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PROCEEDINGS

XXIII International Conference
Ecological Truth

Editors
Radoje V. Pantovic
Zoran S. Marković

EcoIst '15

Hotel "PUTNIK", Kopaonik, SERBIA
17-20 June 2015

UNIVERSITY OF BELGRADE
TECHNICAL FACULTY BOR

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"ECOLOGICAL TRUTH"

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EFFECTS OF SERVICE SMELTING OF IMPORTED COPPER CONCENTRATE IN THE NEW SMELTER OF RTB BOR

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ABSTRACT

The annual capacity of the new RTB Bor smelter is 80 000 t of copper metal. In order to achieve this capacity the smelter requires 400 000 t of copper concentrate. Since the RTB Bor at the moment cannot produce more than 250 000 t of concentrate it is forced to obtain the concentrate from other sources. This article analyzes the effects of service smelting as one of the options in provision of necessary concentrate.

Key words: copper concentrate, service smelting, financial effects.

INTRODUCTION

For over a century RTB Bor has been environmental and ecological black spot. With RTB BOR being one of the European largest copper producers land degradation and air, water and soil pollution due to mining, processing and smelting activities were inevitable. However, the rise of environmental consciousness and introduction of the new environmental standards and legislation triggered a series of actions taken by the RTB Bor in order to mitigate the impact to the environment. The first was the reclamation of the cavity of the closed open pit Bor. The cavity is being filled with overburden from the open pit Veliki Krivelj. In this manner the land degraded by ore extraction from open pit Bor will be reclaimed and no additional land will be covered by the overburden. This was followed with the design for reclamation of South east and Saraka potok overburden dumps and old flotation tailings dumps. In order to provide the possibility for reclamation RTB Bor excluded these facilities from its exploitation field and placed them under government management. Unfortunately, present both domestic and global economic situation prevents this project to be realized and it is on a standstill.

Another project which came to a standstill due to present economic situation is the reconstruction of the Krivelj river collector. The collector reroutes the Krivelj river away from the Veliki Krivelj open pit copper mine. One part of the collector runs beneath the Veliki Krivelj flotation dump. Years of service, aggressive and corrosive waters from the tailings dump and other factors resulted in damage to the collector tube.

There were several attempts to repair the damage but soon it became clear that thorough reconstruction and even partial rerouting is necessary in order to prevent collector collapse and penetration of tailings into the Krivelj river and further on to Bor river, Timok, Danube and finally Black Sea.

Of course, RTB Bor Group as social responsible company, is thinking of mitigating the effects of a century of pollution. Plans are made to clean, reclaim and recultivate the air soil and water and the most ambitious plan is the cleansing of the Bor river downstream basin down to Timok and its confluence to Danube. This endeavor would be one of the largest regional environmental projects and would, most certainly, require the financial support from the international community.

From the aspect of potential health hazard overburden and tailings dumps cannot be compared to the hazardous potential of air pollutants from the smelting facilities. In the past decades there were numerous situations with SO2 concentrations above the maximum allowed limits with extremes reaching 10 000 ppm. Air pollution and the fact that the technology applied was outdated were the two main reasons which lead to the construction of the new smelting line and sulfuric acid factory. The new smelting line officially started with test operation on December 2014 and the first copper started pouring during April 2015.

However, despite the successful start the new smelter operation is faced with some difficulties which must be overcame in order to achieve the primary goal, clean sky over the city of Bor. The new smelter has installed annual capacity of 80 000 t of copper metal. In order to achieve the full capacity and functionality the smelter must be fed with almost 400 000 t of copper concentrate. RTB Bor is capable of producing about 250 000 t of concentrate per year from its own sources meaning that there is a lack of 150 000 t of concentrate. The average price of concentrate at the global market is 1 500 US$/t meaning that RTB Bor would need 225 000 000 US$ per year to buy needed amount. RTB Bor is in restructuring since 2004 and it is impossible for it to take a bank loan. Additionally, RTB Bor is burdened by the loans from previous period and could not take any more debts.

The problem solution could be in the service smelting for international copper producers and traders. There were three basic aspects which defined the terms of service smelting

1. Market processing and market conditions
2. Economy
3. Ecology

MARKET PROCESSING, INTERNAL AND EXTERNAL MARKET IMPACTS

Basic internal impact is a form of mistrust foreigh producers and traders express against the RTB BOR. The reason is the fact that, in previous years, RTB Bor often failed to deliver the ammounts of copper which were agreed under service smelting contracts. Consequently, the 10 000 t debt in copper metal has highly negative influence on further service smelting agreements and RTB Bor`s services are no longer seen as reliable.

External influence which is beyond RTB Bor`s influence is global copper concentrate market behavior. Major market disturbances are:

a) China absorbed all copper concentrate available for procurement and service smelting
b) Several new copper mines appeared in the market mainly to fill the known buyer (China) demand.
c) China used to buy copper product and is now shifting to procurement of copper concentrate. By processing copper in its own facilities, under own technology and with cheaper labor China additionally lowered copper concentrate price and service smelting prices.
d) China is significantly investing in foreign copper mines and in such manner gathers almost whole global copper concentrate production (for example, China imported over 5 million tons of copper concentrate only during December 2014).
e) Copper concentrate market is shifted from the smelters and traders to concentrate producers (both in terms of contract terms and in terms of the manner of quality and quantity measurements and analyses).

The result is the possibility given to concentrate producers to use Chinese smelting services at lower costs than the cost of using RTB Bor services.

ECONOMY

With the average service smelting price of 49.9 US$/t (smelting and refining) for 150 000 t of imported concentrate RTB Bor could reach profit of 6 886 200 US$ only for copper.

150.000t x 8% moisture (12.000 t) = 138 000 t
138.0000 t x 47.96 US$/t, = 6 618 480 US$

Other metals profit is estimated to 50% of copper profit (3 309 240 US$) yielding in profit of 9 927 720 US$ only from service smelting and refining.

However, due to the new technology this profit will be further increased due to higher recovery:

- Copper concentrate should have a minimum copper content of 20 % which is equal to 95 % recovery (20 – 1/20 = 0.95). Since the new technology guaranties the recovery of 98.5 % and RTB Bor is due to deliver metal at 95 % recovery it is evident that excess metal is 3.5 % or 996 t of copper.

The amount of copper RTB Bor should deliver is:

$$\frac{138000 \cdot 20}{100} = 27600 \cdot 0.95 = 26220 \text{ tCu}$$

Meaning the remaining amount of copper is:

27 600 – 26 220 t Cu = 996 t Cu

Financial effect of excess copper is:

996 x 6 146 US$/t (Price on 27.03.2015.) = 6 121 416 US$

In addition, profit is expected from the sale of sulfuric acid in the amount of 731 250 US$ and in savings on coal use (new technology does not use coal) in the amount of 2 446 875 US$. The cost of processing is the cost of oxygen in the sum of 2 074 875 US$.

As opposed to 40 – 50 % of sulfure capture with the old technology the new one captures 98 % resulting in increase in the sulfuric acid production and sale and reduction of the SO_2 emission. If in operation with full annual capacity of 400 000 tons of concentrate the smelting facilities and sulfuric acid plant will produce 390 000 t of sulfuric acid. With a price of 5 US$/t the profit would be 1 950 000 US$, or if only imported concentrate is observed, 731 250 US$.

The new technology does not use coal during the smelting process. The old smelter required 45 000 t of high calorific value coal (27 MJ) with a price of 145 US$/t. For a capacity of 400 000 t of concentrate the old smelter would require 6 525 000 US$ or, observing only 150 000 t of imported concentrate, 2 446 875 US$.

However, RTB Bor is negotiating a 25 000 000 US$ loan necessary to purchase the amount of copper concentrate required for one month operation. The interests and loan preparation costs, for a 60 day payment plan would be 379 166,67 US$ (254 166,67 US$ in interests and 125 000 US$ in loan preparation costs) and this amount would be provided from the service smelting profit.

At the end of period of imported concentrate smelting and refining the effect can be shown as

Smelting and refining	9 927 720 $
Recovery effect	6 121 416 $
Sulfuric acid	731 250 $
Coal savings	2 446 875 $
Oxigen	2 074 875 $
Loan costs	- 379 166 $
Total	**16 773 220 $**

or 121.54 US$ per ton of concentrate processed which is a significant increase compred to previous period (2004 – 2009) when the achieved profit was 27.29 US$/t.

ECOLOGY

New smelting technology is capable of trapping harmful matters (As, Hg, Cd, Pb, Zn etc) in a closed system for water treatment, and consequently, the limit of harmful elements presence in the concentrate can be moved to higher values. The filtering system will prevent harmful elements reaching the air and instead these elements will be disposed to a predefined depot. These matters can be further sold as waste or (requires additional investments) can be treated for copper and other metals recovery.

The main benefit of the new smelter is reduction in air pollution. Due to increase in sulfur capture efficiency and absence of coal in the process the amounts of sulfur dioxide released into the air should be well below maximum allowed limits.

SERVICE SMELTING CONDITIONS

Since the amount of 150 000 t of imported copper concentrate is necessary for normal operation of the new smelter RTB Bor must adapt to all of the conditions and terms dictated by the market. In addition, due to the before mentioned mistrust RTB Bor must accept additional terms required by the concentrate providers. One of the terms is that RTB Bor must guarantee that it will deliver the amounts of copper metal agreed. To guarantee, RTB Bor must have the required amount of copper metal in stock, which will be verified by an independent and reliable international body. Even more radical term RTB Bor is faced with is the obligation to deliver equivalent amount of copper metal at the moment the concentrate is delivered. In other words, the concentrate will be exchanged for the equivalent amount of copper at the Prahovo port.

DOMESTIC CONCENTRATE SMELTING OPERATION EFFECTS

If domestic concentrate smelting is analyzed the financial effects can be presented as

Smelting and refining (250 000dmt x 82.5US$/t x 1,5)	30 900 000 US$
Recovery effect	15 365 000 US$
Sulfuric acid	1 218 750 US$
Coal savings	4 678 125 US$
Subtotal	**51 561 878 US$**
Oxigen	- 3 458 125 US$
Total	**48 103 753 US$**

or 192,41US$/t of concentrate.

CONCLUSION

Due to the lack of domestic copper concentrate RTB Bor is forced to provide imported concentrate in the amount of 150 000 t per year to ensure normal operation of the new smelter. Since the global market conditions, domestic economic situation and the status of the RTB Bor are not favorable, RTB Bor cannot buy the necessary amounts. Instead, the solution is found in service smelting for foreign copper producers and traders. Despite the harsh terms of service smelting imposed by the concentrate providers the service smelting can result in significant profit, both financially and in environmental terms.

The profit obtained from the operation of the new smelter can be further invested in environmental project of the RTB Bor, the reconstruction of the Krivelj river collector before all, reclamation of overburden and tailings dumps and, with the aid of international community cleaning of the Bor river basin. All of these environmental action plans have the goal to provide clean air water and soil for generations to come.

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ENVIRONMENT – SAFETY ASPECTS OF DRILLING ACTIVITIES AS A PART OF GEOLOGICAL EXPLORATION

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ABSTRACT

Every exploitation of mineral resources is preceded by the exploration stage that could have a negative impact on the environment and the very exploitation process. Exploration of mineral resources cannot be done without implementation of exploration drilling, which could pollute the ground up to some extent. In that regard, exploration drilling demands appropriate attention regarding environment protection.

Air, water and land pollution happens when the material in them reaches the level that could have a harmful effect on the population, environment and material assets. In accordance with that, there is a certain legal framework i.e. regulations and limits for polluting environment and ways to protect it.

Key words: geology exploration, ecological aspect, environment, safety and security.

INTRODUCTION

Mineralresources are non-renewable geology resources in such form, with enough quality and quantity, to have rational chances for their possible exploitation. Mineral resources include resources of fossil fuels, metallic and non-metallic mineral resources. In accordance with the growing geological study and reliability, we can divide them in the following classes: inferred, indicated and measured.

In terms of mineral resources and their exploitation, inseparable aspect is, certainly, sustainable development. Sustainable development is development of society with available resources that would satisfy human needs, without putting in jeopardy ecosystems and environment. This would secure a long-term existence of human society and its surroundings.

Sustainable development is most often connected with environment protection. The reason for that, among other things, is actualization of the very term of endangered environment that could be reflected in ecological challenges and problems.

ENVIRONMENT ASPECTS OF GEOLOGICAL DRILLING ACTIVITIES

A large number of unfavorable factors for environment protection is present during the exploration drilling and the following can be identified:

- Harmful impact on air from dust and gases;
- Harmful impact on water i.e. muddied waterways, polluted underground water, waste water, firm material waste, oil and lubricants;
- Degradation of ground;
- Problems of slag disposal;
- Noise and vibrations from the machinery;

Impact of access roads on the environment

The main harmful products of the transport process are creation, spreading to greater distances of: exhaust gases, dust and noise. Motors produce the most of exhaust gases (nitrogen oxides and carbon hydrogen) and noise, and trucks, while moving, create and raise the most of dust. Access roads to the location of drilling are made from the nearest existing road and they can be very long. Thus, the drilling rigs are done by usage of heavy transport assets, but lighter vehicles could be used for shallow drill holes. Drilling time can vary and the location is afterwards abandoned, so the access roads, unless they can be used for something else, must be returned to their original state.

Ground pollution in the drilling setup process

Change in characteristics and pollution of ground in the drilling setup stage is caused by the works on the arrangement of the working site, landfill and buildings. Earthworks are done in order to arrange the workig site, foundations of the drilling rig and additional equipment, reservoirs, sumps, waste etc. These works i.e. their scope, are influenced by the size of the site, terrain, water presence, overgrowth etc. Implemented facility, drilling technology and drill hole depth can have an impact on the platform size.

Spills of additives, fuel and lubricants

Spilling of additives, fuel and lubricants on the working site, can pollute the ground with its quantity and content. Material used in creation of the mud, but especially fuel and lubricants, cannot be dissolved and turn into non-polluting compounds. It is thus necessary to elliminate them by using different processes (physical, chemical or thermal). Together with them, a layer of the ground that was reached by the pollution should be removed.

Usage of the geotextile

Geotextile is a non-woven textile, which is not produced by conventional ways of textile making, but with techonology of creating fleece from high quality synthetic polyester (PES) and polypropylene (PP) fibers, mechanically firmed, by needling i.e. creating loops or tangling fibers into a firm creation similar to felt.

The most important environment protection segment of the geotextile is its chemical resistance. This is the reason why many companies use this material as a background for setting the drilling infrastructure.

Parameters of chemical resistence of geotextile are the following:

- Diluted acids: very good resistence
- Concentrated acids: medium good resistence
- Diluted bases: very good resistence
- Concentrated bases: medium good resistence
- Microorganisms (putridity, mold): very good resistence

Removal of surplus material from mud (Baroid system 360)

Baroid system 360 is designed to remove surplus / unusable material from liquid / mud in order to reuse it in the drilling process. Baroid system 360 is installed for the first time in this part of Europe and this has been done in Brestovac – Metovnica exploration area where Rakita Exploration d.o.o. is doing geological exploration.

Advantages of the Baroid system 360 are:

- Reusing of mud during the process of exploration drilling,
- Separation under pressure of firm material from water in order to make it reusable for the drilling process,
- Reduced water usage up to 75%,
- Enabling safe and easy waste management and disposal at the landfill,
- Increased drilling efficiency.

Area rehabilitation

Rehabilitation is a process that is realized after the end of drilling activities in the location. It includes returning of the complete degradated area into its former state. The drill hole that is abandoned must be closed in accordance with standards and the closing document must be recorded.

Rehabilitation absolutely removes all traces of drilling, starting from the very drill hole, sumps, it refers also to all tools and equipment and everything is returned to the previous state.

ASPECTS OF SAFETY AND TECHNICAL PROTECTION AT WORK AS A PART OF EXPLORATION DRILLING ACTIVITIES

Safety measures at the drilling location

A drilling location in the field is determined in accordance with the current regulations, so that the distance of the axis of the drill hole from the protection zone of the channels, railway, power lines, as well as public buildings and residential buildings, must be at least as the height of the tower increased by 10%. The distance of the axis of the drill hole from the highways and first and second degree roads must be at least 30 meters, and at least 15 meters from other types of roads.

Safety measures during the setup of the drill hole

The tower and the working platform must be designed to endure maximum allowed load during the work. If the working platform is 1 meter above the ground level, it must be fenced with protection fence that is at least 1 meter high and has a 0.15 meter high curb. Access to the working platform must be secured with at least two stairs with handrails, which must not be on the same side as the tower.

The drilling equipment must have a stress indicator and a stress registrator on the hook and pressure on the mud system. A temperature of the device for exhaust gases of the motor used during the drilling must not get over than 350^{o}C. Technical documentation of the drill hole setup gives an insight into technical solutions on implementing technical and protective regulations and it is created based on geology exploration, geophysical measuring and their interpretations.

Protection from eruption

Basic protection measures from eruption in the process of setting up the drill hole are: certain type, quality and quantity of the fluid, as well as certain working regime while performing operations at the drill hole. Outer mud system must have the working fluid in amount of one volume of the achieved depth in the drill hole. In residential zones, besides this quantity of the working fluid, there must be enough material to equal the quantity of volumes of two projected depths of the drill hole, but in case of working outside of residential zone, only up to one quantity of volume of projected depth.

Safety measures while working in residential zones

These measures are implemented during the work in residential zones at the distance of 200 meters from the residential zone. In case where there is no carbon dioxide and sulfur hydrogen, this distance is reduced to 90 meters. Protective area around the drill hole in the residential zone is determined in each separate case. Before the drilling starts, a safe access for vehicles and equipment must be secured and the drill site must be connected by telephone or radio with the management, but also fire department and emergency directly or through the management.

Safety measures while working with hazardous material

Working with hazardous material could be entrusted only with employees who are capable of working with hazardous material in a safe way, and these workers must have appropriate personal protection equipment. Hazardous material neutralization assets and first aid kits must be kept in appropriate location.

Protection from harmful gases

At the locations where poisounous and noxious gases could be expected, each shift must have at least 4 breathing equipments and gas indicators, and at least five employees must be trained and skilled for the usage of this equipment. In the vicinity of mining works at the location that is not jeopardized, a gas protection station must be formed and it should consist of:

- Breathing equipment;
- Gas indicators;
- Necessary parts for this equipment and instruments;
- First aid kits and equipment;

Protection from fire and explosion

For the areas in danger of fire or explosion, a danger zone is determined, preventive measures are implemented and the zone is clearly and visibly marked. During the drilling, finishing and testing of the drill hole, fire danger zone must be at least 30 meters from the drill hole collar. In later mining works (repair etc.), the fire protection zone, for the open system, must be at least 30 meters around the drill hole collar, and 7.5 meters for the closed system.

CONCLUSION

Every socially responsible company must direct its activities towards decreasing negative effects on the environment by implementing risk management strategies. Simultaneously, based on the valid data and implemented scientific findings, it must protect and improve the environment quality in the operating areas.
Equally significant segment of business is, also, creation of safe working environment for employees and contractors, as well as showing a positive contribution to economic environment. A constant goal of each responsible company, besides synchronization with valid laws and environment protection regulations, must be constant improved impact on the environment.

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VALORIZATION OF SECONDARY SULFUR FROM OIL REFINING PROCESS FOR SULFUR CONCRETE PRODUCTION

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ABSTRACT

Modification ofconventional building materials is commonly realized using differentwaste materials. In this research, the use of secondarysulfur as binding agent in concrete was analyzed. Sulfur concrete is a thermoplastic composite made of mineral aggregate and filler, with sulfur as a binder at temperature above the hardening point of sulfur. This relatively new building material can possibly replace conventional Portland cement concrete in many branches of construction. Also, in this research, sulfur concrete properties were examined, as well as its quality in the presence of the induced destruction agent.Destructive and nondestructive methods were applied and the material properties correlated withthe structure.

Key words: secondary sulfur, sulfur concrete, Portland cement concrete, destructive methods, nondestructive methods.

INTRODUCTION

Sulfur is an element that was being removed from the atmosphere by slow natural processes during eons. In these processes, sulfur was bound to metals giving ores. The other natural cycle of sulfur removal, by binding to organic materials through food chains, led to its storage in crude oil. The modern development of industrial society over the last 200 years, the so-called technological revolution, has in fact reversed those natural processes towards restoring sulfur to the environment by exploitation of minerals and crude oil.

Sulfur is the 16th most abundant element in nature. It is found in the earth's crust, in the ocean and even in meteorites. Sulfur occurs naturally all over the world and it is the most prolific where sulfur-rich oil and gas is processed and refined. Canada is the biggest exporter and China is the biggest importer of sulfur [1].

In the last decades, the availability of sulfur has considerably grown mainly due to the current environmental restrictions regarding the petroleum and gas refining processes, which limit the maximum quantity of sulfur present at combustibles. Sulfur from oil processing was stored leading to more or less controlled disposal. Extremely large quantities of sulfur are thus obtained as a by-product of these processes.

Based on literature review and other reliable sources, it is evident that there will be a continuous abundant supply of sulfur in the future due to strict global environmental regulations [2]. The report from the World Business Council for Sustainable Development report, Cement Industry Energy and CO_2 Performance "Getting the Numbers Right" [3], clearly indicates that global production of sulfur will continue to increase, thus assuring its continued availability.

Therefore, the development of new applications for sulfur becomes fundamental.

Building materials come into the focus of interest at the time when waste, industrial or municipal, is becoming increasingly important as a potential raw material. Probable cause for that is the base of building materials- cement which contains numerous waste materials originating from the ingredients or the fuel used for its production. On the one side, the primary application area of building materials has been constantly expanding, but beside these materials, the alternative materials are also taking their place. Modification of conventional building materials is commonly realized using some of the secondary raw materials from various industrial processes. Generally, building materials and their products are important recipients of waste as long as they can provide complete immobilization without degradation of their basic properties.

In this research, possibility of using secondary sulfur as an alternative component of concrete was analized. Waste sulfur is often neglected despite the large amount of globally produced secondary sulfur which possibly exceeds the amount of ash to whom a great importance is given. Therefore, it was necessary to consider alternative ways of sulfur and sulfuric acid valorization in the real process (large scale). In this case, the solutions can be found in application of these types of secondary sulfur for fertilizers production, immobilization of waste materials by conversion into insoluble compounds, and as in the production of building materials.

Production and end use of sulfur is schematically presented in Figure 1.

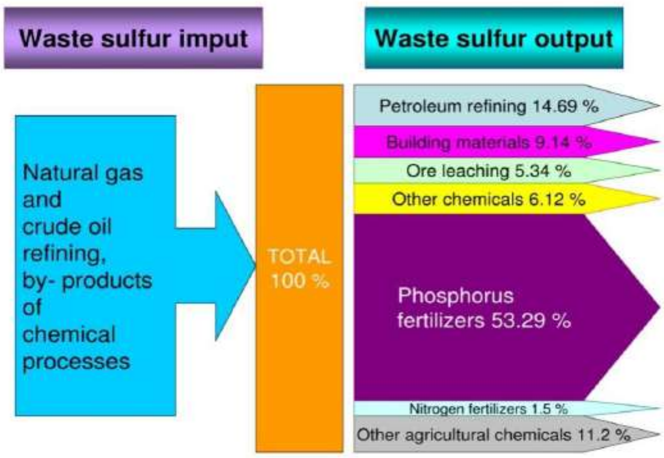

Figure 1. Production and end use of sulfur.

Building materials certainly represent media that should be examined as potential acceptors for large quantities of wastes from various sources.The fact is that wide range of hazardous waste can be inerted by their incorporating into usable building materials.

During the 1960s, there was a remarkable investment in environmental protection against discharge of sulfur into the atmosphere, thus making sulfur a surplus commodity on the market, particularly in the United States and Canada. This was a crucial point, that made the interest for usage of sulfur as a structural binder to grow further, and initiated extensive research programs which became very active in the 1970s and focusing on various properties of the material, including durability [2].

Construction materials such as sulfur concrete and sulfur modified asphalt continue to receive more attention since they are environmentally friendly and cost-effective. Beginning in the 1970s, successful projects in which sulfur concrete has been used as a construction material have been carried out in different levels. Most of these took place mainly in North America. Few and mainly research or test pilot projects have been carried out in Europe, with only Denmark conducting commercial or industrial activities on sulfur concrete.

On the other side, Portland cement may be partially or completely substituted with other binders such as modified heated sulfur to form a stable, hard concrete product. Unlike concrete made from Portland cement (which can be cold mixed), concrete made with modified heated sulfur needs to be heated during production. Although modified sulfur, together with aggregates, needs to be hot mixed (~135°C) when making sulfur concrete, with heat likely obtained from the combustion of fossil fuels, this process uses less energy than conventional cold concrete mixing processes because it avoids the energy needed to heat limestone to 1450°C to manufacture Portland cement. Furthermore, concrete made with modified heated sulfur releases far fewer GHG emissions than concrete made with Portland cement. Modified heated sulfur avoids the process emissions released in the calcination process of clinker production as well as the combustion emissions typically generated to supply heat to the calcination process [1].

It is, therefore, not surprising that such environmental demands and the surplus sulfur draw more attention for the use of sulfur concrete as a construction material. Research activities on sulfur concrete as a construction material are currently reported to be going on in Spain, Italy, and The Netherlands, while interest on medium scale industrial uses of sulfur concrete plans are underway in Poland. In South East Asia, preliminary reports are indicating a growing interest in the use of sulfur concrete as a result of the increase of surplus sulfur from refinery industry. Similar reports come from the Middle East (Saudi Arabia), South America (Chile) and Africa (South Africa), where attempts to use sulfur concrete were reported earlier, or are in progress [2].

Sulfur concrete and mortar are thermoplastic materials made of mineral aggregate and filler, with sulfur as a binder (instead of cement and water) at temperature above the hardening point of sulfur (120 ºC). The proportion of aggregate, filler and binder for the preparation of concrete and mortar mixture may vary depending on the application.

Sulfur implementation for concrete production has started with using unmodified sulfur as a binder. However, despite excellent mechanical properties after preparation, samples exhibited low stability, so spalling and failure occurred after a short period. Namely, exposure of such material to repeated cycles of freezing and defrosting in terms of high humidity or immersion into water caused its degradation and failure**.** This can be explained by sulfur transformation that is occurring during the preparation of sulfur concrete with unmodified sulfur. On cooling of casted liquid mixture, sulfur crystallizes as monoclinic S_β at 114 °C with volume contraction of7%. Below 95.5 °C, it transforms completely into rhombic S_α within 20 h. Since S_α is more dense than S_β high stresses and micro-cracking within the material are induced. This exposes the material to moisture penetration and it fails prematurely.The development of modified sulfur binder contributed to better endurance of sulfur concrete, which focused its application for roads construction and repairing and as a building material. Sulfur itself tends to polymerize to a large extent while chemical modification increases this tendency or prolongs the time required for the polymerization. Except the prevention of sulfur transformation from monoclinic to orthorhombic form, the degree of sulfur polymerization is increased and long chains are created due to modification.Modified sulfur has much lower thermal expansion coefficient compared with unmodified one, therefore shrinkage and residual stresses upon cooling are lower. The polymer prevents the growth of macro- sulfur crystals. Long-term durability of modified sulfur concrete lies in the stability of microcrystalline sulfur [4].

The use of sulfur to produce sulfur concrete and mortar is a relatively new technology that has to be proven in practice. The fact is that these materials are already in use, but refining their application quality is still certainly needed.Sulfur concrete has a relatively simple composition and manufacture, and very interesting characteristics and properties. The recent research programs on sulfur concrete have been continuing to study different properties related to the material performance, most of which are reported to be excellent. Its extremely high corrosion resistance, mechanical strength and fast hardening, make it a high performance material suitable for several applications, especially the ones in which other materials, fail [2]. Furthermore, sulfur concrete can be used for solidification and encapsulation of different waste materials (fly ash, cement kiln dust, phosphogypsum, mercury) into a sulfur-polymer matrix, thus obtaining the sustainable development of construction and industrial sectors and for corrosion protection of reinforcing steel and concrete[1]. Sulfur concrete should also find widespread application in chemical and fertilizer replacement for materials in acid and salt environments as well as in metallurgical operations since they fail in acid and salt environments. Sulfur concrete coated fertilizers were developed to provide better impact strength and controlled- release properties compared to sulfur- coated fertilizers.

In the presented research, the use of secondary sulfur as binding agent in concrete for wide application possibilities was analysed. The starting point was the fact that sulfur is known as a binder and that it can quite possibly be used as a binding agent in building materials. The initial studies were directed towards modification of sulfur for the application in sulfur concrete. Using sulfur to obtain modified sulfur binder is based on its physico-chemical characteristics. According to our terminology, modified sulfur binder considers a mixture of elemental sulfur and modified sulfur- sulfur polymer. Contemporary experience all over the world shows that concrete and mortar with modified sulfur binder instead of cement and water have significant chemical and physico- mechanical advantages comparing with Portland cement- based concrete and mortar [1,5].

The next step in this research was the analysis of technology ie. process of sulfur concrete obtaining in order to optimize the technological parameters for producing high- quality material. This was followed by the researches related to the examination of sulfur concrete properties, as well as testing the new material quality during the exploitation, which was more important. The fact is that the influence of various environmental factors causes a certain degree of destruction and therefore degradation of the basic properties of all materials, so the investigation of the newly obtained material- sulfur concrete was directed towards the analysis of its behavior in the presence of the induced destruction agent.

There are two key elements during the application of this methodology. The first one is a selection of the induced destruction agent, while the other one is a selection of methods, that means methodologies for monitoring and quantifying changes that occur under the influence of the certain agent.

In the scope of this research, hydrochloric acid, sulfuric acid, and sodium chloride were used as induced destruction agents. At the same time these experiments were screening experiments. Based on their results, the induced destruction agent, filler and treatment time for further investigationwere chosen.

In examining the materials properties, as well as in selecting methods for quantifying their changes, classical aspect was not applied. The idea was to implement a number of destructive and nondestructive methods and correlate the material properties with the structure. The structure of the obtained material was analyzed by the methodology of quantification of visual information whereby the images obtained by optical and scanning electron microscopes were used. It means that properties of the material structure were analyzed by different resolutions. The ultrasonic method, which offers defining the homogenity changes of the samples during the treatment time was also applied.

EXPERIMENTAL

Technological procedure for sulfur concrete production

Materials

The initial materials for technological procedure of sulfur concreteobtaining were aggregate, modified sulfur binder and filler.

- Aggregate

Sand with maximum grains size of 2 mm, obtained by sieving of locally available classical building mixture of sand and gravel, was used as an aggregate. Chemical analysis indicated that the aggregate mainly consisted of oxides of silica (89.98%), aluminium (3.61%), calcium (0.84%), iron (0.62%), potassium (0.59%), sodium (0.57%), and magnesium (0.19%).

- Sulfur

Sulfur, the basic component for a modified sulfur binder, originates from oil refining process by Claus's procedure in the Oil Refinery Pancevo, and its purity is 99.9%. Dicyclopentadiene (DCPD), cyclic hydrocarbon, was used for sulfur modification. The procedure performed according to the literature [6]consisted of mixing DCPD and melted sulfur in the temperature range from 120 to 140 ºC and ambient pressure for 30 min, and then rapid cooling and solidification of the obtained sulfur polymer.

- Fillers

Fillers used in this production were: talc (technical quality, China), alumina (Almatis, Germany), microsilica (Sika, Switzerland) and fly ash (Power Plant "Nikola Tesla- A", Obrenovac).

The choice of filler is important because it forms with sulfur paste that coats and binds the aggregate particles. Talc, microsilica and fly ash are fillers that fulfill these requirements and therefore are recommended for the sulfur concrete production [7]. Fine fractions of calcined alumina are used as fillers for refractory concretes [8].

Common characteristic of all selected fillers is their particles size below 75 μm.

Samples preparation

Sulfur concretewas prepared according to the manufacturing technological procedure described in literature [4]. Preheated aggregate and filler (up to 160 ºC) were stirred for about 15 min in a mixer, then melted sulfur and modified sulfur were mixed into homogenized dry mixture of aggregate and filler at sulfur melting temperature, 132-141°C. Preheating is desirable to avoid solidification of the molten sulfur by contact with aggregate at a low temperature and to reduce the mixing time. The heated aggregate and filler were then properly mixed with the molten modified sulfur until a homogenous viscous mixture was obtained. After homogenization and mixing that lasted for 2 minutes, the sulfur concrete mixture was casted into molds preheated at 120ºC and vibrated for 10 seconds. Any extra material was removed to get a well-finish at top surface and left inside the molds at room temperature for hardening. A very important characteristic of sulfur concrete is rapid hardening (from 15 minutes to several hours, depending on size and shape of the sample), which allows removal from the mold and curing in a relatively short period of time (only 24 h at room temperature). Prism samples with dimensions (4 x 4 x 16) cm were prepared. After 3 h of hardening at room temperature, samples were demolded and kept at room temperature of 20ºC for 24 h. Mechanical properties measurements were made after 72 h.

A schematic representation of the mixing process for sulfur concretepreparation is shown in Figure 2.

Characterization of sulfur concrete

The experimental program consisted in performing the following tests on concrete samples.

- *Acid and Salt Resistance*

For sulfur concrete resistance and durability testing the standard testing method [4] was used. The prismatic samples with dimensions of 40 x 40 x 160 mm were immersed in three various aggressive environments: 10 % HCl solution, 20 % H_2SO_4 solution and 3 % NaCl solution.

The destruction of the material during 360 days of immersion was observed by determining variations of mechanical strength and apparent porosity with time.

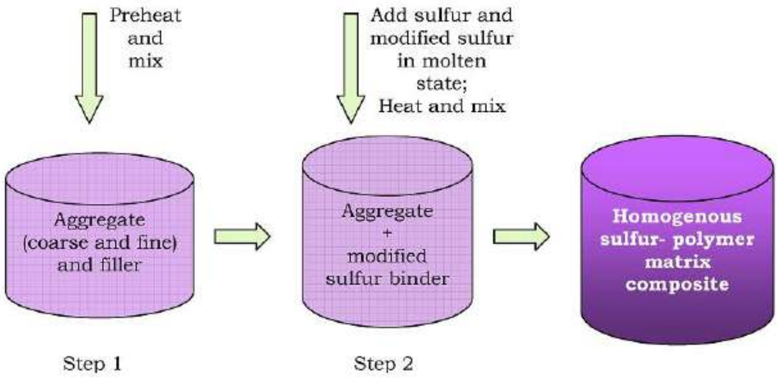

Figure 2. Mixing scheme for sulfur concretepreparation.

- Mechanical Strength Testing

Mechanical strength of the concrete samples before and after immersion tests was conducted using the "Amsler" press with maximum load of 200 kN, and method for testing the strength of concrete according to the standard [9].

- *Apparent Porosity Testing*

Apparent porosity of the samples before and after immersion tests was determined using boiling water saturation technique [10]. The samples were boiled for 5 h and then cooled for 19 h to a final temperature of 20-25 ºC.

- *Image analysis*

The image analysis technique was used for surface destruction monitoring. It was performed using Image Pro Plus Program.

- *Ultrasonic pulse velocity testing*

The measurement of the ultrasonic velocity was used to monitor the internal material degradation with increasing the time of acid treatment. It was performed using the equipment OYO model 5210 according to the standard testing procedure (SRPS D. B8. 121.).

- *SEM analysis*

In order to inspect morphological changes in the inner structure of sulfur concrete, SEM microphotographs were provided using scanning electron microscopeJEOL JSM 5800.

RESULTS AND DISCUSSION

Referent Sulfur Concrete Samples Properties

Physico-mechanical properties of referent sulfur concrete samples, given in Table 1, were determined after removing from the mold and curing at room temperature for 72 h.

Table 1. Physico-mechanical properties of referent sulfur concrete samples after 72 h of curing at room temperature

Sample	Bulk density (g/cm^3)	Mechanical strength (MPa)		Apparent porosity (%)
		Compressive	Flexural	
SC-T	2.33	55.4	8.3	3.14
SC-A	2.34	49.2	8.4	1.38
SC-MS	2.31	50.3	7.2	3.21
SC-FA	2.25	48.9	7.8	4.93

SC-T = sulfur concrete with talc, SC-A = sulfur concrete with alumina,
SC-MS = sulfur concrete with microsilica, SC-FA = sulfur concrete with fly ash.

It can be noticed that mechanical properties of all referent samples of sulfur concrete are mutually similar which can be connected with approximately the same values of their bulk densities.

By comparing properties of prepared sulfur concretewith literature [11], it can be concluded that, regarding mechanical strength, the samples with various fillers have completely satisfying quality.

Mutual differences in mechanical strength and apparent porosity valuesof sulfur concretesamples probably originate from the physical and chemical properties of applied fillers, since the other components were the same.

Durability Testing Results

Sulfur concrete samples in acid and salt environments after 12 months did not show any deterioration and their appearance is shown in Figure 3. For comparison, surfaces of Portland cement concrete samples after 2 months in the same environments are presented in Figure 6.

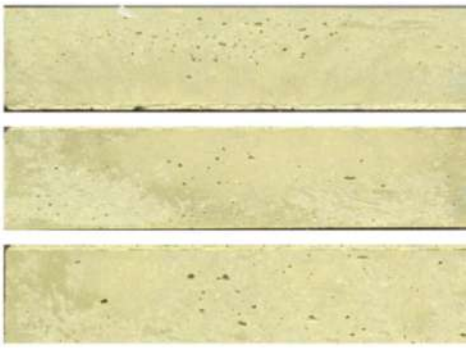

Figure 3. Surfaces of sulfur concrete:
a) with talc in 10 % HCl;
b) with microsilica in 20 % H_2SO_4;
c) with fly ash in 3 % NaCl.

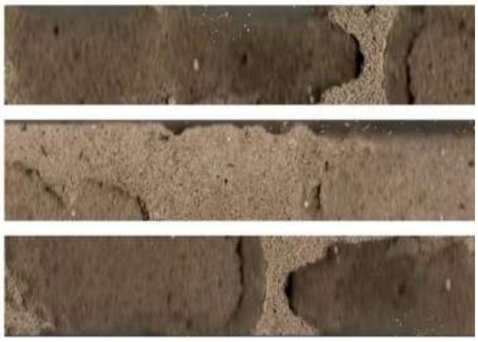

Figure 4. Surfaces of Portland cement concrete:
a) in 10 % HCl; b) in 20 % H_2SO_4;
c) in 3 % NaCl.

a) Compressive strength change of sulfur concrete under acid and salt influence

The obtained results, given in the following diagrams in Figure 5, represent durability of sulfur concrete samples depending on the type of filler and aggressive agent expressed through compressive strength change as a function of time.

The results showed that behavior of the sulfur concrete samples with different fillers regarding compressive strength changes was quite uniform in the investigated aggressive environments. Generally, all sulfur concrete samples after 360 days lost ~ 3 % of their strength in 10 % solution of HCl, and ~ 2 % in 20 % solution of H_2SO_4. Compressive strength loss after 360 days in 3 % solution of NaCl was negligible for all samples of sulfur concrete. It can be concluded that the type of filler did not exhibit significant influence on strength degradation [12].

In all three cases of chemical attack, found compressive strength loss of the treated sulfur concrete samples can be explained by increased porosity because mechanical strength is dependent on the defects in composite microstructure. Porosity is related to the movement of chemical substances into and out of the material and consequently affects durability of concrete, as porosity is connected to many deterioration processes driven by the transport properties of concrete. In sulfur concrete, the majority of the matrix is composed of sulfur coated materials (aggregate and filler) and sulfur accumulated in the voids between particles.

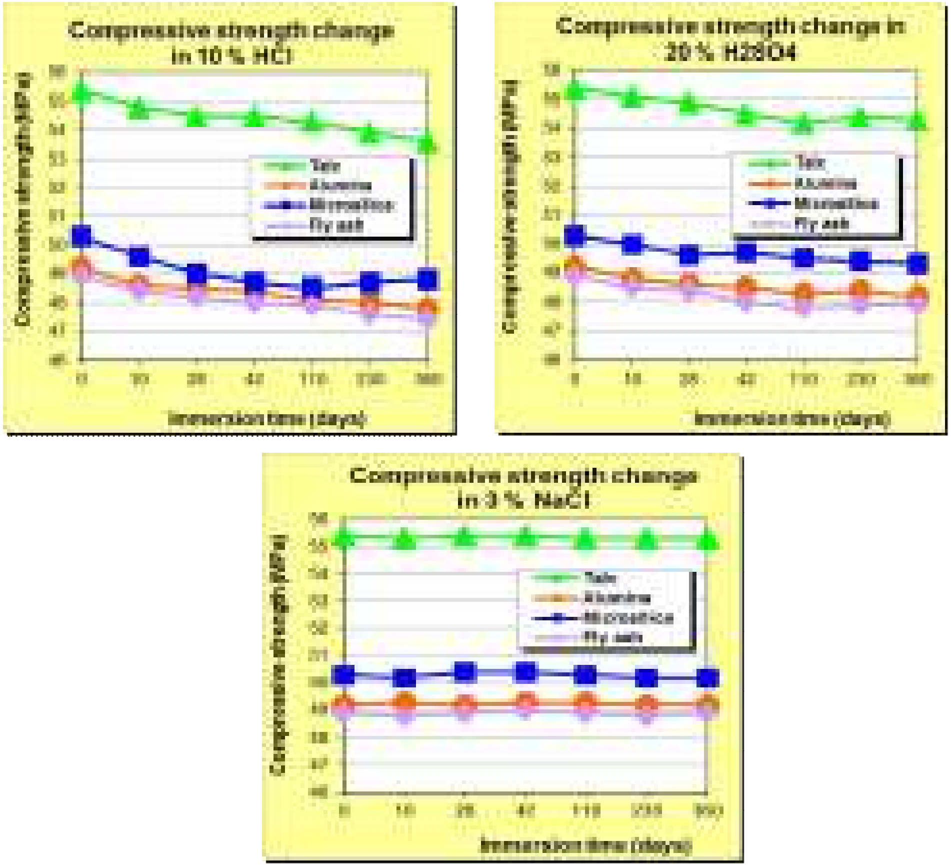

Figure 5. Compressive strength change of sulfur concretewith different fillers in three aggressive environments

During the acid attack, dissolving of basic and amphoteric oxides caused increase in porosity. Acid penetration and therefore corrosion was limited to the surface and open pores that were not coated by sulfur, which in turn resulted in slight porosity increase and slight compressive strength reduction.

During the salt attack, increased porosity is probably a result of a partial detachment between sulfur, aggregate and filler owing to sodium chloride crystals growth. Since sodium chloride penetration is only limited to the outer surface of the sulfur concrete [7], porosity increase was very slight and hence compressive strength loss was practically insignificant.

b) Apparent porosity change of sulfur concrete under acid and salt influence

The obtained results, given in the following diagrams in Figure 6, represent durability of sulfur concrete samples depending on the type of filler and aggressive agent expressed through apparent porosity change as a function of time.

As it was expected, all samples of sulfur concrete exhibited increase of apparent porosity after a year of treatment in the aggressive environments.

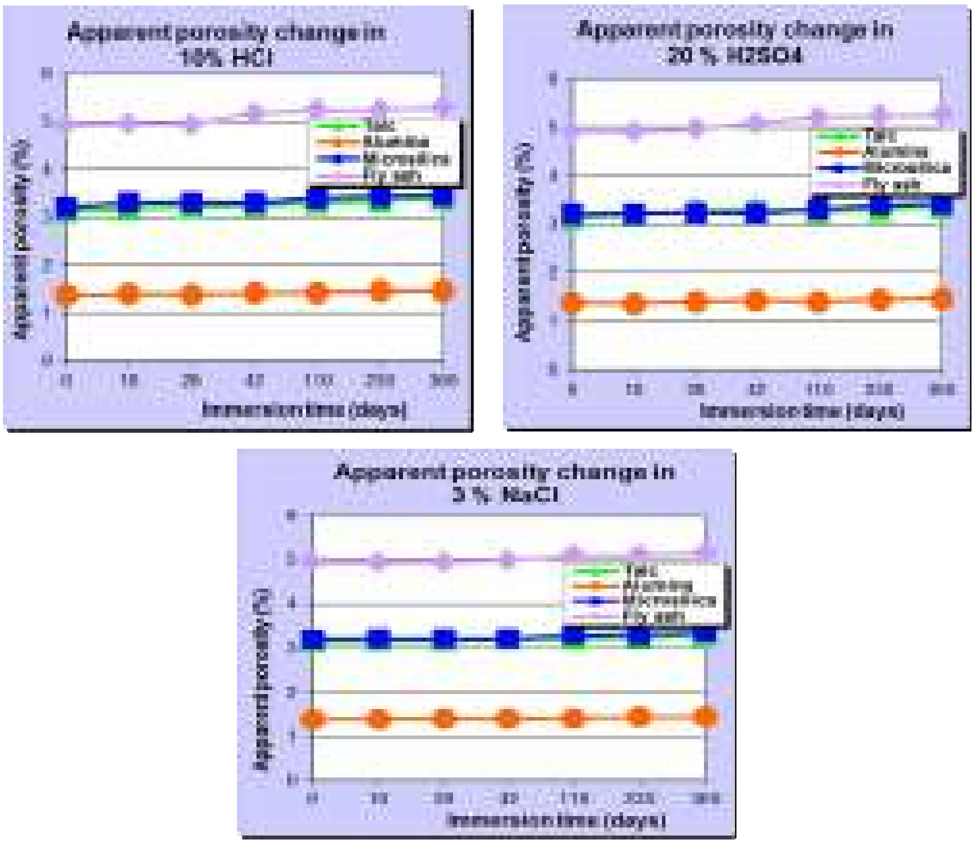

Figure 6. Apparent porosity change of sulfur concrete with different fillers in three aggressive environments

It is obvious that the apparent porosity values were the highest for all samples after a year of immersion in HCl, a bit lower for the samples treated in H_2SO_4, and significantly lower for the samples from NaCl.

The samples treated in HCl underwent the greatest apparent porosity increase of 7.3- 8.3 %, depending on filler. Apparent porosity increase of 6.5- 7.2 % was after treatment in H_2SO_4. In both acids, the samples with talc exhibited the highest apparent porosity changes, unlike those with alumina whose changes were the lowest. The difference between those ending values was ~1 % in HCl, and ~ 0.7 % in H_2SO_4. Apparent porosity increase of only ~ 4.5 % happened for the samples treated in NaCl. Since mutual differences of these changes among the samples were negligible, only 0.3 % between the highest and the lowest values, it can be considered that they were not caused by the type of filler.

Based on the obtained results, it can be concluded that apparent porosity increasement tendency of sulfur concrete samples with different fillers is in accordance with compressive strength loss due to contact with the aggressive agents.

Based onhe presented results, the highest mechanical strength loss and apparent porosity increasement were after treatment with hydrochloric acid. Sulfur concrete sampleswith alumina as filler exhibited great mechanical strength loss in hydrochloric acid accompanied by the lowest apparent porosity increasement.

According to that finding, further investigation was realized on sulfur concrete samples with alumina in hydrochloric acid.Since these samples showed accordance between mechanical strength loss and apparent porosity increasement after only 21 days, treatment time was shortened to 180 days.

Image analysis

The image analysis technique was applied for surface destruction monitoring during durability testing.As addition to the classical porosity test in this research the porosity changes due to chemical influence were followed by the microscopic image analysis. In this case, the samples were analyzed with the minimum resolution in order to characterize only primary interactions between material and the induced stress agents.

Macro image analysis was realized with taking into account the total surface of the samples in order to monitor damage distribution at the surface. For the materials used in engineering, it is very important to analyze the whole sample surface, not only its part, as it is difficult to determine which part is representative for predicting the sample behavior. The level of surface destruction is defined as a ratio of damaged surface area (P) to original surface area before the acid resistance testing (P_0) [13-15].

Diagrams presenting non-damaged surface area (P_{nd}) and surface destruction level (P/P_0) of sulfur concrete samples with alumina in 10 % HCl are given in Figure 7 [16].

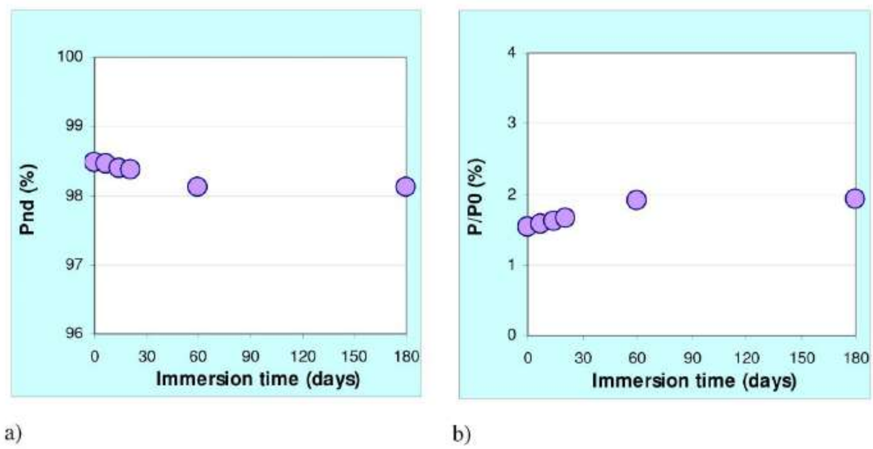

Figure 7. a) Non-damaged surface area of sulfur concrete with alumina in 10% HCl versus immersiontime; b) Surface destruction level of sulfur concrete with alumina in 10% HCl versus immersion time

Certain damage was present on sulfur concrete samples with alumina before the testing in 10 % HCl. Surface destruction level before the testing was 1.5 % and it slightly increased during the immersion time, the value of 1.9 % was reached after 180 days.

Detected surface changes of sulfur concrete samples can be connected with apparent porosity increase results previously presented. Acid penetration is limited to the surface and open pores that were not coated by sulfur, which in turn resulted in slight porosity increase. For the period of 180 days, apparent porosity enhanced from 1.38% to 1.46% (Figure 6). This is in accordance with slight surface destruction increase.

3.4 Ultrasonic pulse velocity

The measurement of the ultrasonic pulse velocities, both longitudinal (V_p) and transversal (V_s), was used to monitor the internal material degradation with increasing the time of acid treatment.

The results of ultrasonic pulse velocity changesin three directions (x, y, z) during the testing time are given in Figure 8.Presented results suggest that the material was very stable during testing, as velocity degradation was not significant- it was less than 5% at the end of the testing which means that the porosity increase is not significant. These results indicate that the samples exhibited excellent resistance to acid influence.

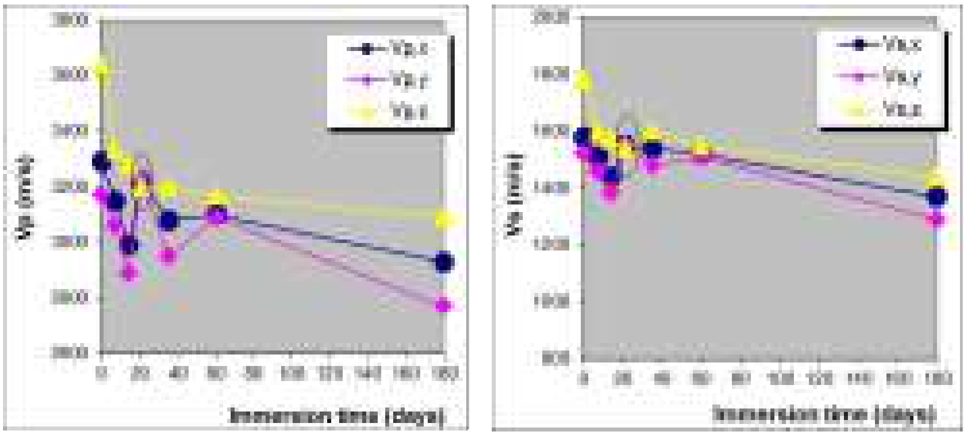

Figure 8. Ultrasonic pulse velocities of sulfur concrete as a function of immersion time

Furthermore, homogeneity of the material can be disscused based on mutual differnences in values of ultrasonic pulse velocities in three directions.

Differences between maximum and minimum values of ultrasonic pulse velocities are presented in Figure 9.

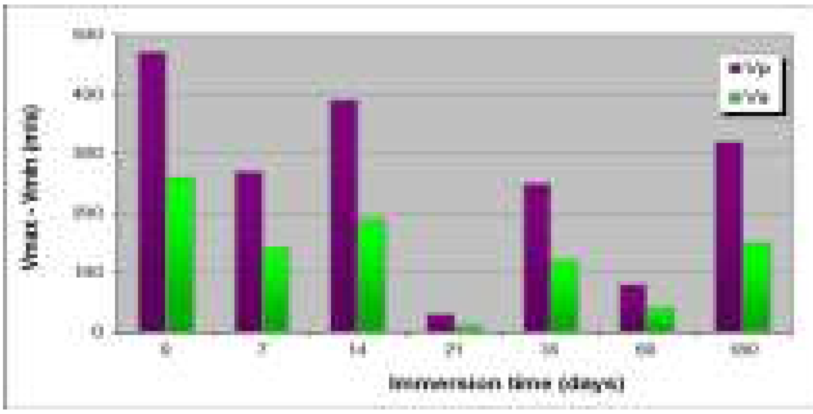

Figure 9. Differences between maximum and minimum values of ultrasonic pulse velocities

Bigger differences between the highest and the lowest values of ultrasonic pulse velocities of untreated samples compared to those treated for 180 days indicate that material after acid treatment became more homogeneous. Since those differences for the treatment period of 21 days are negligible, the material can conditionally be considered as homogenous. For that treatment period compressive strength was the highest. All observed homogeneity changes are the result of material structure rearrangement caused by the influence of acid.

SEM analysis

Bearing in mind that the testing of materials is related to the definition and quantification of the structure and homogeneity of the material, further investigation of the structure with increased resolution, in this case using a scanning electron microscope, was a logical step.For comparison, structural differences between sulfur concrete and Portland cement concrete samples, both treated for 21 days are given in Figure 10.

The analysis of SEM- pictures of sulfur concrete and Portland cement concrete shows two different material changes provoked by the influence of the induced destruction agent.In the case of sulfur concrete, binder phase (sulfur) rearranged and conditionally homogenized the structure. As a result of the treatment, secondary bonding of the aggregate, which additionally homogenized the material, was noticed. It can be concluded that introducing an external disturbance leads to a new quality of the material in terms of its exploitation. Obviously, chemical activation of sulfur concrete, precisely sulfur as a binder, resulted in structural changes of the material. Unlike sulfur concrete, the initial structure of Portland cement concrete was completely degraded, whereby the binder phase was destroyed due to the chemical agent influence. The presented image analysis proves that for both materials changes in the structure on micro scale exist and they are result of interactions with the induced destruction agent, which lead to different scenarios of concretes life circles.

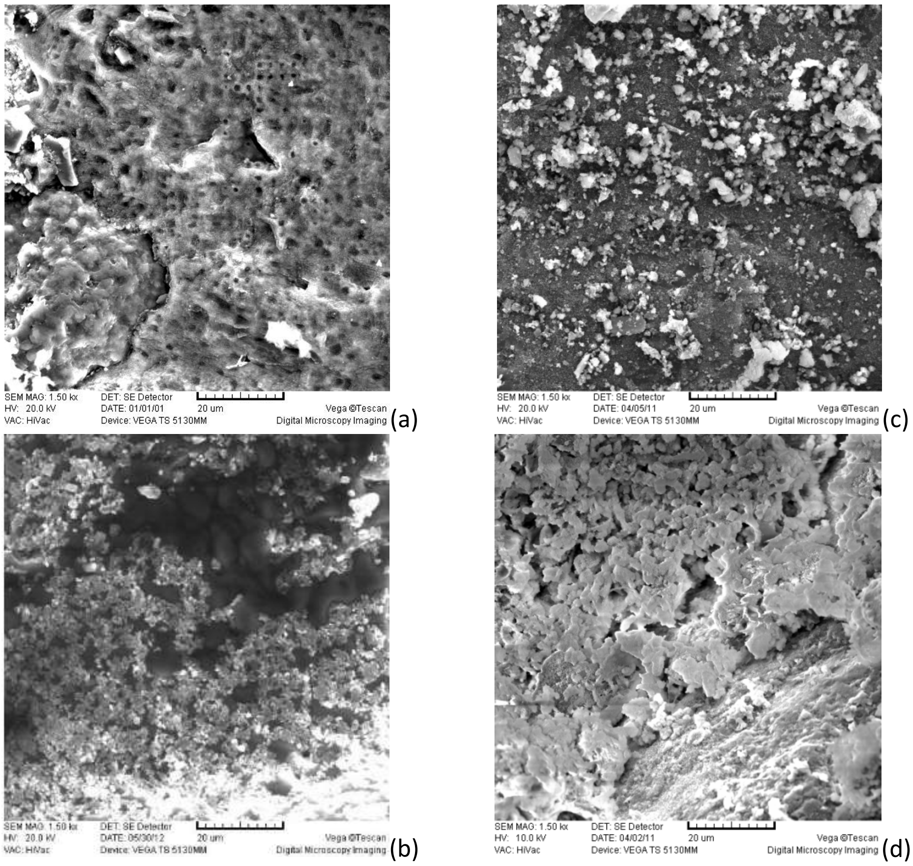

Figure 10. SEM- pictures of:
(a) sulfur concrete untreated, (b) sulfur concrete treated for 21 days,
(c) Portland cement concrete untreated, (d) Portland cement concrete treated for 21 days

CONCLUSION

In this research technological procedure for obtaining sulfur concrete was clearly defined. Sulfur concrete was produced of the secondary sulfur from the oil refining process, sand as an aggregate, and various fillers. Modification of sulfur was performed by cyclic hydrocarbon, dicyclopentadiene. Behavior of produced sulfur concrete in three aggressive environmentsas function of time was investigated.Mechanical testing results showed that sulfur concrete had possessed satisfactory properties and kept them after six months of treatment by the induced destruction agent.Image analysis signified negligible surface changes which are in accordance with slight porosity increase during the treatment.Ultrasonic examination indicated significant homogenity changes during the treatment.Scanning electron microscopy proved a rearrangement of the structure during the treatment which was manifested as enhanced homogeneity.It can be concluded that by adequate technological procedure and selection of the initial components, sulfur concrete with satisfying mechanical strength and good resistance to aggressive solutions was obtained. The obtained results can be used for finding new possibilities of sulfur concrete applying when high resistance to corrosive effect of the environment is required.

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NATURAL SCIENCE RESEARCH IN PROTECTED AREAS OF THE REPUBLIC OF SERBIA

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ABSTRACT

Natural sciences research in protected areas is of great importance not only for Serbia, but for the whole Europe. The main characteristics of the national parks and important natural reserves of Serbia are presented and discussed. The researches of three National Parks - “Fruška Gora”, “Tara” and “Đerdap” - were the results of a joint project, which initiated the idea for gathering important and valuable data on national parks and protected areas on the territory of the Republic of Serbia, including The National Park “Kopaonik” and The Special Nature Reserve "Zasavica”, which are, by their scopes and results of conducted research, in the same range as three mentioned parks. The most important plant and animal species were listed in accordance with their appearance and importance. Protected, rare and endangered species were highlighted. It is given a short overview of importance of such research for agriculture and the practical aspect of obtained results.

Key words: Natural science, Protected areas, National Parks, Serbia, Endemic species, European Red List.

INTRODUCTION

Natural science research, as the outstanding form of interest about the fascinating world around us, is a true step towards overcoming the ignorance of the extraordinary complicated world, full of picture puzzles to solve and enigmas waiting to be explained. Therefore, natural researchers are the biggest admirers, protectors and most sincere adorers of the world in which we live. Comprehensive interest for such fascinating beings, with whom we share our living space on the planet, have no geographical, temporal nor principle limits. Our mind, with all its imperfections and ambivalences, is the only place of permanent inconsistencies and limitation that create and define our existence.

Science development over the millennia, including the evolution of knowledge, discovery of microscope, telescope, photographic techniques, tape recorders, submarines, satellites, computers and other useful things change once acquired attitudes. Gullibility and lack of knowledge have been gradually substituted by scientific knowledge. A chaos related with a variety of information has declined and gave the ground on achievements of modern systems for classification of living creatures and phenomena. By discovering new and unknown parts of the world, by exploring numerous unknown plant and animal species, incomplete and imperfect versions of their classification in the past were modified, and this process of development have been continued up to nowadays. With a strong desire to better know the world, and to more successfully and permanently conquest it, the human race, both individuals and groups, observes the Universe and undertakes various activities in order to systematically define its own position.

State borders drawn on geographic maps represent political, artificially made barriers, but not the biological boundaries of the living world. The defined boundaries of the first, second or third degree of protection in protected areas cannot prevent a seed of the plant to be transferred by wind, or a bird, mammal and insect to spread in their own way all over the habitats.

Extensive long-term natural science researches in the Republic of Serbia have enabled a constitution of the "Regulation on proclamation and protection of strictly protected and protected wild species of plants, animals and fungi"[1]. This Ordinance covers 1,759 strictly protected wild species: 38 species of fungi, 37 species of lichens, 25 mosses, 22 species of ferns, 25 species of algae, 553 seedlings species and 1,059 animal species. Among the animals there are 57 species of mammals, 308 species of birds, 18 species of reptiles, 18 species of amphibians, 30 species of fish and 628 species of invertebrates (91 species of spider-like animals, 4 types branchiopod species, 29 species of centipedes, 25 species of entognata, 377 species of insects, 35 cancers and malacostraca, 1 species of molluscs, 61 species of snails and 5 types of ring worm).

The same regulation includes also 828 protected wild species: 26 species of fungi, 4 species of lichens, 10 species of moss, 9 species of fern, 526 seedlings species and a total of 253 animal species. Protected wild animal species include 27 species of mammals, 29 species of birds, 2 species of reptiles, 3 species of amphibians, 34 species of fish and 158 species of invertebrates (5 species of spider-like animals, 4 types of branchiopod species, 145 insect species, three species of snails and one type of ring worms).

The Nature Protection Act[2], in Article 27, among the protected areas differ: strict nature reserve, special nature reserve, national park, natural monument, protected habitat area, area of exceptional importance and nature park. Areas of the particular importance for preservation and improvement of nature, on the territory of the Republic of Serbia are divided into: 5 national parks, 16 nature parks, 16 area of exceptional importance, 71 strict and special nature reserves, 313 natural monuments of botanic-dendrological, geomorphological, geological and hydrological character and 42 areas with integral cultural-historical and natural values (areas around immovable cultural property and

places of interest). Regarding the special importance of natural history research in protected areas of the Republic of Serbia, it should be pointed out the fact that the entire territory of Serbia is one of the most important refugia and centres of diversity of rare and endemic species on the territory of Europe. The necessity for such research stems from the fact that the Republic of Serbia is a signatory of many conventions which are commitments for conservation of rare and endemic species including their habitats.
Nature research work during the realization of the joint project of the National Parks "Fruška Gora", "Đerdap" and "Tara", together with the examination of other protected areas, generally determines and provides comparability of biodiversity of national parks and other protected natural areas of the Republic of Serbia by forming inventory lists of rare and endemic species, surveys, by highlighting the richness and fascinating diversity of species, as well as the valuation of practical measures of protection and conservation of endangered species.

THE NATIONAL PARK "FRUŠKA GORA"

Fruška Gora is a forest area covering 130.000 hectares, with slightly less than 23.000 hectares of the forest area included in the National Park "Fruška Gora". The central part of the massif is covered with forest vegetation dominated by forest oak, *Quercus petraea*. Going lower to the south of the massif, in the Srem loess plateau, this mesic forests have been gradually replaced with thermophilic forests community of *Quercetum frainetto-cerris pannonicum* and forests of *Acer tatarici-Quercion* forest-steppe areas[3]. Within the zone of thermophilic forests occur xerophyl herbaceous steppe formation types, like meadow steppes[4]. Currently, many areas of the Fruška Gora are covered with meadows, wasteland, arable fields, bushes, orchards and low and coppice forests[5].

Landscape types map in Former Yugoslavia[6] reveals that the area of Fruška Gora mountain has several landscape types: the central massif belongs to the Type 3 (area of mainly southern European deciduous forest), part of the hills and areas next to the Danube river belong to Type 2 (submediterranean area, mainly deciduous forests and shrubs) while a part of the plateau on the south side of Fruška Gora belongs to the Type 6 (steppes and forest-steppe area). According to Matvejev[7] and his review of distribution of steppes and semi-desert areas on the Balkan Peninsula, Fruška Gora was designated as a part of the western province of Pontic-Caspian steppe. Jovanović et al.[8] reported a range of community spaces that characterize the mountain and significantly contribute to their knowledge. Mišić[9] and Janković & Mišić[10] present data about depleted relict communities of beech and linden refuges, on Fruška Gora as well, with the habitat as refugia. On Fruška Gora mountain, transitional stands from polydominant forest types of *Fagetum submontanum mixtum silicicolum* to two-dominant forests of beech and linden can be found.

The most important species in Fruška Gora moutain forest comunities, according to Janković & Mišić[10] are: oak (*Quercus petraea*), linden (*Tilia spp.*), hornbeam (*Carpinus betulus*) and beech (*Fagus moesiaca*). Beside these, there are some other forest and shrub plant species: oaks (*Quercus petraea*, *Q. conferta*, *Q. cerris* and *Q. pubescens*), linden (*Tilia qrandifolia*, *T. argentea*, *T. cordata*), maple (*Acer* *pseudoplatanus*, *A. platanoides*), wild cherry (*Prunus avium*), mountain elm (*Ulmus montana*), black ash tree (*Fraxinus ornus*), white ash tree (*F. excelsior*), wild service tree (*Sorbus torminalis*), European bladdernut (*Staphylea pinnata*), maple (*Acer campestre*), Wayfarer (*Viburnum lantana*), large-leaved spindle (*Evonymus latifolia*, *E. europaea* and *E. verrucosa*), dogwood (*Cornus mas*), hazel (*Corylus avellana*), old man's beard (*Clematis vitalba*), elderberry (*Sambucus nigra*), hawthorne (*Crataegus monogyna*), juniper (*Juniperus communis*) and oriental hornbeam (*Carpinus orientalis*).

Fruška Gora, according to Obradović[11], is a home to over 1.454 plant species. Gajić[12] concludes that the influence of flora of southern and eastern parts of Europe is greater to the Fruška Gora then the influence from the North and Western Europe. It is believed that there is a significant impact of Slavonija what is proved by the strong similarities in geology, soil, climate and vegetation diversity. Being an integral part of the Illyrian floral province (Illyricum) Fruška Gora is, according to composition of flora and living conditions, closer to Slavonia than to the rest of Serbia and the Carpathian region.

Animal diversity of Fruška Gora is also rich. Among the 211 bird species in total[13] almost 150 species live in the forest habitats[14]. The same authors recorded 13 species of amphibians and 11 species of reptiles, what makes this area a significant reproductive center of amphibians and reptiles in Serbia and a center of their diversity as well[14,13]. In addition, there were 60 species of mammals recorded in Fruška Gora. On the relatively small area of National Park, there were 6 out of 7 orders of mammals registered and slightly more than a half (51) of the total number of mammal species recorded in the Carpathian Basin and the Balkan peninsula[14].

In protected forest biocenosis of the National Park Fruška Gora, there is a constant observing and identification of entomofauna, which in certain circumstances could be a potential threat to the forest flora and fauna and their sustainable development[15,16]. Monitoring and studying of predatory entomofauna were also conducted, including investigation of other insect species that play a prominent role in maintaining the balance of forest biocenosis[17-21]. The fauna of hoverflies (Syrphidae) is well explored and a certain number of endemic species were recorded: *Pocota personata*, *Cheilosia schnabli*, *Merodon recurvus* while the particularly important species is *Cheilosia griseifacies* whose *locus typicus* is Petrovaradin rit[22,14]. In the area of Fruška Gora, there were 203 species of hoverflies in total, belonging to 60 genera[23]. During a period from 1980 to 2007, there were several ecological investigations on mosquito fauna, familiy Culicidae of Fruška Gora while 17 species were recorded in total[24], including the species *Culex territans* which was recorded for the first time for mosquito fauna of former Yugoslavia at the begining of 1980's[25].

The richness of insect fauna of the Fruška Gora is also proved with almost 1000 species of butterflies and moths recorded so far[26-30,15,31,32,16,33-47]. There were 204 owlet moths species (fam. Noctuidae) and 187 geometer species (fam. Geometridae). There were also 136 species of longhorn beetles recorded[48-52] with 67 species of weevils[53,54], 31 species of scarab beetles, fam. Scarabaeidae[55], 22 species of ladybugs[56], 184 species of ground beetles[57-61], 5 species of checkered beetles, fam. Cleridae[62], 73 species of leaf beetles[63], 46 species of sawflies[64] and many other groups of insects that are in the process of species identification.

THE NATIONAL PARK "KOPAONIK"

High mountainous flora of Kopaonik is represented with 825 species and subspecies belonging to 292 genera and 80 families, so representing 1/5 of total flora of Serbia. The highest forest area over the altitude of 1500 m is covered with dense spruce forests, while at higher altitudes (1750-1900 m) spruce forests are less thick and become communities of low bushes, with predominantly mountain juniper and blueberry. Ice Age, when compared to other parts of Europe, in our mountains destoyed flora only slightly what is evidenced by the numerous relic plants which are the remains of the former ancient flora. Relic plants of Kopaonik are: *Leontopodium alpinum*, *Vaccinium uliginosum*, *Eriophorum latifolium*, *Taxus bocata*, *Acer heldreichii*, *Ostya carpinifolia*, *Trolius europaeus*. In the area of the National Park Kopaonik there are three stenoendemic plant species that grow only here and nowhere else in the world: *Sempervivum kopaonikensis*, *Viola kopaonikensis* and *Cardamine pancicii*.

Within the National Park Kopaonik, there are 91 endemic and 82 sub-endemic plant species, of which as many as 30 species are protected by the Decree on Protection of Natural Rarities of Serbia's territory. Acctually, they are under the regime of absolute protection. There are four plant species recorded in the National Park Kopaonik which are on the International Red List: endemic plants - *Pedicularis heterodonta* and *Stipa mayeri* and non endemic flora - *Alyssum markgrafii* and *Viola elegantula*. In accordance with the categories of the International Association for the Protection of Nature (IUCN) there are species categorized into different risk categories: species in danger to disappear - *Potentilla palustris* and *Gentiana lutea*; vulnerable species - *Pinus silvestris*, *Dactyloriza majalis*, *Trolius europaeus*, *Geum montanum*, *Leontopodium alpinum*; disappeared (unspecified) species - *Anemone narcisiflora*, *Primula minima*, *Geum reptans*, *Silene saxifraga*, *Narcissus radiflorus* and rare species - *Arctostaphilus uva ursi*, *Gentiana cruciata*, *Aster alpinus*, *Iris graminea* etc.

There is an extremely regular substitution of vegetation by increasing elevation on Kopaonik. It starts from the willow-poplar-alder forests in the valley of rivers and continues with thermophilic forests of pine, Turkey and Hungarian oak communities, forests of oak and hornbeam, forests of pubescent oak and black ash forests which are followed with mountain beech and sessile oak forests (up to 1.100 m above sea level), beech and fir forests (up to 1.600 m above sea level) in which penetrates spruce, being a dominant species in the forests of 1.550 to 1.750 meters above sea level. Above 1.750 m above sea level starting zone of prostrate shrub juniper and blueberry with low subalpine spruce form which is followed by alpine mountain pastures, located above 1.950 meters above sea level.

Favorable natural conditions of Kopaonik enabled development of rich and varied animal diversity. Fauna of mammals on Kopaonik consists of 40 species: 9 species of insectivores (Insectivora), 5 species of bats (Chiroptera), 1 species of lagomorphs (Lagomorpha), 14 species of rodents (Rodentia), 9 species of carnivores (Carnivora) and two species of ungulates (Artiodactyla). All these species are native and settled in this area since ancient times, with the exception of American muskrat, which, with the indirect help of man, penetrated 40 years ago in the valley of the Ibar River and streams of north-eastern foothills of Kopaonik. In the last century, four mammal species were eradicated from this area, mainly thanks to the negative influence of man: bear (*Ursus arctos*), which over the last few years can be seen, but it is considered only in passing without a permanent place of residence, lynx (*Lynx lynx*), chamois (*Rupicapra rupicapra*) and red deer (*Cervus elaphus*). According to the International Red List of Europe (European Red List, UNESCO, New York, 1991) there are two species recored in the National Park Kopaonik: *Muscardinus avellanarius* (Rodentia) and *Canis lupus* (Carnivora), both with an indication of vulnerable species on the global level.

Waters in the National Park "Kopaonik" belong to salmonid, trout region and are distinguished only by fish settlements of native brown trout (*Salmo truta*), with a significant presence of otters along watercourses. Brown trout is a semi-migratory species (with strong freshwater migrations during feeding, especially during spawning) which inhabits cold and fast streams, rich in oxygen, with bottom covered with stones and cobbles. Brown trout is, according to the Law on Protection of Nature, on the list of "protected species" which protection, management, hunt, utilization and improvement of populations shall be governed by the regulations in the field of fisheries.

Since the 19th century, there have been about 180 species of birds in the area of Kopaonik. The actual number of species that can be encountered in this area is certainly bigger and it is estimated to be about 210 species. From so far recorded species on Kopaonik, there have been 125 nesting species. Due to the disappearance of several former nesting bird species of Kopaonik, the number of species that are now nesting here is around 115. Among the species the dominant ones are birds of forest habitats, open mountain habitats and birds of cultural landscapes. Because of the great diversity, richness of bird fauna and the presence of rare and endangered species, Kopaonik was in 1997 included in the list of internationally Important Bird Areas (IBA). Typical nesting forest species in Kopaonik are: European honey-buzzard *Pernis apivorus*, short-toed snake eagle *Circaetus gallicus*, Ural owl *Strix uralensis*, boreal owl *Aegolius funereus*, white-backed woodpecker *Dendrocopos leucotos*, three-toed woodpecker *Picoides trydactilus*, hasel grouse *Bonasa bonasia*, red-breasted flycatcher *Ficedula parva*, wood warbler *Phylloscopus sibilatrix* and mountain tit *Parus montanus*. Alpine pastures and turfs are inhabitats with: horned lark *Eremophila alpestris*, common rock thrush *Monticola saxatilis*, rock partridge *Alectoris graeca* and alpine accentor *Prunella collaris*. On the rocky cliffs and river canyons nest: golden eagle *Aquila chrysaetos*, peregrine falcon *Falco peregrinus* and Eurasian eagle-owl *Bubo Bubo*. Landscapes with meadows and orchards are inhabitats with corn crake *Crex crex*, scops owl *Otus scops*, hoopoe *Upupa epops*, red backed shrike *Lanius collurio*, forest lark *Lullula arborea*, sombre tit *Parus lugubris* and ortolan bunting *Emberiza hortulana*. Several species that have been once regularly nested on Kopaonik, nowadays stopped nesting due to expressed anthropogenic pressures. These are: western capercaillie *Tetrao urogallus*, red-billed chough *Pyrrocorax pyrrocorax*, Alpine chough *Pyrrocorax graculus*, griffo *Gyps flavus*, black vulture *Aegypius monachus*, booted eagle *Hierateus pennatus*, wallcreeper *Trichodroma muraria* and European roller *Coracias garrulus*. A series of protective measures are implemented on the territory of the National Park such as: installation of artificial nesting houses, harmonization of activities in the park with the needs of birds' protection and similar actions that would contribute to a greater number of settled species and continuation of their normal life activities.

Although scarce, existing data suggest the possibility of the presence of a number of animal species, which development positively affects a mosaic set of forests, grassland, bare rock and water. In the area of Kopaonik, there is a total of 14 species of batrahi and herpetofauna recorded (six amphibian and eight reptile species). This area is not included in areas with high diversity of amphibians and reptiles fauna. With an exception of three species of frogs of the genus *Rana*, including horned viper (*Vipera ammodytes*) which are protected species, other species are strictly protected and can be found in the annexes of the Ordinance on proclamation and protection of strictly protected and protected wild species of plants, animals and fungi. Species that are not found in a certain degree of protection are green lizard (*Lacerta viridis*) and wall lizard (*Podarcis muralis*). Species of amphibians and reptiles are extremely sensitive to almost any type of change, even the smallest ones, and can serve as bioindicators of the environment. Amphibians are on Kopaonik represented with the species: fire salamander (*Salamandra salamandra*), Alpine newt (*Triturus alpestris*), yellow-bellied toad (*Bombina variegata*), a large green frog (*Rana ridibunda*), meadow frog (*Rana dalmatina*) and ginger frog (*Rana temporaria*). The reptiles recorded on Kopaonik are: green lizard (*Lacerta viridis*), viviparous lizard (*Lacerta vivipara*), wall lizard (*Podarcis muralis*), grass snake (*Natrix natrix*), dice snake (*Natrix tessellata*), Aesculapian snake (*Elaphe longissima*), viper (*Vipera ammodytes*) and common European viper (*Vipera berus*).

Faunistic richness is conditioned by the central position of the Kopaonik mountain in the Balkan Peninsula and richness of flora and habitats. These pre-conditions, combined with a long geologic historical period of development and low impact of glaciation, caused the presence of 138 species of butterflies. This classified Kopaonik as one of the richest mountain of Balcan Penninsula according to the butterfly fauna. The Balkan Peninsula has a total of 290 butterfly species recorded, so 138 species of Kopaonik makes 47.5% of the total fauna of the Balkan Peninsula. There are 194 known butterfly species in the whole Serbia; therefore fauna of Kopaonik comprises almost 71%.

Endemic and relic butterfly species *Colias balcanica* was found in Kopaonik. Of particular importance is also the presence of species *Coenonympha orientalis* and *Boloria titania,* which record their easternmost distribution on this mountain. Field research on Kopaonik revealed new species of butterflies in Serbia. *Zygaena augelicae* is the species that inhabits northern areas and Slovenia was designated as the southernmost point of its distribution, until its discovery in Kopaonik. Species *Colias caucasica* can be found in the zones of high-mountain rocky area, in open Mediterranean pastures, rocky hillsides and ravines. It represents a relic of the Pliocene, preserved in refugium habitats above the zone of spruce forests. The occurrence of *Phengaris (Maculinea) arion* is of great importance. This myrmecophilous species has an interesting life cycle: the first half of life caterpillars spend in inflorescences of plant species *Origanum* and *Thymus.* Then ants' species *Myrmica sabuleti* and *M. scabrinodis* take them into their anthills where caterpillars feed on ants larvae. *Phengaris (Maculinea) arion* is a significant species which can serve as indicator of natural ecosystems status. Therefore, it is monitored all over the Europe (European Environmental Agency, Butterfly Conservation Europe).

Considerations at the European level showed that there are 17 species of butterflies on Kopaonik known as the target species: *Zerynthia polyxena*, *Parnassius mnemosyne*, *P. apollo, Colias caucasica, Lycaena dispar, Pseudophilotes vicrama, Scolitantides orion, Glaucopsyche alexis, Maculinea arion, M. alcon, Polyommatus eroides, Boloria titania, Polygonia c-album, Euphydryas aurinia, Melitaea aurelia* and *Erebia medusa*. Butterfly species covered by the Natura 2000 program are of European importance are: *Lycaena dispar*, *Polyommatus eroides*, *Nymphalis vaualbum* and *Euphydryas aurinia*. These species are under protection by the Ordinance on proclamation and protection of strictly protected and protected wild species of plants, animals and fungi.

THE NATIONAL PARK "TARA"

Mountain Tara is known as a unique refugium for many rare and endangered species[65]. Special values of this area are endemic, relic and endemic-relic species. The most famous and the most important representative of plants, which is also the symbol of Tara, is endemic-relic species Serbian spruce - *Picea omorika*. Floristic richness of Tara counts over 1.100 plant species, representing almost a third of total flora of Serbia. Previous research revealed the presence of 96 species of lichens, 171 species of mosses, 30 species of ferns, 7 species of gymnosperms and 960 species of angiosperms. Plenty floral elements of the sub-Mediterranean to sub-alpine species can be found on Tara thanks to its specific location, geography and history.

To date, the area of Tara recorded over 76 endemic plant species, among which several are of particular interest: "derventanski različak" (*Centaurea derventana*), "Nikolićeva kandilka" (*Aquilegia grata*), "cvakija" (*Halacsya sendtneri*), "golocvetna mlečika" (*Euphorbia glabriflora*), "Pančićeva bedrenica" (*Pimpinella serbica*), "monaški pupavac" (*Silene monachorum*) and others. Besides spruce, many rare and relict woody species can be found on Tara, such as: common yew (*Taxus baccata*), mountain maple (*Acer heldreichii*) and holly (*Ilex aquifolium*). In rare microhabitats of Tara (gorges and peats) many glacial relics can be found: *Eriophorum latifolium*, *Goodyera repens*, *Viola biflora*, *Leontopodium alpinum*, *Corallorhiza trifida*, *Gentiana pneumonanthe*, *Menyanthes trifoliata* etc.

Thanks to the diversity of edaphic factors, configuration, altitude and other ecological factors in the National park, there are different forests, meadow and wetland habitats developed, which are distributed as mosaic over the entire Tara Mountain. National park "Tara" is typical forest area, and according to its preservation and diversity of forest ecosystems, many of which are relic character, it is one of the richest and most valuable forest areas of Europe. On Tara there are more than 40 broadleaf, deciduous-coniferous and coniferous phytocoenoses identified.

Mountain Tara is a part of Dinaric Alps and belongs to the Illyrian province of Central European region. On its relatively low altitude not exceeding 1.700 meters above sea level, all phenomena of height zoning of vegetation (ecosystems) are not fully manifested. This is reflected with the absence of the subalpine zone of pure coniferous forest, the absence of the upper forest limit, and the alpine zone as well. However, due to the specific orography with slightly wavy surface, at the altitude of 1.100-1.300 meters, where the major parts of limestone alternating serpentinite (southern and western parts of the mountain), at Tara, within the areas of beech on limestone, there are also mixed forest of spruce and fir. These three-dominant forests marked as *Piceo-Abieti-Fagetum* take over 85% of forest areas on Tara[66]. Besides spruce, fir and beech, in areas of 700-1.200 m above sea level there are mixed pine forests or forests of only black or white pine. In this series of forest communities, a special value and rarity are the pure or mixed stands of Serbian spruce (*Omorikae-Pineto-Piceeto-Abieto-Fagetum mixtum*), which are spread out on the limestone, as well as on serpentinit, both on northern and sheltered slopes which have the characteristics of refugia.

Zoning vegetation ecosystems on Tara begins from the canyon of the Drina River, in which the most significant are the thermophilic communities of hornbeam (*Orno-Ostryetum*) that have sub-Mediterranean character. On the steep sides and rocks of Drina and Derventa canyons communities of hornbeam and black pine (*Ostryo-Pinetum nigrae*) are developed. At the foot of the mountains on limestone and serpentinite in more developed soils occur oak forests of Turkey and Hungarian oak (*Quercetum frainetto-cerris*) and in higher areas sessile oak forests (*Quercetum montanum*). The zones with only Turkey oak forests (*Quercetum cerris*) occur at milder southern slopes of the mountain. From the place Kremna to Tara, there are black pine forests (*Pinetum nigrae*), which are replaced at higher altitudes with mixed forests of black and white pine (*Pinetum nigrae-sylvestris*). At the place Kaluđerske bare, the dominant species is white pine (*Pinetum sylvestris*).

In the area of Tara, there are a various types of meadows, although the meadow vegetation in this area is secondary formations, formed at the sites of different former forest communities. So far, there are 19 meadow plant communities, with the highest mountain area significantly represented with *Nardetum* community dominated by *Nardus stricta*.

Vegetation of peat bog and wetland habitats is one of the characteristics of the National Park. It is represented in closed depressions and deep sinkholes with swampy and clay bottom being also around the mountain rivers and streams. Localized, with many small areas all over Tara, it has been found the presence of vegetation associations: *Eriophoro-Caricetum paniculatae*, *Molinio-Deschampsietosum cespitosae*, *Scirpetum silvatici* and *Lythro-Caricetum paniculatae*. Many endemic plants are present on Tara and vegetation in cliffs and canyons is floristic diverse and characterized by a large number of plant communities which are interspersed in a small area.

Animal species present on Tara are also very diverse. One of the most important representatives of the entomofauna of the National Park "Tara" and one of the basic characteristics of biodiversity in this area is a grasshopper species, for the first time noted in the village Mokra Gora by PhD Josif Pančić in 1881. This species is named after Serbia: *Pyrgomorphella serbica*, Pančić's grasshopper. It is a relict and endemic brachipterous species of grasshopper that has survived in relic forests of black pine (*Pinus nigra*) and winter heath (*Erica carnea*). Pančić's grasshopper is a relic of the Pliocene fauna that has been preserved only in the refuge area of the middle course of the Drina River. Twenty three years ago, our famous ornithologist and ortopterologist PhD Sergej Matvejev studied this interesting species, primarily its area of distribution, bionomy, ecology and geographic and biogeographic characteristics of its habitat[67].

There are also extremely important the recent findings of Pančić's grasshopper in the area of Zaovina.

The other groups of insects have been also studied in the previous period in the National Park "Tara". The data are to a greater extent synthesized for a group of daily butterflies (Rhopalocera), of which 23 species are listed in the Red book of butterflies of Serbia[68]. Therefore, the area of the mountain Tara has been included in the areas of importance for the conservation of butterflies[69]. The same area is settled with 115 species of moths (Noctuidae)[70], which can be of great importance for agricultural production. Determining the diversity of Lepidoptera fauna is the result of years of the field work to collect samples, but also of the laboratory work in the analysis of general characteristics, systematic, taxonomy, comparative morphological characteristics and identification of collected specimens. The survey recorded a total number of 138 moths' species belonging to 99 genera, 17 subfamilies, 16 families and 9 super families. According the zoo-geography, dominant are European species (77), followed by Eurasian species (26) and slightly less Palearctic species (18)[71].

Since spring 2013, in the National Park "Tara" significant drying of forests was noticed as a result of the extremely dry conditions in previous years, especially in 2012. Such dried trees, as well as physiologically weak trees usually are material for the development of harmful species of bark beetles (Coleoptera, fam. Curculionidae, subfam. Scolytinae) on conifers. Significant pest species of bark beetles are: *Ips typographus*, *Pityogenes chalcographus* and *Polygraphus polygraphus* on spruce and Serbian Spruce, *Pityokteines curvidens* on fir, *Ips sexdentatus* on pine trees and *Trypodendron lineatum* on spruce, fir and pine trees. Thanks to the donation of the Norwegian Embassy in Belgrade, a very important research, related to monitoring and combating bark beetles in the area of the National Park "Tara", were carried out using pheromone traps. Several hundreds of bark beetle specimens are able to dry a tree about 100 years old, and by the end of the survey 32.000.000 pests specimens were counted in study area[72].

There are 19 fish species in Tara. This area belongs to salmonid (trout) and transitional barbel region with clean and cold mountain water species (brown and lake trout - *Salmo trutta*, huchen - *Hucho hucho* etc.) including domestic cyprinid (carp) fishing species: European chub *Squalius cephalus*, common nase *Chondrostoma nasus*, pigo *Rutilus pigus*, common barbel *Barbus barbus* and others.

In the wider region of Tara, there were recorded 23 species of amphibians and reptiles, including species important for preservation of diversity such as: fire salamander (*Salamandra salamandra*), newt (*Triturus spp.*), European tree frog (*Hyla arborea*), Greek frog (*Rana graeca*), Hermann's tortoise (*Testudo hermanni*), Caspian whipsnake (*Coluber caspius*), Aesculapian snake (*Elaphe longissima*) and viper (*Vipera ammodytes*).

The area of Tara is one of the most important mountain areas in terms of bird fauna. Hence, it is marked as the area of international importance for birds (IBA). So far, in this area there were 140 bird species recorded, while the real number of species could be around 170. The total number of so far recorded nesting species was 125, but today that number is slightly lower (120). One of the most important species of bird fauna is western capercaillie (*Tetrao urogallus*) and Tara is one of the last nesting sites of this species in Serbia. There were also nine species of daily predatory birds which are nesting on Tara [73].

According to the results of previous research, the area of Tara was inhabited by 53 mammal species. A presence of several more species could be expected in future with their findings in near and distant surroundings. The most common group of mammals are bats, according to the number of species in the National Park. They are followed by rodents, carnivores, insectivores, ungulates and rabbits. Area of Tara is primarily significant as habitat for large carnivores, like wolf, *Canis lupus*, and bear, *Ursus arctos*. Currently, the largest population of bears is in this area, with great importance for conservation of this animal in Serbia. One of the important species among mammals, and also the one of the symbols of National Park "Tara", is chamois, *Rupicapra rupicapra*.

THE NATIONAL PARK "ĐERDAP"

Flora of the National Park "Đerdap" is extremely diverse in taxonomic and ecological sense. More than 1000 plant species are located in the narrow coastal region. There is a significant spread of rare plant species, among which the most important are tertiary relics whose range and abundance in Europe has been significantly reduced: hazel (*Corylus colurna*), Pančić's field maple (*Acer intermedium*), European nettle tree (*Celtis australis*), walnut (*Juglans regia*), barberry (*Berberis vulgaris*), common holly (*Ilex aquifolium*), downy oak (*Quercus pubescens*), lilac (*Syringa vulgaris*), smoke tree (*Cotinus coggygria*), butcher's broom (*Ruscus aculeatus*), rustyback (*Ceterach officinarum*) and many others.

About 50 forest and shrub communities were recorded in the area of Đerdap. Extremely valuable for science and education are the relic forest communities such as: *Fago-colurnetum mixtum*, *Querco- colurnetum mixtum*, *Fraxino colurnetum mixtum*, *Syringo-colurnetum mixtum* and *Celto-Juglandetum*. These are rich, mixed structural communities which count more than 20 species of trees and shrubs in size of half a hectare, with over a hundred herbaceous plants species, mosses, ferns and fungi. These communities on limestone rocks usually have one or more tertiary relic species and they are by their characteristics nearest to ancestry, tertiary forest communities from which modern forest communities were originated.

The relic polydominant communities, i.e. *Fago-colurnetum mixtum* have different tree species: beech (*Fagus moesiaca*), sycamore (*Acer pseudoplatanus*), Montpellier maple (*Acer monspessulanum*), field maple (*Acer campestre*), white and black ash (*Fraxinus excelsior* and *F. ornus*), common hornbeam (*Carpinus betulus*), oriental hornbeam (*Carpinus orientalis*), silver linden (*Tilia tomentosa*), hazel *Corylus colurna*, walnut (*Juglans regia*), Austrian oak (*Quercus cerris*) and others.

Writing about his impressions from the Iron Gates Gorge, the famous Soviet scientist Gorišina says: "This area is rich in varied vegetation with preserved relic communities. In favorable climate conditions, with a lot of warm and sunny days, preservation of these forests was enabled with mezzo-climate tempered by the wide, sheltered bays between high rocks above the Danube. In some places the forest goes down to the Danube. They have preserved many rare, endemic and relict species: *Corylus colurna*, *Juglans regia*, *Celtis australis* and more. The most widely distributed associations *Fago-colurnetum mixtum* (subassociation *juglandetosum*) which is characterized by polidominant species (10 to 20 species) and complex structure. Small fragments of thermophilic association *Siringo-colurnetum mixtum* have been preserved as well..."[9].

Inversion of vegetation in Đerdap and many other gorges and canyons of Eastern Serbia is manifested with mesophilic communities in the lowest parts and with thermophilic communities in the highest parts. Cold air in these habitats descends from the higher parts of the slopes to the bottom of the gorge and thus modify the climate. Therefore, highly mountain species grow down to the cold and wet gorges, while thermofilic species of low areas inhabit illuminated habitats along the periphery of the gorge. Beside temperature, relative humidity of air is very important in these habitats, being higher at the bottom than to the higher parts of gorge. Similarly, carbon dioxide concentration is higher close to the bottom. Talus material that comes down the mountain side is deposited on the bottom. In sheltered areas of gorges, there is a low impact of wind, frost and drought[9].

More than 200 bird species inhabit area of the National Park, among which 130 species are nesting species. This area is marked as International IBA area with many rare and endangered species recorded: golden eagle (*Aquila chrysaetos*), snake eagle (*Circaetus gallicus*), white-tailed eagle (*Haliaeetus albicilla*), black stork (*Ciconia nigra)*, grey heron (*Ardea cinerea*) etc. There are also many mammals, with around 50 species recorded: brown bear (*Ursus arctos*), lynx (*Lynx lynx*), jackal (*Canis aureus*), otter (*Lutra lutra*), wild pig (*Sus scrofa*), deer (*Cervus elaphus*), roe deer (*Capreolus capreolus*), chamois (*Rupicapra rupicapra*) etc. The most interesting and the most diverse is fauna of insects, but it is still insufficiently examined[57,74-80]. Research of entomofauna of the whole region of the National Park is missing, bearing in mind that only scarce data are available[81].

THE SPECIAL NATURE RESERVE "ZASAVICA"

In the Zasavica Reserve, according to the available data until to the end of 2014, there were 280-310 species of fungi recorded[82]. There are eight species marked on the Red list of fungi in Europe, while species *Geastrum nanum* is in category B, because its number is decreasing all over Europe or it might be eradicated[83]. There are 46 species of *Bryopsida* in the Reserve, what is about 10.45% of the whole *Bryopsida* fauna of Serbia[84]. On the Red list of mosses and liverworts of Serbia and Montenegro, being endangered according to IUCN from 1994 there are five species: one, *Callicladium haldanianum* – endangered (EN), three species depend of protection (*Brachythecium oxycladum, Isopterygiopsis pulchella, Syntrichia papillosa*) (LR) and one species (*Hypnum fertile*) in DD category[85].

Flora of the Zasavica Reserve counts 650 plant species[86] of which 128 are on the European Red List[87]. Important species from the list are: *Aldrovanda vesiculosa*, globally endangered species with the only one habitat known inside this Reserve (CR A4; B1ab, B2ab)[88]. This species is on the list of HABITAT EU, together with the species *Galanthus nivalis*. Species *Trapa natans* is the relic species with the status of almost endangered species in Europe (LRnt), as well as the rare species *Cyperus michelianus,* which is an indicator species for 3130 priority species of NATURA 2000 habitats[82]. There are also eight plant species (*Aldrovanda vesiculosa. Hippuris vulgaris,* *Hottonia palustris, Urtica kioviensis, Ranunculus lingua, Scirpus triqueter, Stratiotes aloides, Utricularia australis*) which are on the European Red List of priority species for NATURA 2000[86]. From the European Red List, 43 plant species are the indicator species for priority NATURA 2000 habitats[82]. Bulrushes and floating islands are inhabited with the relic species *Urtica kioviensis* and *Schaenoplectus triqueter,* for which this part of Serbia has been the southern border of its distribution[83]. Rare sub-endemic Pannonian species *Achillea asplenifolia* has been found in the wetland of Reserve, and this is known as the southern border of its distribution.

The fern species *Dryopteris carthusiana* is characteristic for the Illyrian maple and oak forests. Two species (*Urtica kioviensis* and *Lindernia procumbens*) are proposed for the second edition of the "Red list of the flora of Serbia"[90]. The species *Viola elatior* is on the European Red List as the endangered species. Forest vegetation consists of various hydrophilic tree species - narrow-leafed ash, mixed with poplars, willows and black alder. The overall forestation of the reserve is 16.74%[91].

There were three species of slugs recorded in the Reserve, and *Tandonia kusceri* is endemic species for Balkan[92]. According to Šćiban et al.[93], there were 68 butterflies species recorded in Zasavica, among which 53 ones are on the European Red List with status LRlc[94]. Three species (*Nymphalus vaualbum, Zerynthia polyxena* and *Lycena dispar*) are on the list of priority species HABITAT Directive EU[95], with species *Lycena dispar* being on the list of priority species NATURA 2000[86]. This is why the Zasavica Reserve is, according to the European convention for butterflies, among 40 areas important for daily butterflies in Serbia[69]. In sampled pool of night butterflies, there was species *Orbona fragariae* recorded for the first time for Serbia[78]. There is a total number of 39 species of Odonata in Reserve[96] comprising 60% of all species of odonata in Serbia with each species on the European Red List with status LRlc[97]. Species *Gomphus flavipes* is on the list of priority species HABITAT directive EU[95] while for species *Epitheca bimaculata,* which was considered as eradicated in Serbia, this Reserve is one of the last habitats in Serbia[98]. There are 31 species of ants recorded in Reserve what makes 1/5 of all known ant fauna of Serbia and species *Bothriomyrmex communistus* was for the first time recorded in Serbia[99]. Among beetles (Coleoptera) which are on the European Red List, there were 16 species recorded, belonging to families: Cerambycidae 9 species; Cetoniidae 3 species; Lucanidae two species and Elateridae and Bostrichidae with one species each[100]. In family Cerambycidae, there were more than 30 species recorded in the Reserve, among which nine species are on the European Red List, seven with status LRlc and two marked as LRnt. The species *Cerambyx cerdo* is on the list of priority species HABITAT directive EU[95]. There are rare species of long horn beetles: *Pilemia tigrina*, *Agapanthia cynarae*, *Lampropterus femoratus*, *Cyrtoclytus capra*, *Agapanthiola leucaspis* with endemic *Stenopterus similatus*[101]. In the family Cetoniidae there were six recorded species[102,82], among which three are on the European Red List: *Osmoderma eremita* (LRnt), *Protaetia cuprina* and *Valgus hemipterus* (LRlc); the first named is on the list of priority species HABITAT directive EU[95]. In family Elateridae there was only one species *Ampedus sanguinolentus* recorded so far, and it is on the European Red List with status LRlc. There were two species recorded belonging to family Lucanidae: *Lucanus cervus* and *Dorcus parallelopipedus*[102,82] which are both on the European Red List. Species *D.*

parallelopupedus is with status LRlc, while *L. cervus* is with status LRnt and it is on the list of priority species HABITAT directive EU[95] as well as it is on the list of priority species NATURA 2000[86]. In family Bostrichidae there was only one species registered, *Bostrichus capucinus*, which is on the European Red List with status LRlc. In the family Curculionidae, there were 86 species recorded among which there were seven species for the first time recorded in Serbia[103]. In the family Carabidae there were 72 recorded species with *Pterostichus (Bothriopterus) quadrifoveolatus* being new for fauna of Serbia[104].

The endemic species of cricket *Zeuneriana amplipennis* was recored in Reserve after more than 30 years brake[105]. According to Skejo & Stanković[106], there were 51 species of Orthoptera in total, among which nine species are on the European Red List: two species (*Barbutustes serrucauda* and *Leptophyes duscoudalus*) with status LRnt, two with status CR (*Pachytrachis gracilis* and *Poecilimon fussii*), three with status LRlc (*Conocephalus dorsatus, Poecilimon schmidtii* and *Ruspolia nitidula*), one DD species (*Phaneroptera nana*) and one EN (*Pholidoptera frivaldskyi*).

Fauna of aquatic Adephaga consists of 47 species among which seven species were not known in Serbia so far. Record of species *Graphoderus bilineatus* is a confirmation of existence of this species in Serbia since it was not recorded more than 30 years and it was only known from literature citations[107,95]. In the most part of Europe this species is close to eradication and it is on every European list of protected nature[108]. This extremely rare species present in Reserve witnesses about high quality of aquatic animals communities in Zasavica[95].

Fauna of terrestrial and freshwater snails according to Karaman[109] consists of 37 species with 24 amphibian and 13 terrestrial species. On European Red List there are 14 species in total with one species with status LRnt and 13 with status LRlc[110]. Slugs are represented by 3 species which are endemic for Balkan. In the fauna of Arachnida, there were 104 species recorded, with eight new records for Serbia, while species *Hipsosinga heri* was recorded for the second time[111]. First record of this species was in Belgrade in 1907. Two spider species (*Cyclosa oculata* and *Dolomedes fimbriatus*) are on the European Red List[112].

In the Zasavica Reserve, there were 23 species of fish, according to Bajić i Stanković[113], among which 15 species are on the European Red List with two species with status VU (*Umbra krameri, Cyprinus carpio,* VU-A2ce)[114]. Four species (*Umbra krameri, Cobitis taenia, Misgurnus fossilis, Rhodeus sericeus*) are on the list of priority species HABITAT directive EU[95] while three species (*Umbra krameri, Carassius carassius, Tinca tinca*) are on the list of priority species NATURA 2000[86]. It is important to mention that Zasavica is one of two remaining habitats of mudminnow and that its population is highly endangered[115].

Herpetofauna of Reserve consists of 14 species and varieties[116]. On European Red List there are 11 species, among which nine species are with status LRlc and two with status LRnt[117]. Nine species (*Emys orbicularis, Coronella austriaca, Coluber caspius, Natrix tesselata, Elaphe longissimus, Lacerta agilis, L.viridis, Podarcis muralis, Testudo hermannii*) are on the list of priority species HABITAT directive EU[95] while two species (*Emys orbicularis* and *Elaphe longissimus*) are on the list of priority species NATURA 2000[86]. There were also two endemic species for Balkan: *Vipera berus bosniensis* and *Lacerta agilis ssp. bosnica*. Boreal elements in Mačva have relic character as they represent remnants from the early Holocene and Pleistocene. This is why the only poisonous snake is present in region of Posavina, *V. berus*, which has a relic character. Beside it, in the Reserve black melanistic subspeciacia *V. berus bosniensis* was identified[116].

Batrahofauna of Reserve consists of 13 species in total[116], of which the European Red List includes 12 species. A total number of 11 species have the status LRlc and one species has the status LRnt[118]. Eight species (*Bombina bombina*, *Bufo viridis*, *Hyla arborea*, *Pelobates fuscus*, *Rana dalmatina*, *R. ridibunda*, *R. lesson* and *Triturus dobrogicus*) are on the list of priority species HABITAT directive EU[95] while four species (*B. bombina*, *H. arborea*, *P. fuscus*, *T. dobrogicus*) are on the list of priority species NATURA 2000[86]. Species *T. dobrogicus* is sub-endemic species for Balkan, to whom the southern border of areal distribution is the Zasavica Reserve with the river Sava is a natural border.

Ornithophauna of the Reserve consists of 198 species of birds Šćiban et al. [119], of which 186 species are on the European Red List: 178 species have the status LRlc, 6 species are LRnt and two additional species have the status VU and EN. Regarding the list of important species at the level of Europe, the status SPEC 1 has 6 species, SPEC 2 16 species of birds. The highest value of ornithofauna reserve and IBA Zasavica is the population of the species *Aythya nyroca*, which is 4.74% of the national population, while the area of the Zasavica Reserve covers 0.054% of the territory of Serbia. This species is globally endangered and its populations distinct all over the world[120].

Teriofauna of the Zasavica Reserve has 65 species of mammals (67.71% of the mammals fauna of Serbia), of which 60 species belong to different IUCN categories of threat. In the area of Zasavica in 2004, European beaver is reintroduced from the wider area of Bavaria. Records of threatened mammal species at European and/or national level make Zasavica an important area for preservation and protection of mammal species[121].

Hydrobiological research reveals that in the Zasavica waters live 5 species of Amphipods. Three species of *Hydrachnidia* are also recorded, of which some are real troglophiles. There are presented Pontocaspian and Central- and South-European elements[122]. *H. geographica* is the first record for the fauna of Serbia, and *H. crassipalpis* is the first record for the fauna of the Balkan Peninsula[123]. Out of 350 species of algae, algae *Tolipella intricata (Charophytha)* and *Nitella confervacea* are new species for Serbia, while the species *Tolypella prolifera* is new for the Balkan[124]. Among 190 species of zooplankton *Rotatoria* 11 species are new for Serbia and 5 are new for the Balkans[125]. Twenty three fish species live in the watercourse of Zasavica, of which 7 species are natural rarities and have the status of endangered species, while 5 species are vulnerable. Fauna of amphibians and reptiles is represented with 27 species among which 3 species are Balkan endemics, 17 species are natural rarities, two species are vulnerable, two endangered while only one species depends on protection. In the the ephemeral waters, the rare and endemic fairy shrimp *Chirocephalus brevipalpis* is recorded, and the Natural Reserve Zasavica represents the westernmost finding and the only one south from the Danube and Sava rivers. In the flooded forests and the riverbed of the river Batar, it is found a living fossil *Lepidurus apus*[126].

All previous researches indicate that the area of the Natural Reserve Zasavica is important for protection of national and interantional species and ecosystems diversity.

Hence, the area of Zasavica was designated as as Ramsar site (2008), Important Bird Area (IBA) (2000) and Important Plant Area (IPA) (nominated 2005)[127]. In 2001, Zasavica has become a member of the EUROPARC Federation.

THE IMPORTANCE OF NATURAL SCIENCE RESEARCH IN PROTECTED AREAS

Protected natural areas of the Republic of Serbia are structural and functional unity of living and inanimate nature, in which natural ecosystems of forest, rivers and lakes alternate with artificially created ecosystems as meadows, arable fields, orchards and fishponds. A dynamic balance of all members of the community is maintained by man who also defines their borders. Since living creatures do not know (artificially) created boundaries, and live in accordance only with natural, biological and ecological limitations, protected natural resources are specific reserves of preserved biodiversity and at the same time important ecosystems in which the nature, with all its members and relationships has been preserved to a greatest possible extent.

Man as the main organizer of the community in which he lives in, with his everyday activities, affects the wildlife in his own surrounding by changing habitats of many plant and animal species, thus influencing their abundance, distribution and significance.

Protected natural resources, as parts of preserved nature and biodiversity, may serve as secondary habitats of pest and/or potentially harmful species for agricultural production - crops, vegetables, orchards, vineyards, fishponds and meadows which are usually in nearby. Ruderal plants very often offer suitable conditions to be a shelter to many animal species, serving at the same time as potential resources of populations which, in certain circumstances can become abundant and significantly harmful for cultivated crops including domestic animals as well. Forest communities can be sources of food for many of these species during the whole year and can be of great importance for surviving during inappropriate living conditions in arable areas. Absence of chemical or similar treatments in protected areas decreases negative influence on animal populations which in such areas find suitable habitats with low predatory activities. Food chains in these areas have many members what decreases the pressure to a certain species. In such term, certain species have better chances to survive. This is more obvious in protected areas, because animals, in accordance with their inner voice and biology, search and migrate to more suitable areas, with less impact to its populations.

There are certain insect species, as wheat bugs, for example (Heteroptera: families Scutelleridae and Pentatomidae), which have two types of habitats during a year: arable fields in agrobiocenosis and mountainous ecosystems dominated by forests and pastures as vegetation types. In the first habitat they spend summer time, feeding on different kinds of cereals and making economic losses. Afterwards, they migrate to the second habitats, close to the forest in hilly areas where they spend winter diapause. These seasonal migrations of economically important species are witnesses about important movement of insects without any possible artificially made border. It is presumed that such behaviour is a kind of evolutionary acquired behaviour and that the named species originally lived on mountainous plants starting to migrate to a plenty of food founded in arable fields, as soon as agricultural production start to develop[128]. Many other animal species migrate to more natural habitats running away from negative influence of man like cutting woods, hunting, use of fire etc. Therefore, natural studies of protected areas are of great importance far beyond the physical boundaries of certain areas and represent significant contribution to the knowledge of the biology and ecology of species within the protected areas including their relationships and impact on seasonal dynamic. Altogether they affect ecosystems that surround them, while agricultural and livestock production areas are biocenosis in which impact of these fluctuations is the most significant.

CONCLUSION

Many plant and animal species change their habitats, behaviour and distribution in accordance to changes of their environment. Therefore, the importance of different kind of natural and scientific researches is great. Beside the scientific value, this knowledge can be of practical importance as well, bearing in mind that by prediction of population dynamic and distribution of pest species, some losses can be exceeded or at least decreased. Only integral approach in the research of natural environment and living beings in it may provide an insight into the natural relationships between plant and animal species, activities of natural enemies and measures which may be conducted without chemical treatment, with the aim to decrease pollution of natural environment. Excessive use of pollutants, industrial waste, pesticides and other agents significantly change the environment for flora, fauna and human population, who is the biggest enemy of the nature. The improvement of the natural habitats and return to the natural principles of life, man could provide to himself and generations to come better conditions for life and survival.

Therefore, the researches of protected natural areas are of multiple importances for many scientific disciplines, particularly biology, ecology, evolution, but also for agriculture, hydro economy, forestry etc.

Presented natural science research in protected areas are a good basis for design a unique and integrated platform, where the comparison of existing and possible results regarding the climate changes, antrophogene impact and other environmental impacts could be used for defining of marginal values of nature protection in the Republic of Serbia. A successful inventarization will complete the list of known living beings in protected areas of nature, and allow successful and sustainable protection in the future.

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Due to the paper length, the list of References will be provided on request from the corresponding author, or they can be found on the website, by following the link:
https://drive.google.com/file/d/0B1B4DwrgRK9mMUY4NTNTejhQdUE/view?usp=sharing

GEOPHYTES IN A FOREST FLORA RESERVE ZASAVICA

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ABSTRACT

The reserve has a total of 27 species were recorded geophita 6 subspecijacija, five of which are species protected by law, the two species are vulnerable to the CITES list. For two species (*Arum maculatum* and *Glechoma hederacea*) were found to be present in the whole reserve in all types of forests. The significant finds include four types geophita *Erythronium dens-canis* and *Isopyrum thalictrum* as mejzijski elements found in Batar, and two orchid species *Cephalanthera damasonium* and *Platanthera bifolia*. Some geophytes are recorded only once, at one site, with a small number of individuals. Generally most species geophita was found in the woods outside the flood zone and high groundwater or where they are present but do not stay long.

Key words: geophyts, Zasavica,plants,forest.

INTRODUCTION

Geophytes a life form perennial plants, which is characterized by unfavorable survival period in the form of underground organs (root, rice, tubers, bulbs) which are then protected in the soil. Unfavourable period is usually drought, but it can be cold. During favorable or favorable period of the year, geophytes develop overhead organs, stem and leaf, and reproductive organs (sporangia, flowers). Name geophytes used for all the species that have an underground stem. There are three types of underground stems which such species reproduce: bulb, tuber and rhizome. Geophytes is often called onion species, which is not entirely true since the bulbs only one of the types of underground stems. (Stevanovic,B.,Janković,M.,2001) In our many years of field research in forest reserve Zasavica according Raunkierov division plants on life forms, we have processed so far ascertained plant geophytes from the group cryptophytes (Janković,M., 1966) These plants are characterized by overwintering buds on the underground organs, which are deep in the ground while above-ground organs after flowering and fruiting - when for their performances unfavorable living conditions. In their underground organs, bulbs, rhizomes, in an underground stem and root tubers stored large amounts of nutrients spare materials and therefore these plants are able to bloom in early spring or even in the winter. The vegetation period of these plants is relatively short, and some with flowering start in the winter. (Obradovic,M. Budak,V., 1979) On the territory of the Zasavica Reserve and surrounding protected zone to 66 km of the coast has been allocated seven forest phytocoenoses (*Calamagrosti-Salicetum cinereae* Soo et Zólyomi.1955; *Populeto-Salicetum* Raj.1950 *subass. ruboetosum* Gajić.1954.,Tóth.1958).em. Erdeši.1971; *Genisto elateaec-quercetum* Horv.1938. *subass.Leucoio-fraxinetosum* Glav.1959; *Brachypodio silvaticae palustris Quercetum* Erdeši 1955; *Genisto elatae Quercetum* Horv.1938. *subass.Carpinetosum betuli* Vuk.1959; *Genisto elatae Quercetum* Horv.1938 *subass. alno-carpinetosum* Glavač.1961.em.Erdeši 1971; *Rusco aculeata-Tilio-Quercetum* Erdeši 1955) at an altitude of 76-84 meters above sea level.Total forest and forest land is 150.0491 hectares in reserve, of which 110 ha are arboriculture hybrid poplar. (Erdeši.J.,Janjatović,G.,2001)

MATERIALS AND METHODS

The inventory of herbarium material and field diary composed list geophita which are found in the forests of the reserve Zasavica as of 2014. For each type are given the following data: date, site, biotope, Legator./ Determined, inventory number in the herbarium, and if there is still some extra data. If the copy is in reservation collection is indicated by the Air Force with or without inventory number, in case the material is deposited in another herbarium collection is indicated BUNS (deposited in the Herbarium of the Department of Biology and Ecology, University of Novi Sad) or PHEJ (if deposited in the Herbarium of private Dr.Josip Erdeš). Plants geophytes are allocated to Šilić,Č.,(1988), Mišić,Lj.,Lakušić,D.,(1990), Obradović,M.,Budak,V.,(1979).

RESULTS AND DISCUSSION

In the reserve Zasavica in the surrounding protection zone so far established the following types of geophita at the following locations:

EQUISETATAE

Fam.Equisetaceae

1. *Equisetum palustre* L.:**Radenković**: Batar, forest-littoral,26.08.2005.,Leg./Det.: Stanković, M, /Perić, R.,HRZ

DICOTYLEDONEAE

Fam.Ranunculaceae

2. *Adonis aestivalis* L.: **Zasavica II:**Turske livade,margin forest, 04.05.2001.,Leg./Det.: Stanković, M.;Turske livade,forest, 04.05.2001.,Leg./Det.:Stanković,M,HRZ- inventory no. 1265; Turske livade,overgrown field with forest,05.05.2010.,Leg./Det.:Stanković,M.; Valjevac pasture, 30.04. 2002.,Leg./Det.:Stanković,M,HRZ-inventory no. 812; 30.04.2002., Leg./ Det.: Stanković,M.;18. 08.2002.,Leg./Det.:Stanković,M/Stojšić,V.,HRZ-inventory no. 186; **Radenković:** Vrbovac, margin forest,25.05.2004.,Leg./Det.:Stanković,M,HRZ-inventory no. 178; **Zasavica I:** Valjavac, pasture, 25.05 2004., Leg./Det.: Stanković,M, HRZ-inventory no. 810; 16.06 2005., Leg./Det.: Stanković, M,HRZ- inventory no.721;30.04 2002., Leg./ Det.: Stanković,M,HRZ- inventory no.15;01.05 2004., Leg./Det.: Stanković, M, HRZ- inventory no. 221;16;

3. *Adonis flammea* Jacq: **Zasavica II**: Turske livade,margin forest,04.05 2001., Leg./Det.: Župunski,B.,BUNS;

4. *Anemone rannunculoides* L.: **Radenković:** Batar,forest, 25.03.2001., Leg./Det.: Stanković, M,HRZ- inventory no.1098;25.05 2001.,Leg./Det.:Župunski,B.,BUNS; 10.04. 2006.,Leg./Det.: Stanković,M,HRZ-inventory no.515; 15.03.2014.,Leg./Det.:Stanković,M,; **Radenković:** Skelice, forest,11.04.2005.,Leg./Det.:Stanković,M,HRZ-inventory no.638; Vrbovac, forest, 14. 03.2014.,Leg./Det.: Stanković,M,;**Banovo Polje:** Batar, forest, 19.04. 2001., Leg./Det.: Stanković, M,HRZ- inventory no.1108;Batar -Crkvine, forest,25.04. 2004., Leg./Det.: Stanković,M,HRZ-inventoryno.833, 281;Trebljevine,forest, 10.04.2006.,Leg./Det.:Stanković, M.;**Noćaj:** Preseka, forest,17.03 2001.,Leg./Det.Erdeši,J.,PHEJ; **Salaš Noćajski:** Lug, forest, 04.04. 2012., Leg. / Det.:Stanković,M,

Variability: 5.1 *Anemone rannunculoides var.genuina*: **Radenković:** Batar, forest,25.03.2001., Leg./Det.:Stanković,M,/Perić,R.,HRZ

5. *Ficaria verna* Hudson. : **Radenković**: Batar, forest,25.03.2001.,Leg./Det.:Župunski,B., BUNS;28.02.2014.,Leg./Det.:Stanković,M.;Skelice,coppice,11.04.2005.,Leg./Det.: Stanković, M,HRZ- inventory no.637;15.03.2014., Leg./Det.:Stanković,M.; Vrbovac, dept.32-36, arboriculture, 11.04.2013.,Leg./Det.: Stanković, M.;Pačija bara, forest, 11.04.2006., Leg./Det.: Stanković,M,;**Salaš Noćajski:** Modran, forest,14.03.2012., Leg. /Det.: Stanković, M.;Ostrovac, forest,14.03.2012., Leg./Det.: Stanković, M.; Lug, forest, 04.04.2012., Leg./ Det.: Stanković,M.; **Noćaj:**Preseka, forest,17.03.2001., Leg./ Det.: Erdeši,J., PHEJ; **Banovo Polje:** Batar, forest, 25.03.2001.,Leg./Det.: Stanković, M,HRZ- inventory no.1110; **Zasavica II:** Turske livade, forest,25.03.2001.,Leg./Det.: Župunski, B.,BUNS;**Zasavica I:** Valjevac, forest, 07.04.2013., Leg./Det.:Stanković,M.;Šumareva ćuprija, arboriculture,14.04,2013., Leg./Det.: Stanković,M.; **Mačvanska Mitrovica:** Modran, forest,11.04.2006.,Leg./Det.: Stanković,M,

Variability: 5.1 *Ficaria verna ssp.bulbifera* (Albert)A&D.Löve : **Radenković:** Vrbovac, forest,10.03.2001.,Leg./Det.:Erdeši.J.,PHEJ

5.2 *Ficaria verna f.nigromaculata* (Schur)Nyár. : **Radenković**: Batar, forest, 28.02.2014.,Leg./Det.:Stanković,M.,HRZ; Skelice,coppice,15.03.2014.,Leg./Det.:Stanković,M.; **Banovo Polje:** Batar,forest,28.02.2014.,Leg./Det.:Stanković,M.; **Zasavica II:** Turske livade, forest, 01.04. 2015., Leg./Det.:Stanković,M

6. *Isopyrum thalictroides* L. : **Radenković:** Batar, forest,01 03.2007.,Leg./Det.:Stanković,M. HRZ-inventory no.233

Fam.Rubiaceae

7. *Asperula odorata* L. : **Crna bara:** Jovača, forest,11.09.1996.,Leg./Det.:Stanković,M,HRZ- inventory no.9

Fam. Oenotheraceae

8. *Circaea lutetiana* L. : **Ravnje:** Staniševac, forest,03.08.2004.,Leg./Det.:Stanković,M,/ Perić,R.,HRZ-inventory no.1425; **Crna bara:** Jovača, forest,19.08.2001.,Leg./Det.:Stanković,M, /Perić,R.,HRZ-inventory no.840,287;**Radenković:** Batar,forest,26.08.2005.,Leg./Det.: Stanković ,M,/Perić,R.,HRZ-inventory no. 1173; **Noćaj:** Preseka, forest,20.07.2001.,Leg./Det.:Erdeši,J., PHEJ; **Banovo Polje:** Trebljevine, forest,19.08.2001.,Leg./Det.:Županski,B.,BUNS

Variability: 8.1 *Circea lutetiana f.luteci* : **Ravnje:** Bostanište, forest,24.07.2000.,Leg./Det.: Stanković,M,/Perić,R.,HRZ-inventory no.1305,255;Staniševac,forest,07.08.2004.,Leg./Det.: Stanković,M,/Perić,R.,HRZ-inventory no. 113

Fam.Papaveraceae

9. *Corydalis cava* (L.)Schweigg&Körte : **Radenković:** Batar, forest,25.04.2000.,Leg./Det.: Stanković,M.,HRZ-inventory no.1151; 27.03.2005.,Leg./Det.:Stanković,M.,HRZ-inventory no. 625; 10.04.2006., Leg./Det.: Stanković,M., HRZ-inventory no.514;Poljane, forest, 27.03.2005., Leg./Det.:Stanković,M.,HRZ-inventory no. 626; **Noćaj:** Cerik, forest,27.03. 2005., Leg./Det.: Stanković,M.,

Fam.Lamiaceae

10. *Glechoma hederacea* L. : Type is present in all forest ban on the reservation and protection zone during all the years of research

Variability: 10.1 *Glechoma hederacea ssp.hederaceum var.micranthum (=syn. G. hederacea var. micrantha* : **Radenković:** Baščine,forest,15.04.2001.,Leg./Det.:Erdeši,J.,PHEJ; **Salaš Noćajski:** Modran,forest,28.04.2001.,Leg./Det.:Erdeši,J.,PHEJ

Fam.Scrophulariaceae

11. *Lathraea squamaria* L. : **Ravnje:** Staniševac, forest,2006., Leg./Det.:Stanković,M.

MONOCOTYLEDONEAE

Fam.Araceae

12. *Arum alpinum* Schott et Kotschy : **Radenković:** Pačija bara,21.03.1999., forest, Leg./ Det.: Stanković,M.;Batar,19.01.2007.,forest, Leg./Det.:Stanković,M.,HRZ-

inventory no. 230; Vrbovac,forest,15.03.2014.,Leg./Det.: Stanković, M.; **Zasavica II:** Turske livade, forest, 09.04. 2010.,Leg./Det.:Stanković,M.; **Zasavica I:** Valjevac, forest,09.04.2010., Leg./Det.: Stanković, M.; **Salaš Noćajski:** Ostrovac-Lug, forest, 14.03. 2012., Leg./Det.: Stanković,M.; Ostrovac, forest,04.04.2012.,Leg./Det.:Stanković,M.; **Ravnje:** Zovik, forest,06.01.2014., Leg./Det.: Stanković,M.; **Crna bara:** Jovača, forest,15.02.2014., Leg./ Det.:Stanković,M.; **Banovo Polje:** Prekopac,forest,15.02.2014., Leg./Det.: Stanković,M.; Batar, forest,28.02. 2014., Leg./Det.: Stanković,M

13. *Arum maculatum* L. : Type is present in all forest ban on the reservation and protection zone during all the years of research

Fam.Liliaceae

14. *Colchicum autumnale* L.: **Noćaj:** Preseka, forest,15.06.2001., Leg./Det.:Erdeši,J.,PHEJ

15. *Convalaria majalis* L. : **Zasavica II:** Turske livade, forest,14.04.2001.,Leg./Det.: Stanković, M,/Perić,R.,HRZ-inventory no.1425; 17.04.2001.,Leg./Det.:Stanković,M,/Perić,R.,HRZ-inventory no.31.; 17.04.2001.,Leg./ Det.:Župunski,B.,BUNS; **Radenković:** Batar, forest, 25.04. 2000.,Leg./Det.:Stanković,M,/Perić,R.,HRZ-inventory no.1039.; 25.04.2000.,Leg./Det.: Stanković,M,HRZ-inventory no.1133.;19.04.2001.,Leg./Det.:Župunski, B.,BUNS;**Banovo Polje:** Batar-Vrtače,forest,29.04.2001.,Leg./Det.: Stankvić, M,HRZ-inventory no.1040.;**Noćaj:** Preseka, forest,14.05.2001.,Leg./Det.: Erdeši,J.,PHEJ

16. *Erythronium dens-canis* L.

Variability: 16.1.*Erythronium dens-canis f. niveum* : **Radenković:** Batar, forest,21.02. 2007.,Leg. /Det.:Stanković,M.,HRZ-inventory no.231

17. *Gagea lutea* (L.)Ker-Gawl. : **Radenković:** Baščine, forest,09.03.2001.,Leg./Det.: Erdeši. J., PHEJ.; Poljane, forest,11.04.2006.,Leg./Det.:Stanković,M.,HRZ-inventory no .511; Batar, forest,28.02.2014.,Leg./Det.:Stanković,M.; **Crna bara:** Jovača,rub forest, 05.09. 1997., Leg./ Det.:Stanković,M.,HRZ-inventory no.173, 1255

18. *Gagea pratensis* (Pers.)Dumort. : **Banovo Polje:** Trebljevine,forest,01.04.2004.,Leg./ Det.: Stanković,M.,HRZ-inventory no. 1401

19. *Gagea pusilla* (Schm.) J.A.et J.|H.Schult : **Noćaj:** Lug, forest edges and gaps,26.02.2014., Leg./Det.:Stanković,M.,

20. *Scilla bifolia* L. : **Salaš Noćajski:** Lađine, forest,13.03.2002.,Leg./Det.:Stanković,M., HRZ-inventory no.102; **Radenković:** Baščine, forest,09.03.2001.,Leg./Det.:Erdeši,J.,PHEJ; **Noćaj:** Preseka,forest,09.03.2001.,Leg./Det.:Erdeši,J.,PHEJ; **Crna bara:** Parašnica,forest,23.02.2008., Leg./Det.:Stanković,M.; **Ravnje:** Zovik, forest, 29.03.2008., Leg. /Det.: Stanković, M.,

Fam.Amararyllidaceae

21. *Leucojum aestivalum* L. : **Zasavica I:** Valjevac, forest,27.04.2006.,Leg./Det.: Stanković, M.,HRZ-inventory no.507.;10.04.2010.,Leg./Det.:Stanković,M.;**Salaš Noćajski:** Lađine, forest,04.05.2001.,Leg./Det.:Stanković,M.; Krivaja,forest,14.04.2001.,Leg./Det.:Erdeši,J., PHEJ
22. *Galanthus nivalis* L. : **Noćaj:** Preseka, forest,09.03.2001., Leg./Det.:Erdeši,J.,PHEJ;Lug, forest,26.02.2014., Leg./Det.: Stanković,M.; **Radenković:** Batar, forest,01.03.2007., Leg./ Det.: Stanković,M.,HRZ-inventory no. 232;15.03.2014.,Leg./Det.:Stanković,M.; Vrbovac, forest,15.03.2014.,Leg./Det.:Stanković, M.; Vrbovac 33 odel.,arboriculture hybrid poplar, 15.03.2014.,Leg./Det.: Stanković, M.; **Ravnje:** Batve, forest, 26.02. 2014.,Leg./ Det.: Stanković, M.; **Zasavica II:** Turske livade, forest,12.04.2014., Leg. /Det.:Stanković,M.,

Fam.Orchidaceae

23. *Cephalanthera damasonium* (Mill.)Druce : **Banovo Polje:** Prekopac,forest-littoral, 25.07. 2003.,Leg./Det.:Perić,R.,BUNS

24. *Platanthera bifolia* (L)L.C.Rich : **Salaš Noćajski:** Modran,forest,20.04.2001.,Leg./Det.: Erdeši,J.,PHEJ

Fam.Asparagaceae

25. *Polygonatum latifolium* (Jacq.)Desf. : **Zasavica II:** Turske livade,forest,04.05.2001., Leg./Det.:Stanković,M.,HRZ-inventory no.389;17.04.2001.,Leg./Det.:Župunski,B,BUNS; **Salaš Noćajski:** Sadžak,forest,26.07.2003.,Leg./Det.:Stanković,M.; **Noćaj:** Preseka, forest,14.05. 2010.,Leg./Det.:Stanković,M.;Leskovik,forest,18.05.2001.,Leg./Det.:Erdeši,J.,PHEJ

Fam.Dioscoreaceae

26. *Tammus communis* L.: **Zasavica I:** Valjevac,forest,25.09.1996., Leg./Det.: Stanković, M., HRZ-inventory no. 48.; 30.05.2006.,Leg./Det.:Stanković,M.,HRZ-inventory no.384.; **Zasavica II:** Turske livade, forest, 04.05.2001.,Leg./Det.: Župunski, B.,BUNS; forest, 04.05.2001., Leg./ Det.:Stanković,M.,HRZ-inventory no.72;**Radenković:** Batar,forest 25.04.2000.,Leg./Det.: Stanković,M.,HRZ-inventory no.1130;06.05.2000.,Leg./Det.: Stanković,M., HRZ-inventory no.1111; **Banovo Polje:** Jovača, forest,30.05.2001.,Leg. /Det.:Župunski,B., BUNS

Fam.Iridaceae

27. *Crocus sp.*: **Radenković:** Poljane,forest,01.04.2006.,Leg.:Stanković,M.,HRZ-inventory no.324

A total of 27 species were recorded geophita 6 subspecijacija. From a total of 28 species, five species are protected by law, the two species are vulnerable to the CITES list. Two species (*Arum maculatum* and *Glechoma hederacea*) are present on the entire reserve in all forest types and three species were recorded at over 10 sites. The significant finds include four types geophita *Erythronium dens-canis* and *Isopyrum thalictrum* as elements mesiae region, and both types are found in Batar in part of the forest with old oak trees, as well as two types of orchid *Cephalanthera damasonium* and *Platanthera bifolia* were found at one site in 2001 and 2003 respectively .god. Discovered orchid *C. damasonium* was to contact the forest *Populeto-Salicetum* Raj.1950. s*ubass.Ruboetosum* Gajic.1954.Tóth1958).em.Erdeši 1971 with reeds. The largest number of findings at the site of Batar and then Turkey meadows while at nine sites we have one finding. During field work in the recording geophita were recorded and the number of animals at the site, which was expressed through the number of individuals counted or percentage coverage of the surface.The largest number of individuals counted was 2014.Vrbovcu to 1000 individuals species *A.ranunculoides* on the surface of 5x4 and 500 individuals species *Galanthus nivalis* on the same site, the same year. Early in the spring the forest floor in all forests except community *Calamagrosti-Salicetum cinereae* Soo et Zólyomi.1955 covered with certain kinds of geophytes. The highest coverage we had 2012. in the forest at the site of Lug, with 80% coverage of the soil in the entire forest with the species *Ficaria verna*, and at the site Valjevac forest species had the same coverage of 70% of the arable soil in 2013 throughout the forest. Some geophytes are recorded only once, at one site,and they are: *A.flammea, C.damasonium, C. autumnale, E. palustre,E.dens-canis,I.thalictrum,G.pratensis,G.pusilla,L.squamara* and *P. bifolia* with a small number of individuals. Generally most species geophita found in forests *Brachypodio silvaticae palustris Quercetum* Erdeš 1955; *Genisto elatae Quercetum* Horv. 1938 *subass. Carpinetosum betuli* Vuk. 1959; *Genisto elatae Quercetum* Horv.1938.*subass.alno-carpinetosum* Glavač.1961. em.Erdeši.1971; *Rusco aculeata-Tilio-Quercetum* Erdeši.1955) followed arboriculture hybrid poplar while the smallest number of species found in the forests *Calamagrosti-Salicetum cinereae* Soo et Zólyomi.1955 and *Populeto-Salicetum* Raj.1950 *subass. Ruboetosum* Gajić. 1954.,Tóth1958).em.Erdeši in 1971.

CONCLUSION

The reserve has a total of 27 species were recorded geophita 6 subspecijacija, five of which are species protected by law, the two species are vulnerable to the CITES list. For two species (*Arum maculatum* and *Glechoma hederacea*) were found to be present in the whole reserve in all types of forests. The significant finds include four types geophita *Erythronium dens-canis* and *Isopyrum thalictrum* as meisis elements found in Batar, and two orchid species *Cephalanthera damasonium* and *Platanthera bifolia*. The largest number of findings at the site of Batar and Turkey meadows. The largest number of individuals counted was 2014. Vrbovcu to 1000 individuals species *A.ranunculoides* on the surface of 5x4 and 500 individuals species *Galanthus nivalis* on the same site, the same year, when we had the highest coverage of 2012.. Lug on the site where there was a 80% coverage of the soil in the entire forest with the species *Ficaria verna*, and at the site Valjevac forest species had the same coverage of 70% of the arable soil in 2013 throughout the forest.Some geophytes are recorded only once, at one site, with a small number of individuals. Generally most species geophita was found in the woods outside the flood zone and high groundwater or where they are present but do not stay long.

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ACTIVITY LEVELS OF ^{137}Cs IN DIFFERENT FUNGI SPECIES IN SERBIA IN THE PERIOD 1999-2013

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ABSTRACT

In the period 1999 to 2013 the following samples were analyzed: 13 fresh *Calocybe gambosa* samples, 16 fresh *Amanita caesaria* samples, 15 black and 21 white fresh truffle samples, 11 fresh samples of *scotch bonnet*, 21 fresh *Lactarius deliciosus* samples, 38 *Lactarius deliciosus* samples in brine solution, 59 samples of dried morel and 98 samples of dried *Craterellus cornucopioides*. The results obtained in this work lead to the conclusion that in the period from 1999 to 2013 the activity levels of ^{137}Cs in fungi reduced indicating lowering of pollution of woodland ecosystems with radiocesium. It is our task to monitor radioactivity in woodland products used for human consumption and also ecosystems where they grow and analyze ^{137}Cs sorption in different fungi species.

Key words: ^{137}Cs, fungi, ^{137}Cs sorption.

INTRODUCTION

Fungi are one of the most significant bioindicators of environment pollution with radionuclides and heavy metals from different land ecosystems[1-5]. High activity values of ^{137}Cs measured in edible mushrooms indicated a potential direct danger for human consumers of forest mushrooms that could indirectly increase through consumption of wild game that injested mushrooms. Immediately after the Chernobyl accident (April 1986) the regulatory commission of the European Union adopted Rule number 737/90 establishing the maximally allowed levels of radiocesium in groceries imported from the so-called "third countries". According to this rule the maximally allowed level of radiocesium in groceries is 370 Bq/kg for milk, milk products and baby food and 600 Bq/kg for all other groceries[6]. In the last few years many groceries have been exempt from this rule, but not fungi as the levels of radiocesium still remain high in them so this rule still applies.

In our previous work we presented activity levels of ^{137}Cs in boletus and chanterelles analyzed in the period 1999 to 2013 intended for export and collected on the territory of Serbia. Investigations showed that twenty seven years after the Chernobyl accident ^{137}Cs was still present[7]. As different fungi species adopt different levels of ^{137}Cs in this work we have presented activity levels of ^{137}Cs in: *Calocybe gambosa*, *Amanita caesaria*, truffle, *Lactarius deliciosu*s, *Marasmius oreades*, *Morchella conica* and *Craterellus cornucopiodes* edible mushrooms, also collected on the territory of Serbia between 1999 and 2013 and intended for export.

Calocybe gambosa is an edible fungi found from the end of March until May, on the edges of woods, in grass and in groves. It is used fresh and frozen. ***Amanita caesarea*** grows in deciduous, coniferous and mixed forests in the summer and during warm Autumn days. According to their colour **truffles** are divided into ***Tuber magnatum*** – white and ***Tuber aestivum*** – black. They are mycorrhizas (have subterraneous bearing meaty bodies, usually an irregular rounded shape) and only develop if they live in symbiosis with trees. During ripening they release an odor enabling animals to find them (pigs, dogs). They have an exceptional taste and medicinal properties. ***Lactarius deliciosus*** is an edible and very tasty mushroom. Its flesh has a pleasant smell and its milk is carrot colored, later becoming grey-green. It grows on limestone soil from July to October. **Scotch bonnet** (***Marasmius oreades***) grows in grass on meadows and wood clearings in large circles from lowland to mountains all year round and appears a few days after stronger rainfall. It is used fresh and dried. **Morel** (***Morchella conica***) is one of the most tasty mushrooms that grows between March and May in deciduous and spruce forests, in parks, on river banks and coppices. This type of mushroom contains high antioxidant levels. ***Craterellus cornucopioides*** is one of the best mushrooms with a sweetish taste and aroma. It grows scattered and in clumps that are sometimes large on damp and muddy ground in deciduous and mixed forests. It appears between August and November[8].

MATERIAL AND METHODS

Samples collected on the territory of Serbia and intended for export in the period from 1999 to 2013 of the following mushrooms were analyzed: *Calocybe gambosa*, *Amanita caesaria*, truffle, *Lactarius deliciosus*, scotch bonnet, morel and *Craterellus cornucopioides*. Gamaspectrometric measurements were until 2002 measured on a NaI detector ORTEC-CANBERRA efficiency 8.7% and resolution 6.7% for ^{137}Cs at 661.6 keV, and from 2002 on a HPGe ORTEC/Ametek detector with 8192 channels, resolution 1.65 keV and relative efficiency of 34% at 1.33 MeV for ^{60}Co. Samples were cleaned from visible impurities (soil, grass) and measured in 1L Marinelli vessels. The measuring time for one sample was 3600s. The relative error of sample preparation and measurement was up to 10%. Spectra analysis was performed using the Gamma Vision 32 software package. Activity levels of ^{137}Cs were determined using the γ-line at the energy of 661.6 keV.

RESULTS AND DISCUSSION

In the period between 1999 and 2013 the following samples were analyzed: 13 fresh *Calocybe gambosa* samples, 16 fresh *Amanita caesaria* samples, 15 black and 20 white fresh truffle samples, 11 fresh samples of scotch bonnet, 21 fresh *Lactarius* *deliciosus* samples, 38 *Lactarius deliciosus* samples in brine solution, 59 samples of dried morel and 98 samples of dried *Craterellus cornucopioides* (Table 1).

In all of the 292 analyzed samples, the presence of ^{137}Cs was confirmed, that verifies the conclusion reached in our previous publication[7] that this isotope is widely distributed in our country after the Chernobyl accident in 1986.

As in this work we have determined the activity levels of ^{137}Cs in 8 fungi species, and in our previous paper for two more species (boletus and chanterelles) and in all individual fungi samples the presence of ^{137}Cs was established, it can be concluded that all fungi species will accumulate this isotope. This means that fungi can be an indicator of the presence of ^{137}Cs on a certain territory, regardless of species, that increases possible pollution control of land with this isotope.

Activity levels of ^{137}Cs in dried mushrooms, morel and *Craterellus cornucopioides* are significantly higher than in fresh samples, in accordance with the results obtained in our previous paper for boletus and chanterelles[7]. It is the consequence of reduced moisture content in the mushroom and not reduction of accumulated ^{137}Cs.

Based on the range of average yearly activity levels of ^{137}Cs, i.e. the lowest and highest values for each analyzed mushroom, they can be grouped into two groups according to their range width. Based on data given in Table 1 and data from our previous publication[7], for boletus and chanterelles, the first group contains *Calocybe gambosa*, *Amanita caesaria*, black and white truffle, where the range of average yearly activities of ^{137}Cs is 0.15-7.3 Bq/kg. The second group consists of scotch bonnet, *Lactarius deliciosus*, boletus and chanterelles where the widest range is 3.0-43 Bq/kg (for boletus 3.6-25.9, and for chanterelles 4.1-18.6 Bq/kg)[7]. There could be two basic reasons for these two groups. The first is lower pollution of the soil where they grow, while the second is the dependence of ^{137}Cs sorption on the fungi species. This second reason is significant as it indicates fungi species more inclined to ^{137}Cs accumulation compared to other species, and thus less suitable, i.e. recommended for human consumption.

The obtained average activity levels of ^{137}Cs for dried morel and *Craterellus cornucopioides* (Table 2) that are in the range 44.9-267 Bq/kg for morel and 0.2-142 for *Craterellus cornucopioides* also indicate different amounts of sorbed ^{137}Cs in different fungi species. Similar differences were also determined for dried chanterelles and boletus in our previous paper[7], in the range 41.6-312 Bq/kg for chanterelles and 45.9-103 Bq/kg for boletus. As these are dried mushrooms these differences, besides the above stated reasons valid for fresh mushrooms can also originate from different water content sorbed by different fungi species, i.e. sorbing ability. Different soil and air moisture and on the growth location also has an influence. Besides this, external water such as rain or snow water can act as a desorber.

Table 1. Average yearly activity levels of ^{137}Cs (Bq/kg), standard deviation and number of fungi samples (*Calocybe gambosa*, *Amanita caesaria*, black and white truffle, scotch bonnet, *Lactarius deliciosus* and *Lactarius deliciosus* in brine solution) collected on the territory of Serbia in the period 1999 - 2013

Year	FRESH						IN BRINE SOLUTION
	Calocybe gambosa	***Amanita caesaria***	**Black truffle**	**White truffle**	**Scotch bonnet**	***Lactarius deliciosus***	***Lactarius deliciosus***
	Activity ± sd (Bq/kg) (sample no.)						
1999	---	7.3 ± 2.3 (3)	---	---	---	9.0 (1)	---
2000	---	---	---	---	26.0 ± 8.5 (2)	---	4.0 ± 1.1 (6)
2001	---	6.3 ± 1.5 (3)	---	---	27.0 ± 5.2 (3)	43.0 ± 0 (5)	4.0 ± 1.4 (2)
2002	---	6.0 (1)	---	---	21.2 ± 14.1 (4)	---	6.0 ± 1.4 (2)
2003	---	---	---	---	7.0 ± 1.4 (2)	---	3.8 ± 3.0 (5)
2004	---	1.1 ± 0.2 (5)	---	---	---	3.0 (1)	---
2005	1.0 ± 0 (5)	---	1.0 (1)	---	---	---	1.5 ± 0.6 (4)
2006	1.0 ± 0 (3)	2.0 (1)	3.6 (1)	0.4 (1)	---	30.5 ± 26.2 (2)	0.9 ± 0.2 (2)
2007	---	---	---	---	---	14.5 ± 20.3 (3)	4.5 ± 3.3 (3)
2008	0.15 ± 0 (2)	0.37 (1)	4.7 ± 1.5 (3)	2.6 ± 0.6 (2)	---	3.1 ± 4.5 (5)	---
2009	0.34 (1)	---	1.5 (1)	1.4 (1)	---	4.6 (1)	1.3 ± 1.3 (4)
2010	1.2 ± 0 (2)	---	0.5 ± 1.4 (2)	2.1 ± 0.4 (4)	---	14.6 ± 10.2 (4)	15.0 ± 7.1 (4)
2011	---	---	0.4 (1)	1.5 ± 0.1 (3)	---	---	1.9 ± 1.0 (3)
2012	---	1.8 ± 1.0 (2)	0.8 ± 0.3 (4)	1.1 ± 0.5 (6)	---	---	---
2013	---	---	0.7 ± 0.3 (2)	1.6 ± 1.4 (3)	---	---	1.3 ± 1.8 (3)
	13 samples	16 samples	15 samples	20 samples	11 samples	22 samples	38 samples

Table 2. Average yearly activity levels of ^{137}Cs (Bq/kg), standard deviation (sd) and number of samples of dried morel and Craterellus cornucopioides collected on the territory of Serbia, minimal (min) and maximal (max) activity values

Year	DRIED			
	Morel		***Craterellus cornucopioides***	
	Activity ± sd (sample no.)	**Min-max**	**Activity ± sd (sample no.)**	**Min-max**
1999	134 (1)	---	49.4 ± 33.8 (7)	10.0-94.0
2000	256 ± 276 (2)	134-451	72.1 ± 46.6 (9)	19.0-137
2001	267 ± 187 (7)	50-559	104 ± 79.7 (10)	12.0-242
2002	190 (1)	---	66.5 ± 92.2 (14)	7.0-348
2003	152 ± 150 (3)	9.0-308	92.0 ± 101 (10)	12.0-320
2004	52.6 ± 53.9 (7)	15.0-155	82.0 ± 106 (3)	12.0-204
2005	53.0 ± 45.5 (2)	35.0-71.0	60.3 ± 66.6 (8)	10.0-201
2006	112 ± 38 (3)	66.0-142	53.7 ± 38.9 (6)	4.0-105
2007	275 (1)	---	133 ± 41.9 (6)	72.0-192
2008	143 ± 119 (17)	18.0-430	66.3 ± 41.9 (3)	28.0-111
2009	123 ± 83.3(7)	20.0-217	142 ± 78.1 (6)	55.0-233
2010	44.9 ± 49.7 (2)	9.7-80.0	83.0 ± 53.2 (5)	44.0-153
2011	66.0 (1)	---	73.0 ± 45.0 (6)	12.0-103
2012	86.0 ± 57.2 (3)	26.0-140	20.2 ± 5.2 (5)	16.0-28.0
2013	169 ± 58.7 (2)	127-210	---	---
	59 samples		98 samples	

That is the consequence of the fact that activity levels of ^{137}Cs are reduced when storing mushrooms in brine solution (Table 2)[7]. The amount of desorbed ^{137}Cs this way will depend on the content of this water and on ^{137}Cs that may be present in it in accidental cases.

Based on all this, the key significance for ^{137}Cs sorption in fungi is establishing the influence of the fungi species on its sorption capacity and thus on the species suitability for utilization, primarily in nutrition.

The obtained data leads to the conclusion that in the period from 1999 to 2013 activity levels of ^{137}Cs in fungi reduced, leading to reduction of the pollution of woodland ecosystems with radiocesium. As removal of radioactivity in woodland and meadow ecosystems is not possible our responsibility is constant control of radioactivity in woodland products used for human consumption.

CONCLUSION

The results presented in this work indicate:

- That even twenty seven years after the Chernobyl accident ^{137}Cs is still present in fungi in Serbia and thus also in ecosystems where they grow,
- That fungi are unavoidable factors of radioecological investigations of woodland ecosystems,
- That monitoring of the environment using fungi is important for evaluation of radiation load of a certain space,
- That it is necessary to establish the sorption capacity for different fungi species.

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THE IMPACT OF MAJOR AND MINOR ELEMENTS FROM SEDIMENTS ON THEIR CONTENT IN *M. galloprovincialis* FROM THE BOKA KOTORSKA BAY, MONTENEGRO

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ABSTRACT

The concentrations of fourteen elements as essential nutrients and highly toxic elements were investigated in the mussel *Mytilus galloprovincialis.* The same elements determined in the surface sediment and their impact on the level in mussels from the Boka Kotorska Bay, Montenegro, by using Energy Dispersive X-ray Fluorescence Spectrometry. Three elements, Al, S and P showed a different accumulation pattern in the *M. galloprovincialis* as compared to their respective concentrations in the surface sediments. Aluminum in the mussels was not detected at all, but P and S concentrations in the mussels were almost 10 times greater than in the surface sediment.

Key words: Mussels, surface sediments, major and trace elements, ED-XRF.

INTRODUCTION

The coastal southeastern part of Adriatic receives large amounts of contaminants introduced by harbor, domestic, industrial, touristic and agricultural activities, rivers, by land erosion and through atmospheric deposition (1, 2). Investigations of southeastern Adriatic marine environment have intensified in the last decade (1- 5). The Boka Kotorska Bay is situated in the southeastern Adriatic Sea along the Montenegro coastline. As one of the most beautiful bays of the world, it is on the UNESCO's World Heritage List. The Boka Kotorska Bay is a semi-enclosed bay divided into smaller bays: the Herceg Novi, Tivat, and Kotor bay. Relief characteristics stimulated the development of urban agglomerations along the Bay coast; especially suitable zones have been placed in the very neighborhood of Kotor, Herceg Novi, and recently Tivat (6). The higher population and industrialization of the Bay coast, such as specific hydrogeology of the Bay have the influence on the surface sediment composition of the Bay (4).

Sediments act as sinks and sources of contaminants in aquatic systems because of their variable physical and chemical properties (7) and demonstrated that metals tend to be trapped in aquatic environment and accumulate in sediments and in the same time can reach marine organisms through the food chain, and thus to the tissues of the mussel (3). Trace and heavy elements are serious pollutants of the marine environment because of their toxicity and persistence, their difficult biodegradability and tendency to concentrate in aquatic organisms. Mussels accumulate a wide range of elements in their soft tissue, some major and minor elements as essential nutrients, but also highly toxic elements too (8). This report presents the investigation of Ca, Si, Al, Fe, Mg, K, S, Mn, Zn, Cr, Cu, As, Pb, and Cd concentrations measured in surface sediments and mussels at the three locations in the Bay by using Energy Dispersive X-ray Fluorescence Spectrometry (ED-XRF). The study aims were: to assess the major and minor elements concentrations in the surface sediment and in the mussel from the same locations and the sediment impact on the elements in mussels.

MATERIALS AND METHODS

The mussel *M. galloprovincialis* and surface sediment samples were collected from three locations: Kotor, with the poor open seawater mixing; Tivat, with a weakened sea current and waves and Herceg Novi impacted with open sea currents and waves, Fig. 1.

Figure 1. The locations of collected mussels and surface sediments samples in the Bay

At every sampling site about 2 kg of mussels were collected, placed in nylon bags with seawater and transported to the laboratory. The biggest 25–30 mussels, of approximately the same size, were washed and cleaned out, opened raw and the flesh scraped out of the shells and freeze-dried at –40°C for 48 h, weighed, homogenized and ground to a fine powder. To reduce particle size effect, the obtained powder was sieved using a 400-mesh sieve. The powdered sample was pressed with a hydraulic press by applying a pressure of 7 t for 20 s. The resulting pellets have a diameter of 32 mm and a uniform mass of 400 ± 3 mg. The samples were prepared in this manner in the form of pressed pellets for ED-XRF.

Sediments were collected using the boat anchored in front of sites usually from the depths of 12 to 20 m. About 1.5 kg of each sample was taken from the upper 15 cm by a grab sampler from the boat and placed in plastic boxes. Before the oven drying at 105 °C for 24 h, each sample was mixed after removal of the coarse fraction (>2 mm) by wet sieving. Sediment samples were prepared as follows: after oven drying, grinding, homogenizing, and sieving (particle size less than 0.071 mm in diameter), the pellets were finally formed by pressing 1.0 g of each powdered sediment samples and 5 g of boric acid added in the mold and pressed into pellets of 32 mm diameter (15 tons pressure, 30 s dwelling time). The standard reference material samples were prepared in the same way as samples pellets and directly measured by ED-XRF under an air condition. Concentration of major, minor and trace elements (Ca, Si, Al, Fe, Mg, K, S, Mn, Zn, Cr, Cu, As, Pb, and Cd) in the investigated samples were determined by using a PANalytical MiniPal 4 EDXRF spectrometer (4), equipped with a 30 kV Rh anode tube (maximum power: 9 W; window: 75 µm Be; maximum high voltage: 30 kV; maximum current: 750 µA; cooling medium: air), a high-resolution Silicon Drift Detector (SDD), a spinner and a 12-position removable sample changer. The resolution of SDD is 145 eV for Mn Kα. Spectral data were analyzed by MiniPal/MiniMate software version 3.0.–63(2.64) (PANalytical, Almelo, The Netherlands). The presented results data are expressed in mg/kg on a dry weight (dw) basis.

RESULTS AND DISCUSSION

In Table 1 is shown the concentrations (in dry weight) of the trace elements studied in the samples of surface sediments and mussels from three locations in Boka Kotorska Bay, Montenegro. The average content of the investigated elements in the surface sediment was found in the following order:

Ca > Si > Al > Fe > Mg > K > S > P > Mn > Cr > Zn > Cu > As > Pb > Cd,

and in the mussel:

Si > S > K > Mg > Ca > P > Fe > Mn > Zn > As > Cr > Cu > Pb > Cd.

Table 1. Concentrations of the elements in surface sediments and mussels from the Bay

Sediment	Ca	Si	Al	Fe	Mg	K	S	P	Mn	Cr	Zn	Cu	As	Pb	Cd
Kotor	154941	162156	46322	28481	13632	12622	1276	1371	805	148	240	44	12	108	0.7
Tivat	200935	92276	26936	17355	15767	8973	3918	409	321	109	46	21	28	16	0.3
H. Novi	236963	103531	33859	19404	12422	8108	1936	418	488	145	47	19	40	19	0.4

Mussels	Ca	Si	Al	Fe	Mg	K	S	P	Mn	Cr	Zn	Cu	As	Pb	Cd
Kotor	6022	26062	n.d	133	6247	8450	13102	8433	89	25	77	11	27	6	1
Tivat	9812	27805	n.d	611	11669	10026	20163	5877	118	25	92	12	38	7	0.8
H. Novi	6807	26576	n.d.	492	7582	8205	18435	5601	119	25	120	10	35	12	1

High concentrations of Al (26,936 - 46,322 mg/kg dw) in sediment samples were determined, but in the mussel samples Al was not detected at all. In the same time in the investigated mussel samples Cr concentrations were the same, 25 mg/kg dw. Also in the surface sediments similar concentration of Cr was found, 148 and 145 mg/kg, in the Kotor and Herceg Novi samples, respectively, and the lowest in the Tivat sediment sample, 109 mg/kg dw. Generally, the Cr concentration in soft parts of *M. galloprovincialis* from Mediterranean countries is from 1.0 to 45.7 mg Cr kg^{-1} dry matter (2). Some other authors have found similar values of Cr in *Mytilus edilus* as in this work (9). They concluded that Cr is metabolised and transported differently from most other metals. As filter feeding organisms, mussels are potentially exposed to more Al, as they come into contact with both particulate (colloidal or ligand-bound) and dissolved metal whilst feeding (10). Aluminum exists in marine sediments as aluminosilicates in inorganic or organic complexes, where it is more or less toxic according to its bioavailable chemical form. Aluminum is a highly reactive element that is never found as a free metal in nature and Al in seawater is not only prevalent as colloidal matter, but also as $Al(OH)^{-}_{4}$ (11,12). The behavior of Al in the environment depends upon its coordination chemistry and characteristics of the local environment, especially pH. High Al concentrations in natural water occur only when the pH is < 5, thus Al is not readily dissolved in the natural seawater with pH range of 7.8–8.2. Also, because of its toxicity to many aquatic organisms, Al has not been bioaccumulated in aquatic organisms to any significant degree (13). Probably *M. galloprovincialis* behaves as *M. edulis,* i.e. the digestive gland is likely to be a short- and medium-term storage site for Al, and the absence of Al in mussel samples is probably due to the inhibition of the mussel filtering activity at the high Al concentrations, as well as the mussel's excretion of accumulated Al (14).

In the investigated mussels the Ca, Si, S, K, P and Mg concentrations are significantly higher in mussels than the remaining tested elements which is understandable since these are macronutrients with many important roles in the organisms (15). On average, in the investigated mussels S (13102-20163 mg/kg dw) and P (5601-8433 mg/kg dw) contents were up to ten times higher than their contents in the sediment compared to the same locations, Table 1. In the case of K content, concentrations range in the mussels is almost the same as his content in the sediment samples. But it is interesting to note that Ca was the highest in surface sediment (154941-236963 mg/kg dw), but was not in mussel tissues. In the mussel tissue Ca and Mg were in the range of 6022 to 9812 and 6250-11700 mg/kg, respectively, and the mussel shells are mainly composed of Ca and Mg carbonates (16). The mussel tissue had the highest concentrations of Si at the all investigated samples, Table 1. The highest content of Si and lower of Ca in the mussel tissue can be explained by their function in mussels and by mussel's way of feeding. Generally, phytoplankton is much higher in K and Si contents than zooplankton, while zooplankton is higher in P than phytoplankton. Samples of phytoplankton and zooplankton are relatively abundant in the Ca and Mg content (17). Between Ca and Mg contents the correlation was almost 1 (0.999), and K and Si were correlated (0.915), but P was not correlated with any other investigated element, Table 2.

Table 1. Correlation coefficients of the mean contents of the elements in *M. galloprovincialis*

Mussels	Si	Fe	Mg	K	S	P	Mn	Zn	Cu	As	Pb	Cd
Ca	0.996	0.821	**0.999**	0.949	0.818	-0.591	0.638	0.025	0.751	0.835	-0.169	-0.981
Si	1.000	0.870	**0.999**	0.915	0.868	-0.664	0.707	0.118	0.686	0.883	-0.076	-0.958
Fe		1.000	0.843	0.598	**1.000**	-0.946	0.964	0.592	0.239	**1.000**	0.424	-0.693
Mg			1.000	0.935	0.841	-0.624	0.669	0.066	0.723	0.857	-0.129	-0.972
K				1.000	0.594	-0.306	0.362	-0.293	0.921	0.618	-0.472	-0.992
S					1.000	-0.948	0.965	0.595	0.235	**1.000**	0.429	-0.689
P						1.000	**-0.998**	-0.821	0.088	-0.938	-0.695	0.422
Mn							1.000	0.786	-0.029	0.956	0.651	-0.474
Zn								1.000	-0.642	0.571	0.981	0.172
Cu									1.000	0.264	-0.778	-0.866
As										1.000	0.401	-0.711
Pb											1.000	0.359
Cd												1.000

Bold values are statistically significant at $p < 0.05$ level; rest of values are statistically significant at $p < 0.10$ level

It is obvious that the much high levels of P in mussels than in sediment, and almost the same content of K in the mussel tissue and sediment, come from a water column: P from filtered zooplankton, but K, Si, Ca and Mg in mussel come from filtered phytoplankton and zooplankton. As Si contents in mussels were the highest, Table 1, and correlated with Fe and Mn (0.870 and 707, respectively), Table 2, it means that the highest level of Si in the mussel can be from the sediment particles also, since Si is the main constituent of clay, and clay is the main constituent of the Bay bottom (5), explaining its similar concentrations and increased level in mussels (2).

Mussels get their food by filter feeding and this leads to the accumulation of metals in the mussels' soft body parts. Consequently, the amount of As, Pb and Cd in these animals reflects the degree of metal pollution in the aquatic environment (8). The highest level of As was in the mussel from Tivat (35 mg/kg), such as S (20163 mg/kg), Table 1. Marine mussels naturally have considerable quantities of organic As compounds, especially arsenobeatine which are mainly non-toxic, and a very small percentage of inorganic As, arsenite and arsenate, which are very toxic forms (5). Majority of As in mussels is present in the organic arsenobetaine, usually the major arsenical form in marine organisms, but since As was highly correlated with S, Table 2, can be assumed existence of a thio-arsenic analogue in marine mussels (18), as have been detected in freshwater mussels (19).

The same as Al and As, Cd, and Pb have no known biological function. It induces behavioral toxicity in aquatic invertebrates (20). The Pb concentration was the highest in the surface sediment of Kotor, 108 mg/kg, but in the mussel the lowest from that location, 6.0 mg/kg. Generally, the Cd concentration was higher in the mussel samples (0.8-1.0 mg/kg) than in the surface sediment (0.3-0.7 mg/kg) at the all locations, Table 1. It is obvious that Cd and Pb in mussels are mainly from a water column rather than from the sediment particles (3). The same case is with Zn (240 and 77 mg/kg, respectively, Table 1) as well as with Cd and Pb, and as a proof of Zn origin from the water column in the mussel (21) is the high correlation between Zn and Pb in mussels (0.981), Table 2.

Similar trend as the S and As concentrations had Fe concentrations in the investigated mussels: the highest content of Fe was in mussels from Tivat bay: 611 mg/kg. In the same time the highest correlation was between Fe and S, and between Fe and As, and was 1. That means that As and S could have the same origin as Fe in the mussels, mainly from the inorganic and organic water particles. This can be confirmed by the Mn correlation Fe (0.964) and S (0.965), Table 2. In addition to Fe, Mn, Cr and Zn, Cu is a micronutrient which has similar concentrations in the Bay mussels: 11.0-12.0 mg/kg. The surface sediment from Kotor had the highest Cu content, 44.0 mg/kg. On the other two locations Cu content was similar in the surface sediment, 19.0 and 21.0 mg/kg dw. Trace metals such as Pb, Cd, and Cu may interact with the metabolic pathway of Ca and Mg (22), therefore the positive correlations between Cu vs. Ca and Cu vs. Mg it is not surprising, Table 2.

CONCLUSION

In conclusion we point out that the mussel *M. glloprovincialis* avoid accumulation of Al and accumulated the same concentration of Cr, regardless of the location and their content in the surface sediment. Mussels had higher content of P, S and Cd than surface sediments in the Bay. Obviously the content of Al, Cr, P, S, and Cd in the surface sediment did not have the impact on the content of these elements in the mussel from the Bay, Montenegro. On the basis of elements correlations in mussels, elements such as Ca, Si, K, Mg, Fe, Cr, Mn, Cu, As and S are mainly accumulated from inorganic and organic water particles, but Cd, Pb, Zn and P in mussels are mainly accumulated from the water.

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STRUCTURAL CHARACTERISTICS OF SILVER LIME AND BLACK LOCUST PLANTATIONS IN DELIBLATO SANDS AREA (SERBIA)

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ABSTRACT

The choice of tree species for afforestation of Deliblato Sands, which was declared as the Special Nature Reserve in Serbia, is a complex issue today. In established plantations on Deliblato Sands, the dominate tree species today on more than 90% of the area are: black locust (*Robinia pseudoacacia* L.) 65% and Austrian and Scots pine (*Pinus nigra* Arn. and *Pinus sylvestris* L.) 27%.

Black locust and pine species are susceptible to fires, and because of short rotation and application of clear-cutting in black locust plantations, maintaining their presence is not in accordance with the modern conservation objectives of Deliblato Sands. It is necessary to pay more attention to the selection of species for afforestation, which are edificators of habitat and can maintain ecosystem stability over a longer period.

Key words: Deliblato Sands, black locust (*Robinia pseudoacacia* L.), silver lime (*Tilia argentea* Desf.), growth elements, afforestation.

INTRODUCTION

Since the beginning of organized work on afforestation of Deliblato Sands (Serbia), from 1818 until today, different stages in the selection of tree species, which are primarily used for afforestation, were present. The selection of species decided different possibilities of arid habitats, historical circumstances, professional attitudes and tendencies in the choice of tree species for afforestation under similar conditions as in the European region. In the period of about 150 years, the afforestation were carried out with the aim of stopping the wind erosion and transformation of Deliblato Sands in the fertile soil and were carried out mostly with poplars and black locust and less with pines (Španović, 1936). After the establishment of the commercial function in the newly afforested forests, and especially since the mid-twentieth century, the afforestation was mainly with pine trees (Popov, 1994). Today, forest vegetation occupies 61.7% (17,552 ha) of total area of the MU „Deliblato Sands“, and within this area the culture of black locust (*Robinia pseudoacacia* L.) are represented on the area of 11,320 ha (64.49%), stands of Austrian and Scots pine (*Pinus nigra* Arn. and *Pinus sylvestris* L.) and other coniferous trees on the area of 4,748 ha (27.05%), while other species occupying an area of 1,483 ha (8.45%) of forest area. Stands of silver lime in the area of Deliblato Sands are represented on 376 ha (Letić and Malešević, 2005).

The structure of forest areas in the Deliblato Sands indicate that, after reaching the main goal to stop wind erosion, determination of planned forest management have largely not focused on the formation of stands with more or less natural species composition and thus are not significantly more supported the process of progressive succession as a logical continuity after fixing soil formations and microclimate by pioneer species (Bobinac, 2005).

This has had significant negative consequences in the history of contemporary Deliblato Sands, because in the period from 1948 to 2009, it was found 259 fires, with a total areas affected by fire of 11,923 ha, and forest area affected by fires of 6,129 hectares (Milenkovic, 2010).

In order to achieve protective but also productive role of forest ecosystems in the Deliblato Sands, which was declared as a Special Nature Reserve in Serbia, the choice of tree species that can meet these basic objectives and also ensure the longevity of stands and their natural continuity, today is an important issue. This paper presents a comparison of the growth elements and structure of white lime and black locust cultures as the most common deciduous species, similar age and silvicultural treatments in the area of Deliblato Sands.

OBJECT OF RESEARCH AND WORK METHOD

In the area of Deliblato Sands, on downy oak (*Quercetum Rhamneto virgilianae*) site, the elements of growth and structure were compared in cultures of silver lime and black locust which are established with seedlings, planting 3 × 1 m, or 3333 trees per hectare (Bobinac, 2005; Andrašev et al., 2014). Culture of white lime was founded on soil type sierozem, on loosely carbonate eolian sand and at the measurement of trees was 44 years old (OP-1), and the black locust culture was established on chernozem soil type, subtype on carbonate eolian sand and at the measurement of trees was 39 years old (EP-2), (2008).

Experimental plots were established in part of stands with the complete canopy and have a size of 30 × 15 m (EP-1) and 30 × 50 m (EP-2). On the experimental plots, on all living trees, the two perpendicular diameters at breast height were measured, with an accuracy of 1 mm and measurement of the height were made with an accuracy of 0.1 m. Based on the three-degree classification on each tree was estimated crown class (CC) and stem quality (SQ), and in trees with CC-1 degree of isolation of the crown (IC) was estimated (Assmann, 1970).

The volume of trees on experimental plots is determined based on volume tables of total volume up to 3 cm for silver lime (Banković et al., 1989), and black locust (Rede et al., 2012). Assessment of site classes for black locust was based on the comparison of mean height by Lorey (h_L) with growth models of mean height by Redei et al. (2014), for tended (modelled) stands of black locust in Hungary. Diameters and height structures of trees are defined based on statistical indicators: mean ($\bar{x}$), standard deviation (s_x), the coefficient of variation (c_v%), minimum (min) and maximum (max), variation width (vw), the skewness (α_3) and kurtosis (α_4).

RESULTS

Top height of 20% of the thickest trees in the culture of silver lime (EP-1), in the age of 44 years, was 18.6 m, and in the culture of black locust (EP-2), at the age of 39 years, was 19.0 m, and the mean heights by Lorey in the cultures were close and amounts 17.2 to 17.4 m. Mean diameters of 20% of the thickest trees had a similar size and amounts 26.5 to 26.6 cm, and the mean quadratic diameter in the culture of silver lime was 18.7 cm and 17.2 cm in culture of black locust. In the culture of silver lime was found 1534 trees per hectare, basal area 41.94 $m^2 \cdot ha^{-1}$ and volume 397.28 $m^3 \cdot ha^{-1}$, and in the culture of black locust was found 1,600 trees per hectare, basal area 37.24 $m^2 \cdot ha^{-1}$ and volume 322,89 $m^3 \cdot ha^{-1}$. Based on the mean Lorey's height (h_L) black locust stands belongs to IV site class, by Redei et al., 2014) (Table 1).

Table 1. Growth elements of trees and stands on experimental plots

<table>
<tr><td rowspan="2">Species</td><td rowspan="2">EP</td><td>Age</td><td>H_g</td><td>h_L</td><td>D_g</td><td>d_g</td><td>N</td><td>G</td><td>V</td><td>Iv_p</td><td colspan="5">Site class</td></tr>
<tr><td>[year]</td><td>[m]</td><td>[m]</td><td>[cm]</td><td>[cm]</td><td>[trees·ha⁻¹]</td><td>[m²·ha⁻¹]</td><td>[m³·ha⁻¹]</td><td>[m³·ha⁻¹ ·year⁻¹]</td><td>1</td><td>2</td><td>3</td><td>4</td><td>5</td></tr>
<tr><td>Silver lime</td><td>1</td><td>44</td><td>18,6</td><td>17,4</td><td>26,5</td><td>18,7</td><td>1534</td><td>41,94</td><td>397,28</td><td>9,03</td><td colspan="5"></td></tr>
<tr><td>Black locust</td><td>2</td><td>39</td><td>19,0</td><td>17,2</td><td>26,6</td><td>17,2</td><td>1600</td><td>37,24</td><td>322,89</td><td>8,28</td><td></td><td></td><td></td><td>*</td><td></td></tr>
</table>

The distribution of height in the culture of lime has a pronounced left asymmetry and mesokurtic flatness, and in culture of black locust left asymmetry and platykurtic flatness are less pronounced. In the culture of black locust a higher variability of height (49.5%) was found, in relation to culture of lime (21.0%) (Table 2). The cumulative curve of height structure indicate that 1/3 of trees in culture of black locust have height less than 8 m, and in the culture of lime below 15 m, that indicates a bimodal height structure in the culture of black locust, that is, in a culture of black locust substantial number trees have slow height growth (Figure 1, left).

Table 2. Numerical indicators of height structure on experimental plots

Species	n [trees]	h_a [m]	s_d [m]	c_v [%]	h_{min} [m]	h_{max} [m]	vw [m]	α_3	α_4
Silver lime	230	15,74	3,31	21,0	6,00	19,80	13,80	-0,991	2,962
Black locust	72	12,70	6,29	49,5	2,07	21,58	19,51	-0,389	1,664

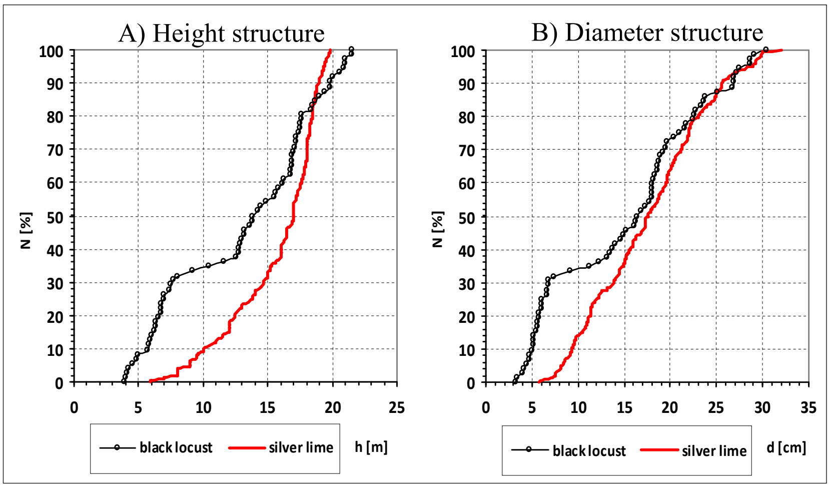

Figure 1. Cumulative curves of height (left) and diameter (right) structure

Diameter structure, both lime and black locust has a poorly expressed positive asymmetry and platykurtic flatness. High variability of diameters at breast height in culture of black locust (52.3%) and expressed platykurtic flatness of diameter distribution, as well as the participation of 1/3 of trees with breast height diameter below 8 cm, indicating the bimodal diameter structure (Table 3, Figure 1, right).

In the summary distribution of height and diameters about 85% of lime trees has a greater height and breast height diameters than black locust, and about 15% of the highest and the tickest lime trees have less height and similar breast height diameters in relation to the black locust.

Table 3. The numerical indicators of diameter distributions of the experimental plots

Species	n [trees]	d_a [cm]	s_d [cm]	c_v [%]	d_{min} [cm]	d_{max} [cm]	vw [cm]	α_3	α_4
Silver lime	230	17,6	6,13	34,8	5,9	32,1	26,2	0,150	2,147
Black locust	72	15,3	8,00	52,3	3,4	30,4	27,0	0,044	1,798

In the culture of black locust, tree differentiation by crown classes is more pronounced in the relation to the culture of lime. The largest number of trees in the researched cultures has a dominant position (1st crown class), 940 trees per hectare (61.3%) in the culture of lime and 667 trees per hectare (41.7%) in the culture of of black locust. These are the trees that are in the diameter degrees of 12.5 cm to 32.5 cm. (Figure 2).

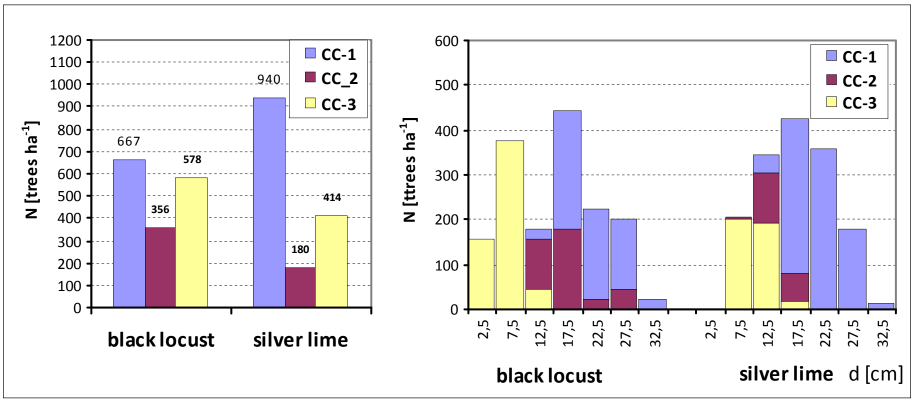

Figure 2. Number of trees per hectare of different crown classes (left) and their distribution through the diameters (right) in the experimental stands

In the culture of silver lime there are 233 trees per hectare with first degree of stem quality, which is 15.2% of the total number of trees, and in the culture of black locust, there are only 67 such trees per hectare, or 4.2% of the total. In black locust culture, trees of the first degree of stem quality are present in medium in of black locust and stronger diameter degrees (17.5 to 27.5 cm), and in silver lime culture, trees of the first quality of stem are present in all diameter degrees (7.5 to 27.5 cm). A large number of trees, 694 tree per hectare or 45.2% of the total number of trees in the culture of lime and 533 per hectare or 33.3% in the culture of of black locust, have a second quality of stem. In the culture of black locust largest number of trees, 1,000 trees per hectare or 62.8% of the total number of trees have poor trunk, and in silver lime culture number of trees with low quality of stem is 607 or 39.6% of the total number of trees (Figure 3).

In the studied cultures, within the trees of the 1^{st} crown class (CC-1), the relative participation of trees with different degree of isolation of the crown (IC) is equal. Trees with a free-standing crown (IC-1) is represented with around 26%, trees with unilaterally reduced crown (IC-2) is represented with around 64%, and the trees with multilateral reduced crown (IC -3), is represented with around 10%. In lime culture trees with IC-1 has 240, and in black locust culture 178 per hectare. In the culture of silver lime trees of IC-1 are represented in diameter degrees from 17.5 to 32.5 cm, and in the culture of black locust in diameter degrees from 17.5 to 27.5 cm. The largest number of trees of the 1^{st} crown class has unilaterally reduced crown class (IC -2), in the lime culture 600 per hectare and in black locust culture 422 per hectare. In the studied stands trees of IC -2 are present in a wide range of breast height diameter (12.5 to 32.5 cm) (Figure 4).

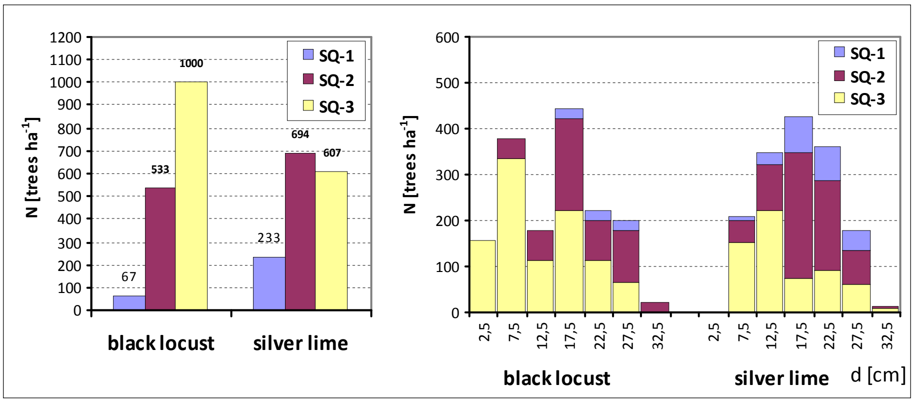

Figure 3. Number of trees per hectare with varying degrees of stem quality (left) and their distribution through the diameters (right) on the experimental plots

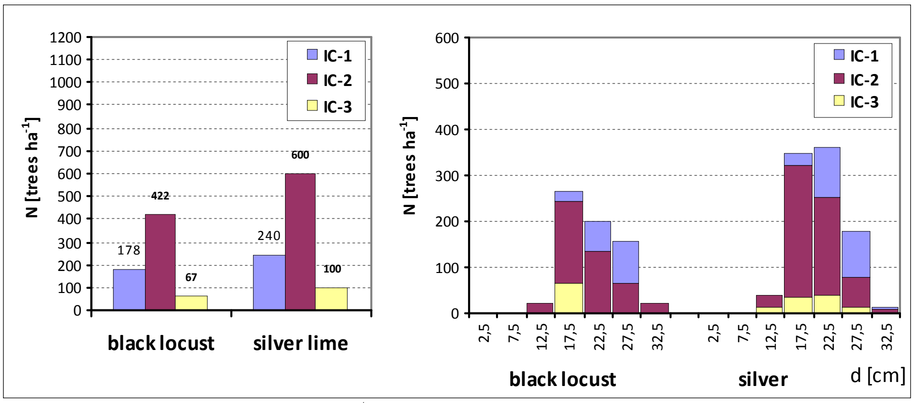

Figure 4. Number of trees of 1st crown class per hectare with different degrees of isolation of the crown (left) and their distribution through the diameter (right) on the experimental plots

CONCLUSION

Based on a comparison of growth elements and structures in cultures of silver lime and black locust in the Deliblato Sands, which are established in the same habitat, with planting 3×1 m, or with 3333 plants per hectare, and which were similar age and silvicultural treatments, may be the following conclusions:

- Cultures are characterized by a large number of trees per hectare, 1534-1600 trees·ha^{-1} and similar growth potential: with basal area of 37.2 to 41.9 m^2·ha^{-1}, volume 322.9 to 397.3 m^3·ha^{-1} and average growth from 8.3 to 9.0 m^2·ha^{-1}·year^{-1};
- In the cultures were determined close amount of growth element and similar diameter and height structure. Mean height by Lorey was 17.2 to 17.4 m, the dominant height from 18.5 to 18.9 m, and the dominant diameter from 26.5 to

26.6 cm. Based on the mean height (h_L) stand of black locust belongs to IV site class, by Rede et al., (2014);

- In the cultures, a different participation of tree qualitative class is determined. Stands of the first stem quality had participation of 15.2% (233 trees per hectare) in the culture of lime and 4.2% (67 trees per hectare) in black locust culture;
- Within trees of the first crown class in both cultures is equally relative participation of trees with different degrees of isolation of the crown. Trees with a free-standing crown (IC-1) are represented by 26% (from 178 to 240 per hectare), a tree with a unilaterally reduced crown (IC-2) are represented with 64% (from 422 to 600 per hectare), and tree with multilateral reduced crown (IC-3), is represented with 10% (67-100 per hectare);
- With the same treatment in the studied cultures, greater participation of silver lime trees which belong to the first stem quality, defines management objectives towards the production of high-quality assortment in considerably longer rotation than black locust, and, therefore, emphasizes the importance of biomeliroative and production of silver lime in relation to the locust.

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TREE SPECIES DIVERSITY IN THE STANDS OF BEECH AND VALUABLE BROADLEAVES IN THE AREA OF THE NP `DJERDAP`

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ABSTRACT

The tree species diversity in mixed stands of beech and valuable broadleaves was researched in the area of the National Park `Djerdap` on fifteen sample plots (total study area of about 5 ha). For this purpose, the following diversity measures were applied: (1) Shannon`s index H', (2) Simpson`s index (Simpson 1949), (3) McIntosh`s diversity index D' (McIntosh 1967), (4) Hill's N1 diversity number, (5) Hill's N2 diversity number and (6) Hill's E5 index. The results showed that the tree species diversity in the study forest stands didn't depend significantly on the type of the index applied to measure diversity.

INTRODUCTION

Among numerous and diversified natural resources and outstanding beauty of the NP `Djerdap`, mixed, even-aged and uneven-aged stands of beech and valuable broadleaves attract special expert and scientific attention. Apart from economic `benefits` (high potential value and quantity of wood and biomass, rapid growth and early attainment of usable dimensions), there are great aesthetic values, high degree of resistance and stability to harmful effects of various abiotic and biotic factors that, according to Drachenfels *et al*. (1984), classify these forests as European forest communities that are the richest in tree species (Stajić 2010, Stajić, Vučković 2012). As such, these stands are of immense importance in studying and quantifying the diversity of tree species and stand structure and represent a constant focus of interest of various scientists.

In the early stages of studying and quantifying diversity, some researchers equated the concepts of *species richness* and *species diversity* or at least considered *species richness* to be one of several measures of diversity (Hulbert 1971). However, a forest stand which has a large number of tree species can be characterized by lower species diversity if the secondary species are unevenly distributed, compared to a stand which has a smaller number of tree species but its individuals are evenly distributed among the species. Therefore, in order to make an accurate assessment of species diversity, it is necessary to apply those diversity indices that account for both *species richness* and *evenness*, or the number of individuals per species. Considering the above, the aim of this study was to use different measures of diversity to find the level of diversity of tree species in mixed stands of beech and valuable broadleaves in the National Park `Djerdap`.

MATERIAL AND METHODS

The study used the data and results by Stajić (2010) as starting material. The stands are located on the territory of the National Park `Djerdap` (north-eastern Serbia). The size of 15 sample plots ranges from 0.25 to 0.45 ha, and the total research area covers about 5 ha. The average number of trees per ha is as follows: 621 (EUa), 401 (EUb), 309 (EUc) and 570 (EUd). The average basal area per ha is: 37. 4 m^2 (EUa), 34.9 m^2 (EUb), 37.3 m^2 (EUc) and 27.9 m^2 (EUd), while the average volume per ha amounts to: 453 m^3 (EUa), 431 m^3 (EUb), 494 m^3 (EUc) and 298 m^3 (EUd). Visual assessment of tree size structure and stand physical appearance reveals that the stands of EUa and EUd are closest to uneven-aged forests and the stands of EUb and EUc to even-aged. The sites belong to the syntaxonomic units *Corylo colurnae-Fagetum*, sub-associations *aceretosum* (EUa – 4 stands) and *typicum* (EUd - 3 stands) and *Fagetum moesiacae montanum*, sub-association *aceretosum* (EUc - 4 stands).

Quantification of tree species diversity was carried out using (1) Shannon`s diversity index H' (Pielou 1977), (2) Simpson`s diversity index λ (Simpson 1949), (3) McIntosh`s diversity index D' (McIntosh 1967), (4) Hill's N1 diversity number (index), (5) Hill's N2 diversity number (index) and (6) Hill's E5 index (Hill 1973). In order to facilitate the analysis and interpretation of the results as well as the comparison of the aforementioned diversity indices (the higher the index size – the greater the diversity), Simpson`s diversity index was further calculated by the equation given by De Jong (1975), Swind *et al*. (1991) and Neumann and Starlinger (2001) and designated λ^*.

RESULTS AND DISCUSSION

Despite certain difficulties and ambiguities related to the calculation of diversity by means of diversity indices, as described by Hulbert (1971), Alatalo (1981), Ludwig and Reynolds (1988), Gove *et al.* (1994), these indices are often applied in ecology, biology and forestry. There are plenty of diversity indices (Hill 1973, Peet 1974, Ludwig, Reynolds 1988).

The size of H' taken as the proportion of each species relative to the number of individual trees (H'_N) ranges from 0.57 to 1.91 (Table 1). The highest value of H'_N was recorded on SP6 where the presence of 11 tree species was determined. However, the size of the index depends not only on the number of species present, but also on their relative proportion in the total number of trees. Thus, for instance the lowest value of H'_N was determined on SP1, which wasn't the plot with the smallest number of tree species. This indicates that the sample plots with a smaller number of species (SP9, SP11 and SP12) have a far evener distribution of secondary species compared to SP1. The fact that the same size of H'_N may be the result of different combinations of species number and their relative proportion is clearly shown in the case of SP12 and SP15. In fact, almost the same size of H'_N (0.93 to 0.95) was determined on the sample plots with 5 (SP12) and 10 (SP15) tree species present.

The highest value of H' per number of trees calculated for different ecological units was recorded in EUb (averagely 1.73), and the lowest in EUa (averagely 0.80). For the purpose of comparing the level of species diversity determined on the basis of H'_N in this research with the results of Fuldner's (1995) research conducted in the mixed forests of beech and valuable broadleaves in the area of Niedersachsen in the Federal Republic of Germany, the size of H' relative to the number of trees was calculated both using the natural and the common logarithm. The values of H'_N calculated using the common logarithm range from 0.25 (SP1) to 0.83 (SP6), while they amount from 0.20 to 0.35 in Fuldner`s research. The results point to a far more pronounced diversity of tree species in the NP `Djerdap` compared to the stands on the territory of Niedersashsen.

With the indices that are based on the relative proportion of species (p_i), p_i may refer to different elements of stand growth, such as number of trees, basal area, volume, crown size, canopy cover (Swindel *et al.* 1991, Füldner 1995, Stajić, Vučković 2005, Sterba, Zingg 2006...). This method of quantifying diversity is considered somehow more appropriate and comprehensive by numerous authors, as diversity quantification includes the real dimensions of trees and shows their impact on not only the diversity and abundance of the young growth, ground flora, and accompanying wildlife, but also on the stability and performance of forest ecosystems. Therefore, in addition to the relative proportion of tree species in the total number of trees (H'_N), H' was calculated as the proportion of tree species in the total basal area (H'_G) and in the total stand volume (H'_V) - Table 1. At the level of sample plots, the highest values of H'_G and H'_V were found on SP7 ($H'_G = 1.74$, $H'_V = 1.60$), and the lowest on SP1 ($H'_G = 0.56$, $H'_V = 0.50$). At the level of ecological units, the highest diversity expressed through H'_G and H'_V was found in EUb (H'_G averaged 1.57 and H'_V 1.44) and the lowest in EUa (H'_G averaged 0.71, H'_V 0.63).

Table 1. Number of tree species (S) and diversity indices (H'_N, H'_G, H'_V, λ_N, λ_G, λ_V, λ^*_N, λ^*_G и λ^*, D', N1, N2 and E5) per sample plots and ecological units.

	Sample plots														
	Ecological unit EUa				***Ecological unit EUb***				***Ecological unit EUc***				***Ecological unit EUd***		
	SP1	SP2	SP3	SP4	SP5	SP6	SP7	SP8	SP9	SP10	SP11	SP12	SP13	SP14	SP15
S	7	11	7	7	9	11	9	8	5	7	6	5	10	10	10
H'_N	0,57	0,98	0,85	0,78	1,51	1,91	1,84	1,66	0,91	1,22	1,26	0,93	1,33	0,83	0,95
H'_G	0,56	0,90	0,68	0,68	1,36	1,70	1,74	1,46	0,90	0,86	1,21	0,91	1,34	1,06	1,02
H'_V	0,50	0,82	0,63	0,58	1,26	1,59	1,60	1,31	0,80	0,73	1,09	0,79	1,28	1,05	1,00
λ_N	0,76	0,56	0,62	0,66	0,30	0,19	0,19	0,22	0,51	0,39	0,35	0,51	0,42	0,65	0,61
λ_G	0,77	0,61	0,70	0,72	0,35	0,24	0,23	0,32	0,54	0,58	0,40	0,55	0,38	0,50	0,54
λ_V	0,80	0,65	0,70	0,76	0,40	0,28	0,29	0,39	0,61	0,65	0,47	0,61	0,40	0,50	0,55
λ^*_N	0,24	0,44	0,38	0,34	0,70	0,81	0,81	0,78	0,49	0,61	0,65	0,49	0,58	0,35	0,39
λ^*_G	0,23	0,39	0,30	0,28	0,65	0,76	0,77	0,68	0,46	0,42	0,60	0,45	0,62	0,50	0,46
λ^*_V	0,20	0,35	0,30	0,24	0,60	0,72	0,71	0,61	0,39	0,35	0,53	0,39	0,60	0,50	0,45
D'	0,13	0,26	0,23	0,20	0,49	0,63	0,62	0,59	0,32	0,42	0,45	0,32	0,37	0,21	0,24
N1	1,76	2,69	2,35	2,18	4,53	6,73	6,29	5,25	2,48	3,38	3,53	2,55	3,77	2,30	2,57
N2	1,31	1,78	1,60	1,51	3,30	5,40	5,16	4,56	1,96	2,58	2,83	1,97	2,37	1,53	1,65
E	0,29	0,41	0,44	0,40	0,69	0,79	0,84	0,80	0,56	0,63	0,70	0,58	0,58	0,36	0,41
E5	0,41	0,46	0,45	0,43	0,65	0,77	0,79	0,84	0,56	0,67	0,72	0,62	0,50	0,41	0,41

Comparing the sizes of H'_N, H'_G and H'_V, we can see that the species diversity calculated on the basis of the number of trees is greater than the diversity based on the basal area or volume in all stands and ecological units, except in EUd. In this ecological unit, the size of H'_N is approximately the same (SP13) or even smaller (SP14 and SP15) than the size of H'_G and H'_V. The results can be explained by the fact that the beech, as the most common tree species, has a stronger participation in the total basal area and volume of EUa, EUb and EUc stands than in the total number of trees. The relations between the beech and the secondary species in terms of abundance are more favourable within EUd, since it dominates other secondary species in number, but not in size. In the case of ranking sample plots according to the lowest level of diversity, the differences between H'_N, H'_G and H'_V were not determined, because all three variants of H' found the lowest level of diversity on SP1.

Simpson diversity index is the measure of diversity less sensitive to rare species than H'. The results of this research show that the level of diversity determined by λ^* is not substantially different from the level of diversity determined by H'. The greatest diversity calculated by λ^*_N (number of trees) was determined, as in the case of H'_N on SP 6 (0.81) and the smallest on SP 1 (0.24). At the level of ecological units, the highest diversity was found on the sample plots of EUb (on average λ^*_N was 0.78), and the smallest on the sample plots of EUa (on average λ^*_N was 0.35).

Apart from the relative proportion of each tree species in the total number of trees (λ_N, λ^*_N), both variants of Simpson`s index were further calculated as the proportion of individual species in the total basal area (λ_G, λ^*_G)) and the total stand volume (λ_V, λ^*_V – Table 1). Comparing the values of λ^*_N, λ^*_G and λ^* , we can conclude that, similarly to H', the level of tree species diversity calculated by the number of trees is greater than the level of species diversity calculated by the basal area or volume in all stands and ecological units, except in EUd. In this ecological unit, the values of λ^*_N are smaller than the values of λ^*_G and λ^*_V. There is no difference in ranking sample plots and ecological units by the level of diversity when the species diversity is calculated by λ^*_G and λ^*_V from the one based on λ^*_N. In other words, the greatest diversity was recorded on SP6 and within EUb, and the smallest on SP1 and within EUa.

Since McIntosh diversity index D' (McIntosh 1967) takes into account the number of individuals per species and the total number of individuals, the calculation of D' within the framework of this research was carried out only by the number of trees. The size of D' ranges between 0.13 and 0.63 (Table 1). The highest value of D' was recorded on SP6, and the lowest on SP1. Regarding ecological units, the highest average value of D' was recorded within EUb (averagely 0.58), and lowest within EUa (averagely 0.21).

Ludwig and Reynolds (1988) indicate that the quantification of diversity using the so-called Hill's diversity numbers (Hill 1973) provides results which are much easier to interpret. Therefore, we further defined the level of diversity on the basis of N1 and N2 diversity numbers (Table 1). According to Hill (1973), N1 is *the number of abundant species*, *i.e.* the species with a large relative proportion. Compared to H', the measure of N1 gives the number of species that would, if each were equally common, produce the same H' as sample (Ludwig, Reynolds 1988). . The values of N1 range from 1.76 (SP1) to 6.73 (SP6) at the level of sample plots, while they average between 2.25 (EUa) and

5.70 (EUb) at the level of ecological units. The results indicate that the greatest diversity, quantified by this measure, was determined within EUb, which again had the greatest number of abundant, dominant species whose individuals are evenly distributed among species. On the other hand, the small value of N1 in EUa can be explained by the fact that this ecological unit has on average only 2.25 abundant and evenly distributed tree species, whose abundance is much greater compared to other secondary tree species.

N2 index refers to the number of very abundant species (Hill 1973). N2 values range from 1.31 (SP1) to 5.40 (SP6), and averagely 1.55 (EUa) to 3.84 (EUb) for different ecological units - Table 1. The results show that there are no differences in terms of ranking sample plots and ecological units using N1 or N2. It is also obvious that much smaller diversity within EUa compared to EUb, results from the fact that EUa has on average 1.55 abundant tree species, while EUb has 3.55. Therefore, the existing relations between very abundant and remaining secondary species within EUa in terms of their relative proportion contributed to the lowest average distribution of species and thus to the lowest diversity of this ecological unit compared to the others.

E5-evenness (equitability) indices, which are in the available literature generally classified as diversity indices, were also used to characterize the level of diversity in this paper. E5 is a more appropriate than other indices of evenness, since it is less affected by the number of species (Ludwig and Reynolds, 1988). At the level of sample plots, the values of E5 range from 0.41 (SP1, SP14, SP15) to 0.84 (SP8), and 0.44 (EUa) to 0.65 (EUb) for ecological units.

Table 2. Correlation coefficients between different measures of diversity ($\alpha = 0.01$)

	H'_N	H'_G	H'_V	λ_N	λ_G	λ_V	λ^*_N	λ^*_G	λ^*_V	D'	N1	N2	E5
H'_N	1.00												
H'_G	0.94	1.00											
H'_V	0.91	0.99	1.00										
λ_N	-0.97	-0.89	-0.84	1.00									
λ_G	-0.93	-0.99	-0.98	0.91	1.00								
λ_V	-0.90	-0.99	-0.99	0.86	0.99	1.00							
λ^*_N	0.97	0.89	0.84	-1.00	-0.91	-0.86	1.00						
λ^*_G	0.93	0.99	0.98	-0.91	-1.00	-0.99	0.91	1.00					
λ^*_V	0.90	0.99	0.99	-0.86	-0.99	-1.00	0.86	0.99	1.00				
D'	0.98	0.90	0.85	-0.99	-0.91	-0.85	0.99	0.91	0.85	1.00			
N1	0.99	0.93	0.90	-0.94	-0.90	-0.88	0.94	0.90	0.88	0.95	1.00		
N2	0.96	0.90	0.86	-0.93	-0.87	-0.84	0.93	0.87	0.84	0.96	0.99	1.00	
E5	0.86	0.75	0.68	-0.94	-0.78	-0.70	0.94	0.78	0.70	0.95	0.84	0.89	1.00

Correlation analysis was conducted in order to test the interdependence of the diversity indices applied to assess the level of species diversity. The results are presented in Table 2. All the correlations between the applied indices of tree species diversity were highly significant, at the 0.01 level of significance. A negative correlation, due to the nature of the indices and their mutual relations, was established between the two variants of Simpson`s index ($\lambda_N$, $\lambda_G$, $\lambda_{V,}$ on the one hand and $\lambda^*_N$, $\lambda^*_G$ and $\lambda^*_,$ on the other), as well as between Shannon`s index ($H'_{N,}$ H'_G and H'_V) and Simpson index (λ_N, λ_G, λ_V). Furthermore, λ had a negative correlation with $D^'$, N1, N2 and E5.

CONCLUSIONS

In general, the measurement and quantification of different elements of diversity in the forestry in our country has often been conducted using in some aspects inadequate and too general methodology and equating diversity with the number of woody plants, herbaceous species, plant communities or soil types. However, the number of species is largely dependent on the sample size. The larger the sample, the greater the number of species, since such samples are more likely to include some rare species. In addition, diversity refers not only to the number of species within a population of a specific area, but also to the way individuals of each species are distributed in the population. In principle, the methodology of diversity assessment depends on the time and money available to carry it out, desired level of the quantification accuracy and may also vary depending on the goal to be achieved. In this study, species diversity in the study stands was determined using diversity indices.

Based on the above, it can be concluded that in terms of ranking sample plots and ecological units by the level of diversity there are no significant differences if diversity is determined using different indices of diversity. Out of the total of 13 diversity indices used, 8 indices ($H'_{N,}$ λ_N, λ_V, λ^*_N, λ^*, D', N1, N2) found the largest level of diversity on SP6, while all 13 diversity indices used in this study measured the lowest diversity on SP1. At the level of ecological units, all the indices measured the highest species diversity in EUb, and the lowest in EUa. The results show that there is high correlation among different measures (indices) of diversity, which proves that the assessment of the level of diversity and the ranking of the study stands and ecological units did not depend much on the applied methods and measures of diversity.

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HEIGHT GROWTH OF WHITE ASH (*Fraxinus excelsior* L.) IN THE REGION OF MAJDANPECKA DOMENA

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ABSTRACT

This paper considers the height growth characteristics of white ash in the region of Majdanpečka Domena. The regularities of height growth of this species were analyzed in 10 young stands (with 30 dominant trees felled for growth reconstruction), for different site conditions. For the purpose of comparing the growth of white ash and the other individually recorded species, six additional trees of sessile oak, wild service tree and aspen (two of each) were felled. Defined models of growth and incremen thave confirmed that white ash is a fast-growing tree species, with early culmination of current height increment (6-8 years), which indicates the time period when it is biologically suitable to carry out the most intensive treatment, by which the complete management of these species' stands becomes far more effective.

Key words: height growth, white ash, time of increment culmination, silvicultural importance.

INTRODUCTION

In the past, areas covered by valueble broadleaves throughout Europe, including those where we are, were far more widespread. However, a lack of silvicultural measures, along with excessive and uncontrolled use, have brought these areas to a state of neglect (Stajić, 2003). An increased share of valuable deciduous trees, in addition to economic gain (rapid achievement of usable dimensions, high-quality and appreciated wood type etc.), would also be biologically and ecologically significant due to increase in stability and resilience of pure beech and oak stands against the effects of various abiotic and biotic factors (Burschel, 1990; Stamenković, Vučković, 1998; Stajić, 2010, etc.).

Economically and ecologically speaking, white ash (*Fraxinus excelsior*) represents one of the most interesting species in the valuable broadleaves tree species category. Numerous uncertainties, which are related to environmental requirements and the selection of appropriate sites, the type of growth in different site conditions, the character of silvicultural operations, the duration of the production cycle (rotation) and the production effect of white ash, are all hampering the development of relevant concepts of how to manage pure and mixed ash stands in particular. Therefore, great practical significance is given to doing research on this species's growth characteristics under different site conditions, which enables the existing knowledge to be complemented, deepened or rectified as its scope and quality are still insufficient.

MATERIAL AND METHODS

The research object (10 sample plots in pure stands of white ash) is located in the area of north-eastern Serbia (Majdanpek), within the M. U."Crna Reka" in Educational Base of the Faculty of Forestry in Belgrade. The climate is mild-humid (B1), i.e.it belongs to low-forest humid climate. The analyzed stands are classified into two ecological units: ecological unit A (EUa) – the site of sessile oak and hornbeam (*Querco - Carpinetum moesiacum*Rudski (40) 1945) on humus-siliceous soil on andesite (SP1-5), and ecological unit B (EUb) - the site of sessile oak and hornbeam (*Querco - Carpinetum moesiacum* Rudski (40) 1945) on eutric brown soils on andesite-amphibolite schists (SP6-10). Stand age is about 23 years.

The aim of the study is to investigate the regularities of growth and define height growth models of white ash for the analyzed sites and thereby indicate the applicability of the information obtained. For this purpose, three dominant trees from each sample plots were felled (a total of 30 trees) and cross-sectional slices were taken at every 0.5 m from the base to the top of the trees. In addition, for the purpose of comparison of growth and increment trends, two more dominant trees were felled of each of the mixed species: sessile oak, wild service tree and aspen (a total of 6). In order to determine the existence of statistically significant differences in the growth of the trees analyzed on white ash sample plots, analysis of variance was applied.

For the presentation of height growth depending on age, the Chapman-Richards function was applied:

$$h = a \cdot \left(1 - e^{-b \cdot T}\right)^{c}$$

Current height increment is obtained as the first derivative of the growth function:

$$i_{th} = f(T) = F'(T) = \frac{dh}{dT}$$

Average height increment is obtained on the basis of the formula:

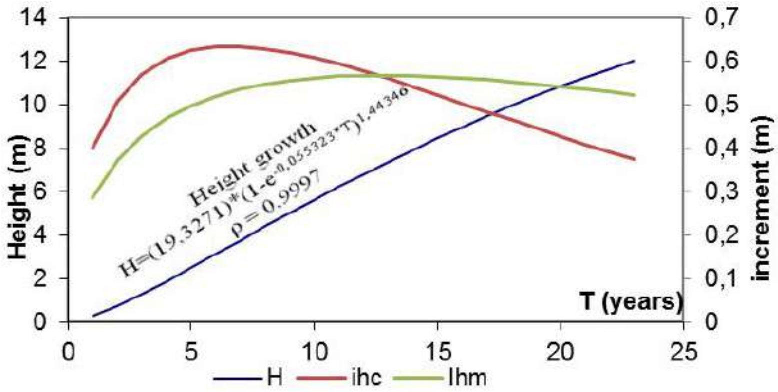
$$i_{ph} = \frac{h_t}{T} = \frac{\int_0^T f(T) \cdot dT}{T} = \frac{F(T)}{T},$$

or as the quotient of reached tree height (h_t) and age (T).

RESULTS

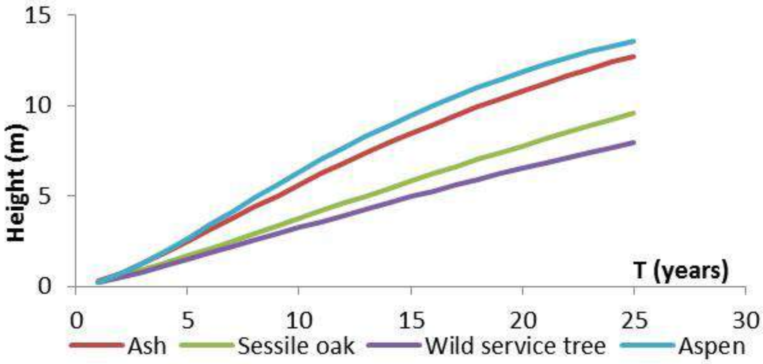
Although very small differences in height growth of dominant trees were established among the analyzed sample plots, in order to define the significance of the differences observed, an analysis of variance was carried out, related to achieved height of dominant trees within each ecological unit at 5, 10, 15, 20 and 23 years of age. Established empirical values of F-test in EUa (0.17, 2.88, 3.01, 1.00, 0.35) and EUb (1.0, 1.25, 0.50, 0.55, 2.15) at all analyzed ages were smaller than the critical value (F_{crit} = 3.48), indicating a lack of statistically significant differences in the heights of dominant trees with respect to sample plots within ecological units. In order to come to conclusions about whether the observed differences in heights of analyzed dominant trees between EUa and EUb were of accidental nature or there was a significant difference, the reached heights at the aforementioned ages were tested using the t-test.Calculated t-values (1.52, -0.51, -0.84, -1.99 and 1.92) were always smaller than the critical value from the t-distribution table (t_{crit} = 2.05), so a hypothesis of equal trees heights between the EUs in all observed periods was acceptible. On the basis of these facts, i.e. on the basis of all the data on the analyzed trees at the ages of 5, 10, 15, 20 and 23, a height growth model of white ash trees for both ecological units was established.The defined height growth model of dominant trees for both ecological units, as well as graphic illustrations of height growth and current (i_{hc}) and mean height increment (i_{hm}) are presented in Graph 1.

With all of the 30 analyzed white ash trees, i_{hc} culminated between 6 and 8 years of age, with values ranging from 0.60 m to 0.67 m, and i_{hm} between 11 and 14 years of age. With all the trees, as it had already been stated earlier, there was a non-significant variation in height growth. Therefore, on the basis of a defined model for the representation of height growth for both ecological units, it was concluded that the culmination of i_{hc} occurred in year 7 with the value of 0.63 m, and the culmination of i_{hm} in year 13 with the value of 0.57 m.



Graph 1. Height growth model of dominant trees for both ecological units and curves of height growth, current and mean height increment

In order to compare the growth dynamics of white ash and mixed species, height growth models of sessile oak, wild service tree and aspen were defined. Height growth lines of all the tree species are shown in Graph 2. In year 23, aspen reaches the biggest height (13.0 m), followed by ash (12.0 m), sessile oak (8.9 m) and wild service tree (7.4 m).

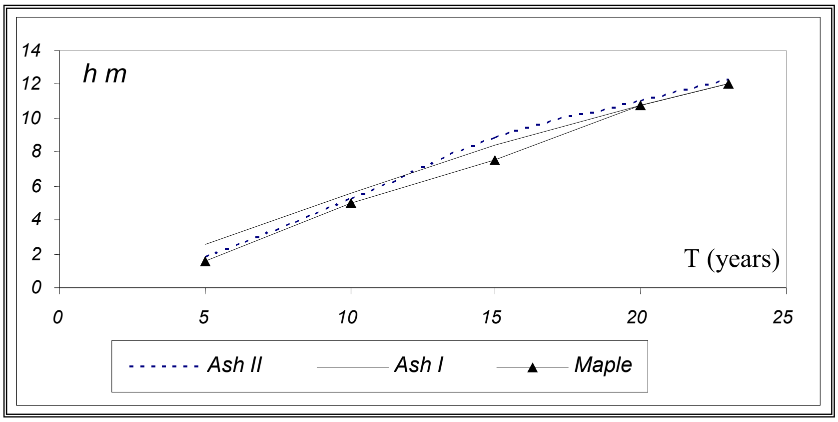


Graph 2. Height growth of white ash, sessile oak, wild service tree and aspen

DISCUSSION

According to Plavšić (1960), initial research on growth and increment of white ash was done by Schuberg (1887) and Endres (1888) who published their results on 20 ash trees aged between 52 and 107. The first detailed technical data on the growth and increment of individual white ash trees and stands in Serbia were a result of research by Miščević and Stamenković (1972, 1976). Stamenković et al. (1991), Stamenković and Vučković (1995, 1998), Vučković et al. (2001) and Stajić (2003, 2004, 2010) continued further research on growth characteristics of white ash in pure and mixed stands in Serbia.

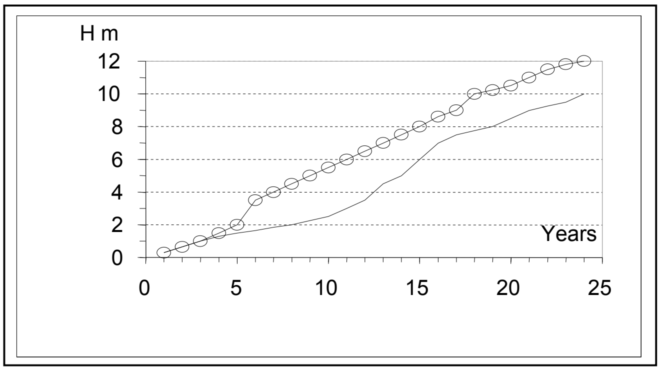
In principle, white ash falls into the category of fast-growing tree species. Defined models of height growth and increment of dominant trees in this research have confirmed the aforementioned statement that white ash is a rapidly growing species in youth, with a very early culmination of current height increment (between the years of 6 and 8) and a relatively rapid decline of current increment after the peak. Misčević and Stamenković (1972) discuss a similar growth rate and age at the time of culmination, whereby they emphasize that in the analysis of 12 white ash trees of different biological positions, a culmination of current height increment with the 2 highest trees is established in year 7. Kadunc (2004a) also points to rapid height growth of young white ash, and notes that a maximum height increment is achieved by year 10, and the average height increment by year 20. According to Faliński and Pawlaczyk, height increment of white ash culminates depending on the site conditions in the period between years 10 and 25 (Dobrowolska et al. 2008). Current height increment of white ash trees in the area of "Đerdap" National Park culminates in years 11 and 12 (Stajić 2010). According to the data from European textbooks on the subject matter of growth and forest increment (Assmann 1961, Erteld, Hengs 1966, Krammer 1988, Wenk et al., 1990, Kotar 2005), white ash is added to the group of woody species where culmination of height increment occurs over a period of 2 -15 years.



Graph 3. Height growth of white ash and Norway maple

For the purpose of analysis and comparison, trends of height growth of white ash (ash I - the result of research in this paper) and white ash and Norway maple (ash II and Norway maple - the result of research by Stamenković and Vučković 1998) are presented in *Graph 3.* The results show that the established trends of height growth are very similar according to height growth dynamics, both to each other and in relation to Norway maple. In addition, if trends of height growth are analyzed for the purpose of evaluating competitive ability of tree species recorded in this stand, the fastest growth up to approximately year 25 is to be found in aspen and ash, followed by sessile oak and wild service tree (*Graph 2.*).

Early culmination of height increment of white ash indicates to the necessity of intensive silvicultural treatment of this species from an early age, which can significantly speed up and "facilitate" undisturbed growth of individual trees and boost their competitive ability and resilience against the effects of a number of adverse factors (Stajić 2010). It is known that during the period or development phase of a large height increment, trees have the strongest respond to increased growth space and that space regulation for growth has its full biological sense and economic justification. An illustrative example, which confirms the aforementioned, is given through research results by Vučković et al. (2001). According to these authors, all up to year 5, height growth of white ash was even to a high degree on two analyzed surfaces (*Graph 4*). After year 5, when on sample plots II (growth in height during the age represented by a line with circles) the number of trees started to be reduced, a strong growth and increment differentiation of ash was initiated on the treated and non-treated areas, whereby the strongest effects of reduction had already been achieved between years 5 and 10. Similar conclusions can be drawn in relation to the here analyzed growth trends of white ash and aspen. It is clear that from approx. year 5, aspen constantly dominates growth compared to white ash, hindering it progressively through more pronounced shading, reduction of canopy and competitive interference. On the other hand, white ash dominates growth and competitively interferes and dampens the growth of sessile oak and wild service tree. Therefore, with the aim of preserving the mixture and quality of these two species, appropriate practical professional operations must be applied towards reducing competitive ability of white ash and "supporting" sessile oak and wild service tree. It is evident that cleaning at the sapling stage is generally considered important for growing ash stands of good quality, and it is also believed that ash needs intensive tending (Dobrowolski et al. 2011).



Graph 4. Height growth of white ash of one treated (line with circles) and one non-treated young stand (***Source:*** *Vučković et al. 2001*)

A pronounced decline in height increment of white ash after culmination, which was determined based on conducted research study, clearly points to the conclusion that any further delay in silvicultural intervention would represent a belated and forced-choice management measure depending on the situation existing prior to it, due to its trivial effect and considerably intensified dangers to stand stability, whereby there is a deterioration and damage to a large number of trees. In this case, after cutting devitalized, bent and broken trees, an inadequate number of trees with adequate production potential is often left in stands that are unevenly distributed on the surface, so considerable losses in increment occur that are multiplied depending on rotation length (Vučković, Stajić 2003).

CONCLUSIONS

White ash is a forest tree species that is characterized by beauty and quality of its wood, but also intensive growth in youth and early achievement of usable dimensions (Stajić 2004). According to Kadunc (2004b), white ash can reach a 50 cm diameter at breast height already at the age of 70. At good sites, pure stands of white ash can have a capacity of up to 700 $m^3 \cdot ha^{-1}$(Knorr 1987). One of the most impressive white ash trees in Serbia (height of 44 m, breast-height diameter of 192 cm) has been recorded in the area of "Đerdap" National Park.

In order to make the management of this forest type as efficient as possible, both economically and environmentally, it is necessary to practically detect growth regularities of white ash in different site conditions. In addition, special importance and attention paid by the relevant profession and science must be directed towards determining the characteristics of height growth, given that height growth contains within itself two components whose knowledge enables adequate planning and execution of management: growth of species depending on age and the species's relationship to the site (Vučković 1989). In this way, an approach which assumes permanent monitoring of height increment trends, a good-quality biological basis is provided for early separation of the future trees and their proper tending, a timely and appropriate implementation of an overall effective silvicultural treatment and, consequently, intensive growth, stability and quality of economically interesting stands of white ash. At the same time, realistic assumptions are made for the return of white ash to the forests in our area, which proves a great deal of attention that has been paid to this species by professional and scientific circles in European forestry in recent decades. After all, white ash undoubtedly represents an elite tree species in the majority of European forests and should be treated as such.

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ELEMENTS OF GROWTH, BIOLOGICAL AND QUALITATIVE STRUCTURE OF TREES IN VEGETATIVE ORIGIN BLACK LOCUST STANDS ON CHERNOZEM

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ABSTRACT

The researches were conducted on the permanent sample plots in two vegetative origins black locust stands close in age (31 and 33 years), which were established on chernozem soil type. The stands were under different silvicultural treatment and differ in the number of trees per hectare, mean and dominant heights and diameters, whilst not differ in volume per hectare.

In thinned stand (EP-2), the total number of trees per hectare is in accordance with the number of trees in the modelled stands, and in unthinned stand (EP-1) number of trees per hectare is twice higher.

Based on determined number of trees in the sample plots the share of the dominant trees was closely, and by the biological structure on the EP-1 there were a significantly greater number of trees with slow in growth. Qualitative structure of stems shows not enough equal participation of trees with the first quality of stems on both experimental plots, but much lower participation of trees with the third quality of stems on the tended experimental plots in relation to the untended plot.

Key words: black locust, vegetative origin, elements of growth, crown class structure, stem quality structure.

INTRODUCTION

Black locust (*Robinia pseudoacacia* L.) is an introduced species of trees (neophytes) from North America in the early seventeenth century, and today in Europe and Serbia is economically important species. It was used in the reforestation of different habitats due to good adaptability, fast growth and significant yield, possibilities of vegetative regeneration, very hard and long-lasting wood, nitrogen fixation from the air with the help of *Rhizobium* bacteria on the roots, drought tolerance, honey and decorative qualities (Keresztesi, 1983; Barrett et al, 1990; Guzina et al., 1997; DeGomez i Wagner , 2001; Redei et al., 2012).

In the area of today's Serbia black locust have largely used in binding "live sand" in Deliblato and Subotica sands in the middle of XIX century (Guzina, 2006).

At the same time with the afforestation of Deliblato Sands, black locust was afforested and throughout Vojvodina and other parts of Serbia. In the structure of forests in Serbia black locust, with birch and aspen as pioneering companions, occupies an area of 223.200 ha or 8.5% of the total area of forests and forest land of 2,634,800 hectares (Banković et al, 2009).

Researches in black locust stands on the Deliblato Sands (Vucetic, 2009) and the wider area of the Vojvodina Province outside the Subotica and Deliblato Sands (Andrašev et al., 2014) indicate the presence of a large number of trees per hectare compared to the modelled stands in the region (Rede et al. 2014) in similar climatic and edaphic conditions. The presence of a large number of trees in the study stands of black locust, compared to modelled stands of similar origin, indicates the lack of adequate tending in the stands. In the study black locust stands was found unfavourable quality structure of stems so the tending measures in the stands need to focus on improving the quality structure of stems (Andrašev et al., 2014b). Based on the research conducted so far the effects of the application of tending to the development of black locust stands have been insufficiently known.

The task of the research is to study the elements of growth and structure of black locust stands, which differ in the previous tending treatment, and are located in similar site conditions in age that is close to the length of the production cycle.

THE OBJECT OF RESEARCH AND WORK METHODS

The researches were conducted in two vegetative origin black locust stands in Management Unit (MU) "Bagremara" (Public Company "Vojvodinašume" Forest Holding Novi Sad, Forest Administration Backa Palanka): experimental plot 1 (EP-1) and section 8, subdivision and, 31 years old , and experimental plot 2 (EP-2) and section 2, subdivision and 33 years old.

In the stands were made cleaning measures in the age between 5 and 10 years, and after this period on EP-1 thinning have not been carried out, while on EP-2 two thinning were conducted: the first in the age of 20 years and the other in the age of 30 years (so-called "increment thinning" by Rede et al, 2011).

The study was conducted on permanent sample plots, EP-1 with an area of 0.16 ha, and EP-2 with an area of 0.18 ha. On the sample plots two perpendicular diameters were measured on all trees, with an accuracy of 1 mm, and at least 5 trees height in diameter degrees of 5 cm wide with hypsometer type Vertex III, with accuracy of 0.1 m. On each sample plot, pedological profile was opened and collected data for the assessment of morphological description and systematic affiliation of soil.

Measured diameters and heights were used for the construction of height curves (model: $h = 1.3 + a \cdot e^{-b/dbh}$, h - height, dbh – breast height diameter, a, b - parameters to be estimated) for each stand and assessment of stands volume.

Assessment of site classes at each experimental plot was based on the comparison of mean height by Lorey (h_L) with mean height from growth models by Redei et al. (2014) for modelled tended black locust stands in Hungary. Since mentioned height growth models are proportional site class models, i.e., heights of individual site classes of the same age have the same relationship, so assessment of particular site class was determined by the ratio of mean Lorey's height from experimental plot and mean height of the first site class from growth model for the appropriate age, in percentages.

The volume of trees was obtained on the basis of volume tables by Redei et al., (2012), while total volume per hectare was obtained as the sum of the volume of trees on experimental plots multiplied by the appropriate factor.

During the measurement, crown class (CC) and stem quality (SQ) was estimated for every tree based on the classification by Assmann (1970):

– Crown class (CC): tree crown is in upper storey (1), tree crown is in middle storey (2), tree crown is in lower storey (3);

– Stem quality (SQ): (1) evidently straight, smooth utilizable stem, at least one-third of the tree length being free from branches, (2) a bole which, owing to minor faults, does not entirely fulfil the stipulations made for the 1st class, being not entirely straight or slightly inferior in quality owing to a maximum of three thin branches or one thicker branch within the lower one-third of the tree length or some other defect slightly spoiling the quality of the stem, and a curved but utilizable bole of medium quality; (3) a bole which is bent or coarse or has too many branches and with fairly serious technical faults.

RESULTS

By classification of Škorić et al (1985) soils on experimental plots belong to the same systematic unit: chernozem type, subtype on loess and loess-like sediments, variety brownised, form medium deep. Differences in mean heights (h_L) for a given age, or reduced to approximately the same age of 33 years[1] amount to over 4 m, which was considerably higher than the difference between the two site classes that for the specified age is 2.6 m (Redei et al, 2014). The differences in the top heights (H_{100}) approximately reduced to the age of 33 years was 2.1 m which is less than the difference between the two site classes and indicates that the stated habitats are close by productivity (Table 1).

On the EP-1 mean height by Lorey (h_L) is 73.1% of the amount of height of the first site class by Redei et al (2104) and stand belonged to IV site class, while on the EP-2 mean height is 92.6% of height of the first site class and stand belonged to the II site class (Table 2).

Table 1. Growth elements of trees and stands on experimental plots.

EP	Age	H_{100}	h_L	D_{100}	d_g	N	G	V	I_{Vp}	Site class				
	[year]	[m]	[m]	[cm]	[cm]	[trees ha^{-1}]	[m^2 ha^{-1}]	[m^3 ha^{-1}]	[m^3 ha^{-1} $year^{-1}$]	1	2	3	4	5
EP-1	31	21.16	18.25	25.2	14.7	1756	29.84	320.23	10.33				*	
EP-2	33	24.67	23.55	32.4	26.5	469	25.96	310.34	9.40		*			

Legend: EP - experimental plot; *Age* – age of culture since establishment; H_{100} – top height; h_L – mean Loray's height; D_{100} – diameter at breast height of dominant tree; d_g – diameter at breast height of mean tree; *N* – number of trees per hectare; *G* – basal areas per hectare; *V* – volumes per hectare; I_{Vp} – mean volume increments per hectare; *Site class* – site class by Redei et al. (2014).

[1]Adding twice the amount of average height increment at the age of 31 years is reasonably possible considering the early culmination of height increment of black locust (up to 10 years) and the small size of current height increment, as well as its variation in the age of 31-33 years (Vučetić, 2009).

Table 2. The relationship between mean heights and mean diameters of the study stands and data from the table by Redei et al (2014).

EP	Age	N	Height		Diameter		Difference	
			1st y.c.	Y.cl.	1st y.c.	Y.cl.	Δy.c.	Δd_h
	year	[trees·ha^{-1}]	[%h]	[h_L]	[%d_g]	[d_g]	[h_L-d_g]	[cm]
EP-1	31	1756	73,1	IV	56,1	V	-1	-3,2
EP-2	33	469	92,6	II	97,6	I	1	2,2

***Legend**:* EP - experimental plot; *Age* – age of culture since establishment; *N* – number of trees per hectare; *1st y.c._h* – mean tree height by Lorey's in relation to the height of the first site class by Redei et al., (2014) for the corresponding age in percentages; *Y.cl._h* – corresponding height growth model of mean tree by Redei et al. (2014); *1st y.c._d* – mean tree quadratic diameter in relation to the diameter of the first site class by Redei et al., (2014) for the corresponding age in percentages; *Y.cl._d* – corresponding diameter growth model of mean tree by Redei et al. (2014); *Δy.c.* – differences in site classes on the basis of achieved mean height and mean diameter at breast height by Redei et al., (2014); Δd_h – difference between achieved breast height diameters and breast height diameters by Redei et al., (2014) for the corresponding site class.

Mean diameter (d_g) on EP-1 is 56.1% while on EP-2 average diameter is 97.6% of the of the mean diameter of the first site class by Redei et al (2014). Average diameter on EP-1 is 3.2 cm less than the mean diameter of the IV site class, while on the EP-1 is increased by 2.2 cm of mean diameter of the II site class by Redei et al (2014) (Table 1, 2).

In the unthinned stand (EP-1) at 31 years it was determined fixed number of trees per hectare of 1756, that is higher by 891 tree per hectare or 103% compared to modelled tended black locust stands of the IV site class. In the thinned stand (EP-2) at 33 year it was determined only 469 trees per hectare, which is 44 trees per hectare or 10.5% more than the number of trees per hectare the second site class by Redei et al (2014), (Table 3).

The number of trees per hectare is in strong dependence on the mean diameter at breast height ($N_0=f(d_g)$). For the modelled values of the number of trees per hectare of different site classes by Redei et al (2014) was constructed the dependence of the number of trees from mean diameter at breast (Andrašev et al, 2014). For such a defined modelled number of trees per hectare on EP-1, was found 1058 trees per hectare or 151.5% more, while on EP-2 was determined 20 trees per hectare or 4.1% less than the number of trees for proper site classes by Redei et al, (2014) (Table 3) .

In the relation to the volume displayed on the site class by Redei et al (2014) volume per hectare on EP-1 of 320 m^3·ha^{-1} is higher by 162 m^3·ha^{-1}, while the volume per hectare on EP-2 is higher by 50 m^3·ha^{-1} (Table l, 3).

Table 3. The relationship between numbers of trees and volumes per hectare of the study stands and data from the table by Redei et al (2014).

EP	Age	N	*$N_0=f(Age)$*			*$N_0=f(d_g)$*			*Volume per hectare*				
			N_{0_Age}	ΔN_{Age}	$(N-N_0)/N_0$	N_{0_dg}	ΔN_{dg}	$(N-N_0)/N_0$	1st y.c.	Y.cl.	Δy.c.	ΔV	ΔV
	year	[trees·ha^{-1}]	[trees·ha^{-1}]	[trees·ha^{-1}]	[%]	[trees·ha^{-1}]	[trees·ha^{-1}]	[%]	[%V]	[V]	[h_L-V]	[m^3·ha^{-1}]	[%]
EP-1	31	1756	865	891	102,9	698	1058	151,5	106,0	I	3	161,71	102,0
EP-2	33	469	425	44	10,5	489	-20	-4,1	98,7	I	1	50,30	19,3

***Legend**: EP* - experimental plot; *Age* – age of culture since establishment; *N* – number of trees per hectare; N_{0_Age} – number of trees per hectare obtained by model: $N_0=f(Age)$; ΔN_{Age} – difference between achieved number of trees per hectare and number of trees obtained by model; $(N-N_0)/N_0$ – the percentage difference between achieved number of trees per hectare and number of trees obtained by model; N_{0_dg} – number of trees per hectare obtained by model: $N_0=f(d_g)$; *1st y.c.* – volume per hectare in relation to volume per hectare of the first site class by Redei et al., (2014) for the corresponding age in percentages; *Y.cl.* – the corresponding growth model of volume per hectare by Redei et al. (2014); *Δy.c.* – differences in site classes on the basis of achieved volume per hectare and volume per hectare by Redei et al., (2014); *ΔV* – difference between achieved volume per hectare and volume per hectare by Redei et al., (2014) for the corresponding site class.

Of the total number of trees in the EP-2 416 trees per hectare were found in the upper storey (89%) and only 53 trees (11%) in the middle storey, while in the EP-1 725 trees per hectare (41%) were in the upper storey, 244 trees per hectare (14%) in the middle storey, and 788 trees per hectare (45%) in the lower storey.

Diameters of trees in the upper storey on the EP-1 were 12.5-32.5 cm, with the largest share in the diameter degree of 17.5 cm, while on the EP-2 trees in the upper storey had diameters of 17.5-37.5 cm, with the largest share in the diameter degree of 27.5 cm. On the EP-1, 54% of trees from the lower storey had a diameter less than 5 cm (Figure 1).

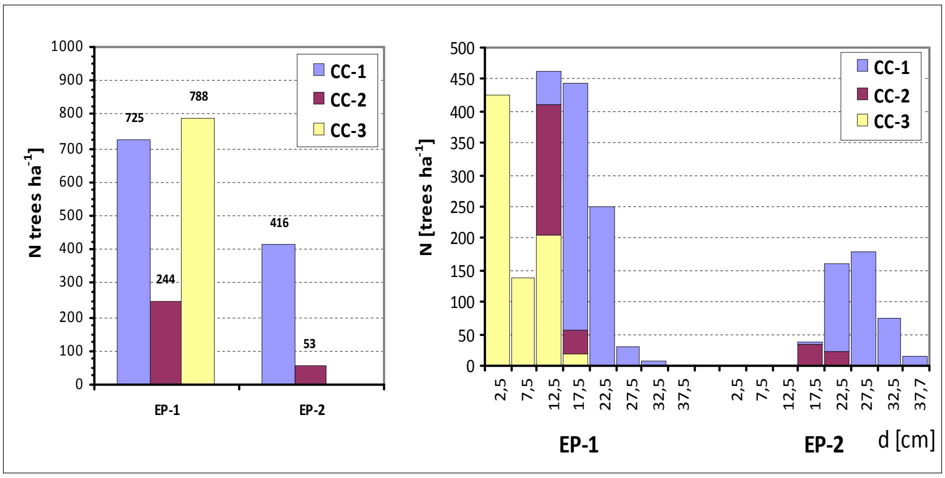

Figure 1. Number of trees per hectare of different crown classes (left) and their diameter distribution (right) on the studied plots.

Of the total number of trees in the EP-1 306 trees per hectare (17%) were found with the first stem quality, 500 trees (29%) with II stem quality and 950 trees (54%) with III stem quality, while in the EP-2 213 trees per hectare (45%) were found with I stem quality, 219 trees (47%) with II stem quality and 37 trees (8%) with III stem quality.

Trees with I stem quality in the EP-1 had diameters of 12.5-32.5 cm diameter degrees and the largest share in the diameter degree of 22.5 cm, while trees in the EP-2 were located in diameter degrees of 17.5-37.5 cm and had the largest share in the diameter degree of 27.5 cm. In the EP-1, more than half of the trees with III stem quality had a diameter smaller than 10 cm (Figure 2).

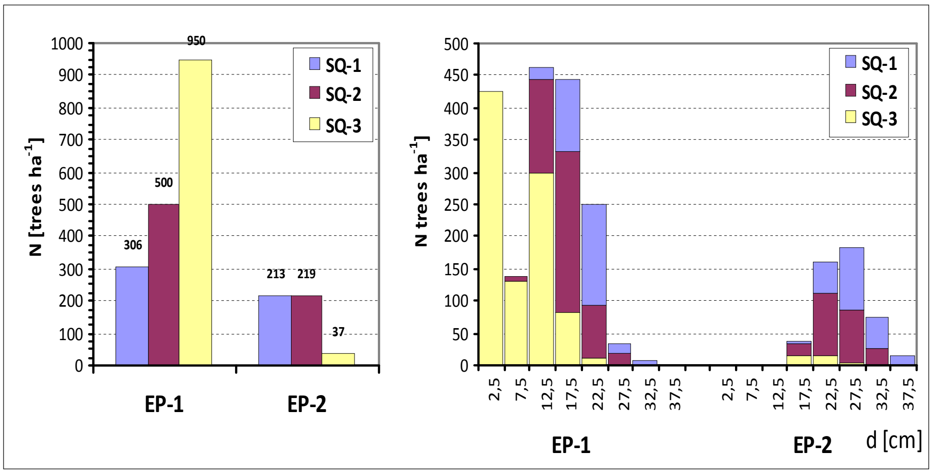

Figure 2. Number of trees per hectare of different trunk quality classes (left) and their diameter distribution (right) on the studied plots.

DISCUSSION AND CONCLUSIONS

Studied black locust stands of vegetative origin on chernozem soil, which were under different silvicultural treatment, show a strong dependence of tree growth elements from habitat and the number of trees. Differences between the heights of dominant trees of studied vegetative origin black locust stands are less than the difference between two adjacent site classes by Redei et al, (2014), which indicates that the stated habitats are close by productivity. Mean heights of study stands differ by two site classes, according to Redei et al (2014) as a result of the different number of trees or silvicultural treatment in studied black locust stands. In unthinned stand (EP-1) top height (H_{100}) are greater than the mean heights (h_L) by 16%, and in thinned stand (EP-2) by only 5%. Greater differences between dominant and mean heights indicate to lagged inventory in the stand.

On the EP-2 the number of trees per hectare is in accordance with modelled stands, and on the EP-1 were found more than 100% higher trees per hectare than modelled managed stands by Redei et al (2014). However, by biological classification on the both experimental plots determined number of trees per hectare in the upper storey (CC-1) is consistent with the modelled managed stands by Redei et al (2014).

As a consequence of the lack of thinning on the EP-1 has been intensified differentiation of trees. The mean diameter was in the level of 56% of the diameter of the I site class (Redei et al, 2014).

Increased participation of black locust trees with I stem quality can be expected only in cultures established with known genotype (Keresztesi, 1983). The research results are consistent with the above and show that in the studied stands 213-306 trees per hectare has a trunk with I stem quality, which enables the production of so-called. "industrial wood". The research results show that in the thinned stand total number of trees decreased by more than 70%, and the number of trees with I stem quality decreased by 30%. In thinned stand (EP-2) more than 200 trees per hectare had diameters above 20 cm, of which more than 60 trees per hectare is thicker than 30 cm, as opposed to the unthinned stand (EP-1) where 175 trees per hectare is thicker than 20 cm, and only 6 trees per hectare are thicker than 30 cm.

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THE ASSESSMENT OF SITE CLASSES OF BLACK LOCUST STANDS IN MU "BAGREMARA"

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ABSTRACT

The paper shows the possibility of obtaining estimates of height site classes of black locust stands in the area of a forest management unit ("Bagremara"), which is uniform in soil characteristics. The research was based on data collected by forest inventory for the purpose of making forest management plan by the methodology applied in Serbia.

The results showed that, by the majority of sample plots, the most common is the III site class, by Redei et al (2014), and that the II, III and IV site classes cover over 80% of the management unit. It is emphasized that the resulting increased variability of site classes depends on usage of mean height and that it is necessary to create height site classes based on top height in the black locust stands in Serbia.

Key words: black locust, site class, mean height, sample plot.

INTRODUCTION

Black locust (*Robinia pseudoacacia* L.) is an introduced tree species (neophytes) from North America in the early seventeenth century, and today in Europe and Serbia is economically important species. It was used in the reforestation of different habitats due to good adaptability, fast growth and significant yield, possibilities of vegetative regeneration, very hard and long-lasting wood, nitrogen fixation from the air with the help of *Rhizobium* bacteria on the roots, drought tolerance, honey and decorative qualities (Keresztesi, 1983; Barrett et al, 1990; Guzina et al., 1997; DeGomez i Wagner , 2001; Redei et al., 2012).

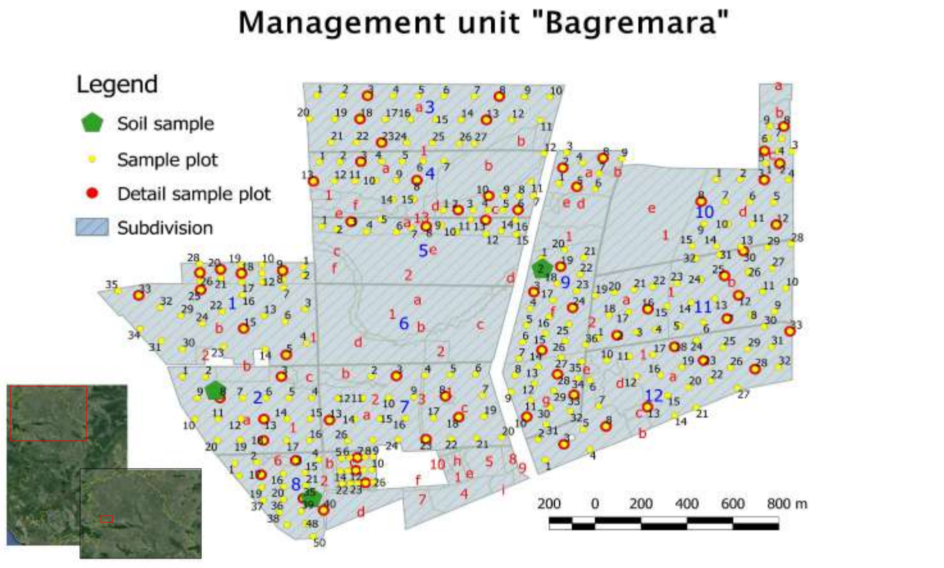
On the territory of today's Serbia black locust was mostly used in binding so-called „live sands" in Deliblato and Subotica sands in middle of the nineteenth century (Guzina, 2006). Parallel with the afforestation of the Deliblato Sands, black locust was afforested and throughout Vojvodina and other parts of Serbia. In the structure of forests in Serbia black locust, with birch and aspen as pioneering companions, occupies an area of 223.200 ha or 8.5% of the total area of forests and forest land of 2,634,800 hectares (Banković et al, 2009).

The research and information of productivity of stands and growth characteristics of black locust in our conditions are rare and are not in accordance with the proportion of black locust and its importance in the growing stock. Significant research is mainly related to the area of Deliblato Sands (Guzina et al, 1994; Vučetić, 2009) as the area where he is most present. Recent research in black locust stands on the Deliblato Sands (Vučetić, 2009) and wide area of Vojvodina outside the Subotica and Deliblato Sands (Andrašev et al., 2014) indicate the presence of a large number of trees per hectare compared to the model stands in the region (Redei et al., 2014) in similar climatic and edaphic conditions.

The aim of this work is to study the production potential of black locust stands on the example of a management unit (MU) which will enable obtaining more reliable basis for making management plans, applying appropriate silvicultural measures in studied and similar stands over a wider area of Serbia.

OBJECT OF RESEARCH

Investigations were carried out in the MU "Bagremara" which is located in the north-western part of Serbia, ie western part of the Vojvodina province, north of Bačka Palanka (Map 1). Management unit belongs to the Public Company "Vojvodinašume" Forest Holding Novi Sad, Forest Administration Bačka Palanka, total area of 395.50 hectares, with total forest area of 373.18 ha (94.4%), where the dominant species is black locust (*Robinia pseudoacacia* L) with 359.12 hectares or 96.2% forest area (2014).



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Map 1. Location of MU "Bagremara" and sample plots

WORKING METHOD

For research were used data measurement of trees on sample plots in the MU "Bagremara" in 2013 year with the aim to make forest management plan according to the methodology used in Serbia (Banković, Pantić, 2006). The network of sample plots with circle shape was set up in each compartments depending on the so-called. „degree of homogeneity", while the size of a plot (1, 2, 5 or 10 ares) is conditioned by the number of trees per hectare, which should be 15-25 trees on a plot. Breast height diameters (dbh) of all trees were measured on sample plots, with an accuracy of 1 cm, and on average every fifth sample plot (ie. a detailed sample plot), in addition to the diameter, and height were measured with an accuracy of 10 cm. On the map 1 are shown the location of each sample plots, as well as detailed sample plots, in the MU "Bagremara". Researches were conducted in 31 subdivisions, where 330 sample plots were set up, of which 77 were detailed sample plots.

The paper presents data measurement of trees on three types of samples: (A) detailed sample plot, (B) sample plot, and (C) subdivision (obtained as the sum of all sample plots in the subdivision).

Based on the measurement of tree heights on detailed sample plots (type A) height curves were constructed, according to the model of Mihailov:

$$h = ae^{-\frac{b}{dbh}} + 1.3$$

where: h - height, dbh - diameters at breast height, a, b - parameters to be estimated.

Height measured on detailed sample plots (type A) and obtained from the height curves (type B and C) were used for the assessment of mean height by Lorey for all three types of samples according to the formula:

$$h_L = \frac{\sum_{i=1}^{n} d_i^2 h_i}{\sum_{i=1}^{n} d_i^2}$$

where: d_i – diameter at breast height of trees in a sample plot, h_i - height of trees in a sample plot, n - the number of trees in a sample plot.

Mean heights by Lorey were compared with the height growth models of different site classes by Redei et al (2014). Data from height site classes by Redei et al. (2014), presented in tabular form, were used to obtain the growth model of mean height for each site classes according to the model:

$$y = a(1 - e^{-bx})^c$$

where: y - height of a tree, x - age, a, b, i - parameters to be estimated.

Height site classes by Redei et al. (2014) are constructed on a proportional basis, which means that have the same relationship to each other. This principle was used to define the range of each site classes based on the ratio of mean height of II-VI site classes and mean height of the first site class obtained from the model. Affiliation to adequate site classes was obtained on the basis of the ratio of mean height by Lorey (h_L) of each sample plots and the height of the first site class obtained from height growth model for appropriate age, as well as a defined range for each site class.

RESULTS OF THE RESEARCH

Height growth models of mean tree for each site classes were constructed based on the data of height site classes given in tabular form by Redei et al, (2014). Ranges of each site class, defined as the percentages of mean height of II-VI site classes and mean height of the first site class, were also obtained. The coefficients of determination (R^2) shows a high degree of agreement in tabular given height of site classes (Redei et al, 2014) and height growth models (Table 1, Figure 1).

Age of stands in MU „Bagremara" ranged from 8 to 57 years and the average age was 24 years. Mean diameter (d_g) ranged between 6.6-32.1 cm, while the mean height by Lorey (h_L) ranged from 10.3 to 24.3 m (Table 2).

Table 1. Parameters of the height growth models of mean trees for each site class and ranges of the percentage of the height of the individual site class and height of the I site class, by Redei et al, (2014).

Site class	Parameters of model			R^2	Range*
	a	b	c		
I	28,60077	0,07039	1,13797	0,99996	> 94.7%
II	25,52765	0,07041	1,13344	0,99985	84.1 – 94.7%
III	22,52129	0,06996	1,13142	0,99990	73.4 – 84.1%
IV	19,51397	0,06979	1,1352	0,99992	62.7 – 73.4%
V	16,40471	0,07157	1,15846	0,99990	52.0 – 62.7%
VI	13,44303	0,07021	1,15404	0,99998	< 52.0%

*Range of height site classes in relation to the I site class.

Table 2. Basic information of sample plots.

Type of sample			Age				Mean diameter - d_g				Mean height – h_L			
		n	mean	sd	min	max	mean	sd	min	max	mean	sd	min	max
A	Detail sample plots	77	23	8	8	37	15.3	4.7	7.8	25.0	17.0	3.4	11.1	24.3
B	Sample plots	330	24	9	8	57	15.5	4.6	6.6	32.1	17.1	3.3	10.3	24.3
C	Subdivisions	31	24	10	8	57	15.4	5.3	8.0	32.1	16.9	3.4	10.9	23.9

Legend: n – number of sample plot; mean – average value; sd – standard deviation; min – minimum; max – maximum.

On the basis of the measured height of the detailed sample plots (type A) reserached black locust stands belong to I-V site classes, by Redei et al (2014) (Figure 1). Average height (h_L) on 32.5% of detailed sample plots belonged to III site class, on 27.3% belonged to II site class, and 23.4% belonged to IV site class by Redei et al (2014) (Figure 2).

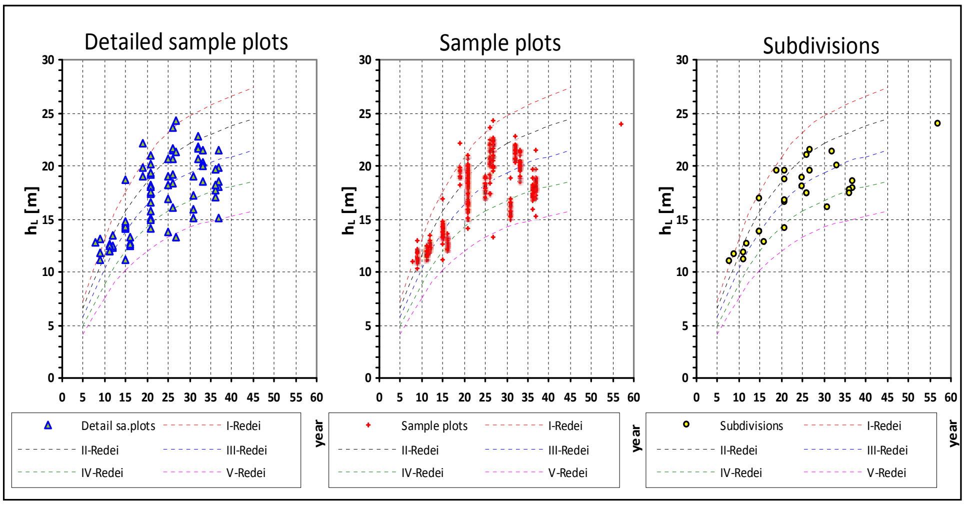

Figure 1. Mean height by Lorey (h_L) in three different type of samples in MU „Bagremara“ and site classes by Redei et al (2014).

On sample plots type B, where mean heights were obtained from the height curves, they were highly variable also, and belonged to different height site classes by Redei et al (2014) (Figure 1). The largest number of mean heights, 36.7%, belonged to III site class, while considerable number of mean heights belonged to II (30%) and IV (23.9%) site classes. In the I site class belonged 7% of mean heights, and at least mean heights belonged to V site class (Figure 2).

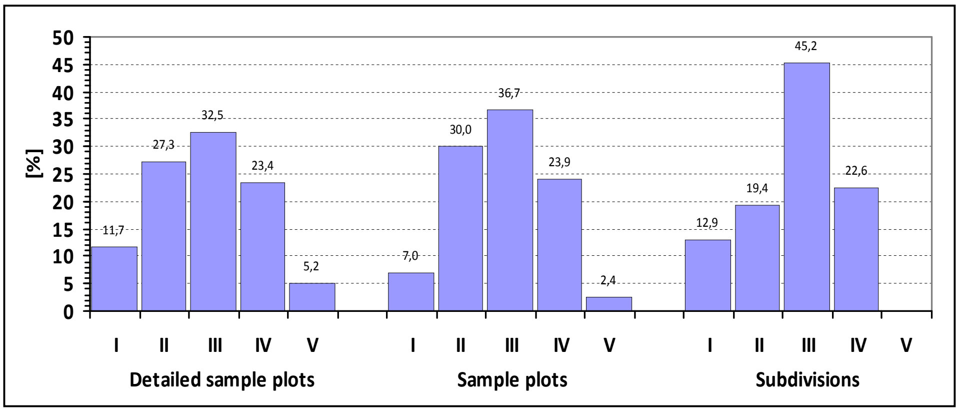

Figure 2. Percentage of site classes by Redei et al, (2014) in three different type of samples.

Combining sample plots (sample type B) in the subdivision (sample type C) the largest number of mean heights, over 45%, belonged to III site class, and almost half to

II and IV site classes. By sample type C, compared to other types of samples, the largest number of samples (subdivisions) belonged to I site class (12.9%), and has not been found any sample that belonged to V site class (Figure 2).

DISCUSSION AND CONCLUSIONS

By pedological map (Nejgebauer et al, 1971) soil on an area of MU"Bagremara" belongs to once type, chernozemlike meadow brownized soil. The similarity with the aforementioned characteristics of soils were also confirmed on three pedological profiles within the MU (Map 1) where, by the classification of Škorić et al (1985), confirmed the similarity of systematic units to the level of form: chernozem soil type, subtype on loess and loess-like sediments, variety brownized, form medium deep (Andrašev et al, 2014).

Results of research showed that stands of black locust in the MU "Bagremara", although entire MU located on a chernozem soil type, in terms of production belong to different site classes by Redei et al (2014). For the most of sample plots, as well as detailed sample plots, mean heights indicate that black locust stands have mean productivity, and that over 80% of sample plots belong to II-IV site classes by Redei et al. (2014). Considering the spatial arrangement of sample plots over an area of MU can be concluded a high degree of representativeness area of soil with data obtained from sample plots (Map 1).

The strongest relationship of characteristics of soil and growth elements exists at the top height, while mean height are under significant influence of stand conditions, primarily tending treatments (Assmann, 1970). Larger differences between the upper (H_{100}) and mean height (h_L) were obtained in black locust stands in MU „Bagremara" with a larger number trees per hectare, compared to modelled tended stands (Andrašev et al., 2015). The authors emphasize that these differences in heights caused by the absence of tending measures during the production cycle. The authors showed that on two experimental plots, that by top heights differ within one site classes, by mean heights one stand belonged to II, and the other to IV site class by Redei et al (2014).

The research results indicate the possibilities to estimate site classes of black locust stands in a wider area MU based on measurement of trees on sample plots for the purpose of making forest management plan on the basis of pre-defined site classes in other areas (Redei et al., 2014). Since the site classes by Redei et al (2014), defined as relationship of mean height on age, obtained greater variability of habitat in the area of MU "Bagremara" would be decreased if top heights would be used, which are less influenced by silvicultural treatment of stands. This indicates the necessity of making site classes on the basis of top heights depending on age in black locust stands in Serbia.

Acknowledgement

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ANALISYS OF AN INDUCTOR WITH DIFFERENTIATED DOMAINS OF THE ELECTROMAGNETIC AND THERMAL FIELD

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ABSTRACT

Recently the issue related to the distribution of temperature along an inductor for volumetric induction heating of cylindrical workpieces has become more and more topical. There are only few publications linked to this area because of the sophisticated modeling and complex experimental recording of temperature. The present paper considers modeling of the thermal and electromagnetic field of a volumetric heating inductor of R-ITO-630/1-A-L type. The equivalent parameters of the equivalent inductor-piece system are calculated taking into consideration the differentiated domains of the thermal and electromagnetic field in the inductor.

Key words: induction heating, steel workpieces, electromagnetic field, thermal field.

INTRODUCTION

Globally energy efficiency is a world problem, which plays a key role in the management strategies of both small and large enterprises. Management of energy consumption costs is an essential aspect of overall management, which should result in reducing the price of a given product and increasing enterprise market competitiveness.
The minimum theoretical energy expenditure to produce a given product can be usually determined in the course of work and standard energy costs can be established for it. Such a minimum standard for particular energy costs is difficult to accept but it could serve as an indicator of the size of the opportunity for energy saving.

The starting point to reduce energy costs should be to achieve minimum possible costs with the existing equipment and processes or to upgrade or modernize the existing equipment. [1].

The main distinguishing feature of induction heating, compared to other types of heating, is to give out heat directly in the heated metal workpiece by concentrating the electromagnetic energy in a limited volume, upon which it is transformed into thermal energy. As a result there is high thermal efficiency and temperature gradient.
To analyze and model induction heating processes, interrelated phenomena of different physical nature should be considered. Generally the induction heating system is described by the interrelated partitive differential equations of electromagnetism and heat

conduction with nonlinear coefficients. Nonlinearity within heating processes is related to the dependence of the thermophysical properties of bodies, heat transfer coefficients, on the temperature T whereas within electromagnetic processes it is linked to the dependence of the electrophysical properties on the temperature and the magnetic field strength.

The interrelation of the thermal and electromagnetic field is determined by the fact that the heat sources in the heated workpiece are defined by the development of the electromagnetic processes in the inductor-workpiece system. It is also known that the magnetic permeability μ and the resistivity ρ in the metal depend on temperature. These dependencies are nonlinear and of different nature, including a jump-like one – for example the dependence $\mu = f(T)$ in the Curie point.

The volumetric induction heating inductors are of a length from a few centimeters to a few meters depending on the specific application and the workpiece volume. They are multi-turn inductors, much longer than the workpiece being heated.
The workpieces pass successively through the inductor and gradually reach the required technological temperature of 1250 – 1300°C. In this way there is enough time to uniformly heat the workpieces and to provide admissible energy parameters of the supply source. At the inductor output the temperature difference across the section of the workpiece does not exceed 100 – 150 °C, кwhich is the requirement of the next operation. The volumetric heating inductor is shown in fig.1.

With volumetric heating of ferromagnetic workpieces temperature zones of 25 – 1300 °C are formed along the inductor. They correspond to the temperature of the separate workpieces. The electromagnetic parameters are determined, to a great extent, by the temperature zones because of the dependence of the magnetic permeability μ and resistivity ρ on the temperature. The length of the temperature zones is defined by the geometric dimensions of the inductor, the insulation, the electrical and magnetic parameters of the inductor-workpiece system, and the stroke of feeding the workpieces.

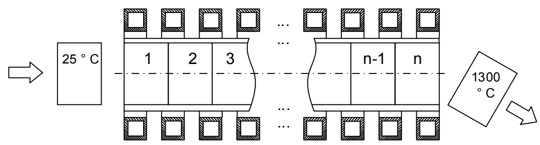

Figure 1. General view of the volumetric heating inductor

The first stage of the analysis is to model the thermal field in the inductor. Three zones that are directly linked to the magnetic properties and the equivalent parameters of the inductor-workpiece system are accepted as temperature zones.

1. Cold zone - from 25 to 500-600 0C. It covers a limited number of workpieces. It starts from the beginning of the inductor, along its length, and at the end of the temperature zone the temperature of the last workpiece does not exceed 600 ÷ 680 0C. In this zone the magnetic permeability μ and resistivity ρ on the surface are determined by the physical properties of the steel workpiece being heated.

2. Intermediate zone – from 650 to 850 °C. The temperature of the workpieces is just before the Curie point. It covers a limited number of workpieces along the

inductor and at the end of the temperature zone the temperature of the last workpiece does not exceed 800 ÷ 850 0C. The electrical and magnetic modes determine considerable changes in the magnetic permeability μ and resistivity ρ, which are analyzed and known.

3. Hot zone – from 850 to 1300 °C. It covers a limited number of workpieces until the end of the inductor. In this zone a temperature of 1300 0C is reached for the forge-press treatment of workpieces. The magnetic permeability μ drops sharply and reaches 1. The resistivity ρ varies with temperature [2,3].

The present paper has two objectives: 1. to analyze and model a volumetric induction heating inductor with differential domains of the electromagnetic and thermal field in it; 2. to define the equivalent parameters of the inductor-workpiece system taking into consideration the differentiated zones of the electromagnetic field.

SYNOPSIS

With induction heating for forge-press operations an inductor of R-ITO-630/1-A-L type is used. The inductor consists of three cylindrical inductors connected in series, which are 1 m long and have 13 turns. It is used for heating cylindrical workpieces of radius 1 m and length 0.15 m. To achieve the set production schedule, an inductor of considerable length (in comparison with the length of the workpiece being heated) is used. The supply source is an inverter of SMK UB 2F2 630/1.5/0.6-R type.

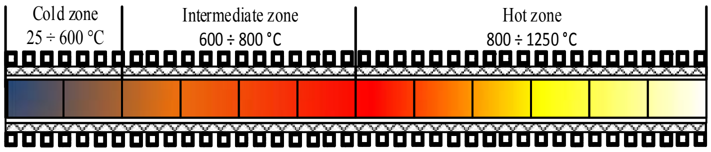

Figure 2. Inductor with zones formed upon heating identical workpieces

The system described is one of the possible examples where the resultant magnetic field and the equivalent electromagnetic parameters of the inductor-workpiece system will be formed by zones with differentiating parameters of their magnetic field. A model distribution of the temperature zones along the inductor is shown in fig. 2.

The inductor is modeled by using the finite element method in Comsol Multiphysics 5.0. The set problem is solved by going through two stages. The first stage refers to the modeling of the propagation of the electromagnetic waves in the inductor and workpieces, and the formation and circulation of eddy currents in the workpiece. The second stage involves the modeling of the thermal field and the temperature resultant from the eddy currents, as well as the heat generated by the latter in the workpieces. The temperature field is also viewed in terms of the inductor current-carrying parts (copper buses and supply conductors, as well as in terms of their cooling).

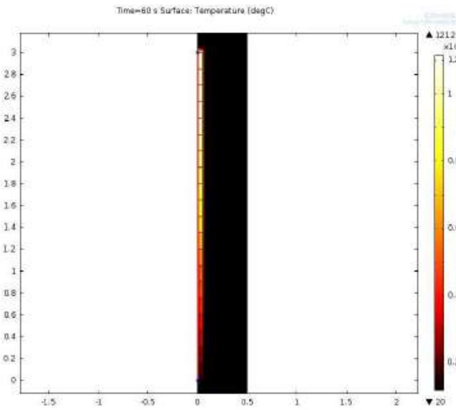

Figure 3. Picture of the temperature field of a long inductor of diameter ø 180 mm and workpiece of diameter ø 110 mm and length 150 mm at a stroke for feeding workpieces of 60 s

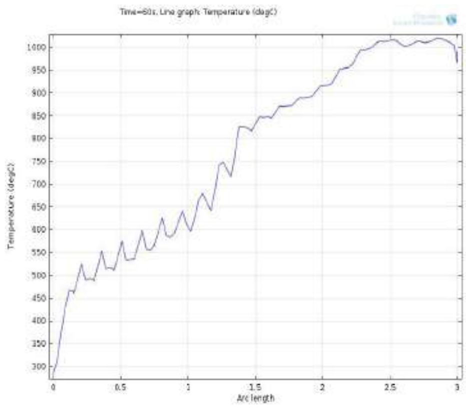

Figure 4. Distribution of temperature in the centre of the workpieces along the inductor at a stroke of feeding workpieces of 60 s, upon identical workpieces

Figure 3 shows modeling of the temperature field of an inductor of diameter ø 180, for volumetric induction heating with a workpiece ø 110 and of lenth 150 mm at a stroke for feeding workpieces of 60 s, after 20 strokes.

Figure 3 clearly indicates the homogeneous distribution in the workpieces placed in the inductor. The maximum temperature is on the surface of the 20th workpiece 1212 °C, which is enough for the next forge-press operation. Figure 4 shows the temperature inside the 20th workpiece, which is uniformly distributed and is approximately 1050 °C, which is admissible and meets the set requirement for maximum temperature difference "surface/workpiece centre". At the end of the last workpiece the temperature in the centre is lower. This could be explained with the fact that it is at the end of the inductor and there are radiation losses. We can precisely determine the length of the three zones – cold, intermediate and hot. The cold zone completely encompasses the firs five workpieces and part of the sixth one. Its length is approximately 0,8 m. The intermediate zone encompasses part of the sixth workpiece and the seventh and eighth workpiece. It has a length of around 0,45 m. The hot zone is of length 1.8 m. There the workpieces are kept at a certain temperature in terms of the temperature difference "surface/workpiece centre" and they are heated completely by the active losses caused by the circulation of their eddy currents.

Figure 5 presents the modeling of the magnetic field strength of an inductor of diameter ø 180, for volumetric induction heating and an workpiece of diameter ø 110 and length 150 mm at a stroke of feeding workpieces of 60 s.

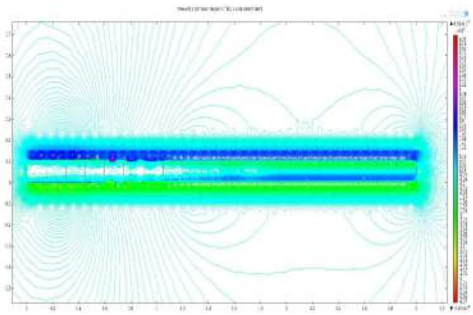

Figure 5. Distribution of magnetic field along the inductor at a stroke of feeding workpieces of 60 s, upon identical workpieces

From the modeling at a stroke of 60 s it is clearly seen that there are three magnetic domains in the inductor. These domains coincide with the temperature zones. The first domain is of length 0.8 m. It coincides with the cold temperature zone. There is a comparatively slight change of the magnetic permeability. The second domain has a length of 0.5 m and coincides with the intermediate temperature zone. The third zone is the longest one – around 1.8 m. It coincides with the hot temperature zone, where the magnetic permeability is approximately 1. Domains caused by the end effect are formed at the two ends of the inductor. In the cold zone the magnetic field strength lines are more that those in the intermediate zone whereas in the cold zone they are few. This is due to the branching of the magnetic flux in the cold and intermediate zones and the generation of additional magnetic fields in these zones. The availability of lines which encompass two zones (cold and intermediate, intermediate and hot) proves the magnetic energy transfer between them. In the cold and intermediate zones we observe refraction of the magnetic field strength lines which is caused by the sharp change of the inductor properties and the metal being heated in those points with respect to the magnetic permeability μ.

The results from the modeling of the volumetric induction heating inductor show three magnetically connected sectors formed in one inductor and bound up with the values of the temperature-dependent equivalent parameters of the inductor-metal system. The temperature zones determine domains of different magnetic vector potential which, in turn, defines domains of different magnetic induction and magnetic flux. As a result local domains are formed in the inductor, where the magnetic field strength self-closes. The boundary of each domain is related to the temperature dependence of the magnetic permeability μ.

Taking into account the above mentioned we can divide the inductor into three separate smaller inductors coinciding with the domains described above. The calculation of the equivalent parameters of each domain is presented as a problem with constant parameters of the magnetic field by determined magnetic domains. It is done by using the methods shown in [3].

The first stage of the proposed method requires calculations of the equivalent parameters by inductor domains. The results are presented in Table 1. The second stage of the proposed method is an addition to the method of induction heating of metals.

Actually it is calculation of the total equivalent parameters of the inductor-workpiece system.

Table 1. Equivalent parameters

Equivalent parameters	Cold zone I domain	Intermediate zone II domain	Hot zone III domain
r_{ei}	$8{,}36.10^{-4}$ Ω	$3{,}4.\ 10^{-4}$ Ω	$25.\ 10^{-4}$ Ω
X_{ei}	$32.\ 10^{-4}$ Ω	$144.\ 10^{-4}$ Ω	$46.\ 10^{-4}$ Ω
L_{Di}	$0{,}64.10^{-6}$ H	$2{,}9.\ 10^{-6}$ H	$0{,}92.\ 10^{-6}$ H

The domains in the inductor are combined by a replacing electromagnetic circuit shown in fig. 6. An equation by the inductor current is worked out with the help of the defined and unchanging values for the inductances and the mutual inductance by defined domains in the course of heating.

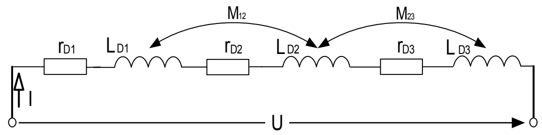

Figure 6. Equivalent replacing inductor circuit with domains defined by electromagnetic parameters

$$U = (r_{D1} + r_{D2} + r_{D3})I + L_{D1}\frac{dI}{dt} + L_{D2}\frac{dI}{dt} + +L_{D3}\frac{dI}{dt} + 2M_{12}\frac{dI}{dt} + 2M_{23}\frac{dI}{dt} \quad (1)$$

where: r_{D1}, r_{D2}, r_{D3}- equivalent active resistances by domains; L_{D1}, L_{D2}, L_{D3}- equivalent inductances of the three domains; M_{12}, M_{13} - mutual inductances between the separate domains.

To determine the mutual inductances M_{12} and M_{13}, the principle of interchanging lengths in a solenoid is applied [4].

$$M_{12} = \frac{\pi}{8}\mu_0 wW\frac{d^2}{a_1 a_2}[(a_1 + a_2)K_{a12} - a_1K_{a1} - a_2K_{a2}] \quad (2)$$

where: μ_0- magnetic permeability of the vacuum, equal to $\mu_0 = 4\pi.10^{-7}$ H/m , w,W- number of turns of the two domains; d – inductor diameter;a_1, a_2 - length of domains I and II [m]; $K_{a1,}$ $K_{a2,}$ K_{a12} – coefficients whose values depend on the relationship α=ai/d, where ai –the length of the respective domain in [m]; d is the inductor diameter [m]. For this particular case K_{a12}=0,91 , K_{a1}=0,66 , K_{a2}=0,89.

$$M_{23} = \frac{\pi}{8}\mu_0 \omega W\frac{d^2}{a_2 a_3}[(a_2 + a_3)K_{a23} - a_2K_{a2} - a_3K_{a3}] \quad (3)$$

where: a_2, a_3 - length of domains II and III [m]; K_{a23}, K_{a2}, K_{a3} – coefficients whose values depend on the relationship $\alpha = a_i/d$, where a_i - the length of the respective domain in [m]; d is the inductor diameter [m]. For this particular case K_{a23} = 0,92 , K_{a2} =0,89 , K_{a3}=0,71.

The third stage of the proposed method refers to the calculation of the inductor energy parameters and mutual inductances at set voltage and operational frequency, and heating time of one workpiece. The results from the calculation of the equivalent parameters for an inductor with differentiated domains of the magnetic field are shown in Table 2.

Table 2. Inductor equivalent parameters

r	$3{,}68.\ 10^{-4}\ \Omega$
x	$2{,}54.\ 10^{-2}\ \Omega$
L	$5{,}06.\ 10^{-6}$ H
z	$2{,}54.\ 10^{-2}\ \Omega$
P	77,21 kW
I	1743,5 A
M_{12}	$0{,}12\ .10^{-6}$ [H]
M_{23}	$0{,}18.10^{-6}$ [H]

The presented calculation of a volumetric induction heating inductor considers the fact that the properties of the workpiece being heated change with temperature. In this way we can calculate the dynamically changing equivalent parameters of the system in the course of heating. These calculations can be used for controlling parameters in supply source control systems.

CONCLUSIONS

The present paper views the modeling of the electromagnetic and thermal field of a volumetric heating inductor of R-ITO-630/1-A-L type. The modeling results show three magnetically connected sectors formed in one inductor and bound up with the values of the temperature-dependent equivalent parameters of the inductor-metal system. The temperature zones determine domains of different magnetic vector potential, which, in turn, define domains of different induction and magnetic flux. As a result local domains where the magnetic field strength self-closes are formed. The boundary of each domain is connected with the temperature dependence of the magnetic permeability μ.
With the help of the proposed methodology the equivalent parameters of the inductor-workpiece system are calculated by taking into consideration the separate magnetic domains.

The paper completes the induction heating theory and proposes a methodology for calculating the electromagnetic parameters of an inductor-workpiece system with differentiated temperature zones and magnetic domains along a volumetric heating inductor.

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THE NORMALIZATION OF GASEOUS EFFLUENTS POLLUTANTS FROM LARGE COMBUSTION PLANTS

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ABSTRACT

From the perspective of environmental protection, the most important area of human activities is the industry.

Electricity is a clean form of energy but often, its production is based on fossil fuel combustion processes.

Within the European Union, operators of large combustion plants are required under the provisions of Directive 2001/80 / EC (LCP), to monitor particulate emissions, sulfur dioxide and nitrogen oxides.

INCD INSEMEX Petrosani determines the concentration of gaseous components of industrial emissions from large combustion plants and the concentration of VOCs from various industrial processes, endowed with advanced equipment.

This paper presents the calculation of pollutant concentrations measured at stationary sources.

Key words: Large combustion plants, pollution, emissions measurements, normalization.

INTRODUCTION

One of the most important environmental issues in Romania is the air pollution, which is a highly complex phenomenon.

Emissions from large industrial facilities are a significant part of the total emissions of key air pollutants environmental effects. Power plants are designed as basic power for the National Power System

The main parts of a plant are:

- Household fuel (solid) - to supply energy blocks;:
- Household liquid fuel tanks fitted with oil under / overground;
- Ash and slag deposits from the combustion of fuels;
- The boiler and related facilities;
- Steam turbines and related facilities;
- Energy blocks - containing electrical installations;
- Household electrical wiring and automation;

- Installations for the retention, disposal and dispersion of pollutants in the environment evidenced by electro-filters for retaining dust and various gas cleaning systems of combustion.

Large combustion plant operators are required under Art. 17 of GD. 541/2003 to monitor the emissions of sulfur dioxide and nitrogen oxides.

Evaluation of gaseous pollutants in the large combustion plants is carried out in accordance with the technical requirements established by Order No. MAPPM. 462/1993, governing the methodology for determination of emissions of air pollutants produced by stationary sources.

EMISSIONS ARISING FROM BURNING

Pollutants resulting from large combustion plants considered in the protection of the atmosphere (by Order 462/1993) are: sulfur dioxide (SO_2), nitrogen dioxide (NO_2), nitrogen oxides (NO_x), carbon monoxide (CO) . and particulate matter (PM_{10} and $PM_{2.5}$).

Effects of pollutants listed below are presented further.

Sulphur dioxide (SO_2) - a colorless, bitter, non-flammable, with a pungent odor that irritates the eyes and respiratory system.

The effects on health are based on the concentration and exposure time.

Exposure to a high concentration of sulfur dioxide in a short period of time, can cause serious breathing difficulties. Are particularly affected people with asthma, children, the elderly and people with chronic respiratory diseases. Exposure to reduced concentrations of sulfur dioxide in the long term can lead to infection of the respiratory tract.

Nitrogen oxides (NO_x) – are a group of highly reactive gases which contain nitrogen and oxygen in varying amounts. Most of the nitrogen oxides are colorless and odorless gas. It is known to be very toxic gas both to humans and animals (the degree of toxicity dioxide is four times higher than that of nitrogen monoxide). Exposure to high levels could be fatal, and at low levels affects the lung tissue.

Population exposed to such pollutants can have breathing difficulties, respiratory irritation, lung dysfunction. Long-term exposure to a low concentration can destroy lung tissue resulting in emphysema. The people most affected by exposure to this pollutant are children.

Carbon monoxide (CO) – is a colorless, odorless, tasteless gas. It is a toxic gas in high concentrations is lethal (at concentrations of about 100 mg/m^3) by reducing the oxygen carrying capacity of blood, with consequences on the cardiovascular system Respirators system. At relatively low concentrations of the central nervous system, reduce heart rate, thus decreasing blood volume in the body distribution, reduced visual acuity and physical ability, exposure for a short period can cause severe fatigue may cause shortness of breath and pain in the chest those diseases cardiovascular causes irritability, headache, tachypnea, lack of coordination, nausea, dizziness, confusion, reduced ability to concentrate.

Segment of the population most affected by exposure to carbon monoxide is children, the elderly, people with respiratory and cardiovascular diseases, anemic people and smokers.

Particulate matter (PM_{10} and $PM_{2,5}$) – is a complex mixture of small particles and aerosols.

Particle size is directly related to the potential to cause effects. An important issue is the particle diameter less than 10 micrometers, passing through the nose and throat and enters the pulmonary alveoli causing inflammation and poisoning. Are particularly affected people with cardiovascular and respiratory diseases, children, the elderly and asthmatics.

Children older than 15 years inhale more air, and therefore more pollutants. They breathe faster than adults and tend to breathe more on his mouth, practically bypassing natural filter and nose are especially vulnerable because their lungs are not developed and developing lung tissue is more sensitive.

GENERAL REQUIREMENTS FOR MONITORING DISCONTINUOUS LARGE COMBUSTION PLANTS

Discontinuous measurements of emissions have as result emission behavior of plant, punctual and limited in time.

Monitoring by discontinuous measurements of SO_2, NO_x and dust is made in all cases where continuous monitoring is not requiredIn the event of non continuous measurements, the competent authority for environmental protection have performed discontinuous measurements or other appropriate determination procedures, verified and approved it, leading in evaluation of the quantities of emissions of sulfur dioxide, nitrogen oxides and dust, with a frequency at least every 6 months.

Discontinuous measurements shall be performed in the following cases:

- For large combustion plants whose life is more than 10,000 hours;
- Emissions of sulfur dioxide and dust emissions from the combustion of natural gas in boilers or gas turbines;
- Sulfur dioxide emissions from gas turbines or boilers which burn oil with known sulfur content, if they do not have desulphurisation equipment;
- Sulfur dioxide emissions from boilers using biomass combustion process, provided that the holder activity to justify technically that emissions of sulfur dioxide can be in no case greater than the limit emission set.

Measuring pollutants SO_2, NO_x and particulate involve in Annex 2 of GD. 541/2003, simultaneously measure the relevant process parameters: temperature, pressure, oxygen content of the flue gas water vapor as required by the methods of measurement used.

In order to draw some conclusions on the emissions of installations operating continuously applying measurement procedures in a limited amount of time, measurements must be made in such a way that the results are representative of the emission behavior of the system. Therefore the planning of this activity is an extremely important factor.

The purpose of the current surveillance installations that do not require continuous monitoring to establish a monitoring program to be approved batch by the competent authority for environmental protection environment and is included in the integrated environmental authorization. In determining the measurement program are taken into account technological features of the system.

Measurement program must cover all phases of operation of the plant. Measurements should be relevant for all situations - known operating conditions (operating cycles, fuel switching, changes which affect emissions etc.)

DETERMINATION OF GASEOUS POLLUTANTS WITH TESTO 350 XL EQUIPMENT

Determining method for gaseous components from industrial emissions is the direct method with Multigas unit.

The test method is to determine the concentration of gas samples taken from emissions from stationary sources (industrial chimneys, pipes) using Testo 350XL equipment.

Multigas analyzer TESTO 350 L is composed of the sampling probe unit for analyzing and control unit Figure 1 (A, B, C). Samples are taken with internal pump unit and on the route the suction gas is cooled to 4-8 ° C, water vapor is condensed directly results in the lowest moisture absorption by NO_2 and SO_2. The condensate is pumped at regular intervals Desiccator body installed on equipment.

Dry gas is passed through filters that are designed to retain the suspension. The filters also have function to retain water vapor. If filters are waterlogged, their pores closed and protects the pump and internal sensors. A very small proportion of the gas passes through the sensor membrane, where the concentration of the gas is converted into electrical signals, excess gas is removed.

For gaseous effluent, sampling is used a stainless steel metal probe provided inside with a thermocouple to determine the temperature of the effluent.

Analysis and control unit is composed of:

- Sampling pump - the role of extracting a sample from inside the chimney / pipe through sampling system (probe);
- Primary filter to retain particles with a diameter less than 10 micrometres (mounted at the tip of the sample probe), which will clean up after each determination to avoid condensation reactions between gases measured which would lead to erroneous results;
- Secondary filter to remove particulates in order to protect the pump (analyzer). It is included in the sampling line as well. The use of this filter for retaining the particles with a diameter greater than 1 μm.
- Water vapor elimiarea device operating on the principle of condensation / cooling water vapor;
- Measuring cells, which are intended to produce an electro-optical or chemical response corresponding to the gas concentration.

B. Control unit C. Logger

Figure 1. Multigas analyzer TESTO 350 XL

A.	**B.**	**C.**
1 Control unit	1 Printer	1 Status led
2 Logger	2 Toolbari	2 Tool holder
3 Sampling probe	3 Display	3 Direct contacts
	4 Toolbar functions	4 Connections
	5 Function key	5 Sampling probe
	6 Toggle Keys	
	7 Network Connection	
	8 PC interface	

EXPRESSION OF RESULTS BY NORMALIZATION

The measured results are shown in the file generated by the application saved in the computer, which is expressed in mg / m^3 or % vol depending on specific parameters.

The final value is obtained by normalizing the outcome. Thus it relates to standard conditions of temperature, volume fraction of oxygen and moisture.

Recalculation of values is performed according to the equations below:

Mass concentration C_M measured at T_M temperature will become C_{RT} concentration at standard temperature T_{ref} by the equation:

$$C_{R_T} = C_M \cdot \frac{T_M}{T_{ref}}, \quad mg / Nm^3$$

where:

- C_M - pollutant concentration measured;
- T_M – Measured temperature of the gas drawn;
- T_{ref} – absolute standard temperature;
- C_{RT} – C_M concentration at standard temperature;

Mass concentration C_M measured for a oxygen volume fraction O_M will become C_{RO} concentration in standard conditions trough oxygen volume fraction O_{ref} by the equation:

$$C_{R_O} = C_M \cdot \frac{21\% - O_{ref}}{21\% - O_M}, \quad mg / Nm^3$$

where:

- C_M - pollutant concentration measured;
- C_{RO} – pollutant concentration adjusted to a reference oxygen content, % vol;
- O_M – measured oxygen content, % vol;
- O_{ref} – reference oxygen content, % vol;

Reference oxygen content in the flue gas:

- 3 % in volume of liquid or gaseous fuels;
- 6 % in volume, in the case of solid fuels;
- 15 % the volume at of gas turbines.

F_h conversion factor for converting the measured volume content of water vapor h_m at standard conditions to the water vapor content by the equation:

$$F_h = \frac{100\% - h_m}{100\% - h_{ref}},$$

in which:

- h_{ref} standard content of water vapor (volume fraction, $h_{ref} = 0\%$ in dry conditions);
- h_m Measuring water vapor content of the sampled gas (volume fraction).

Above equations will be combined to obtain mass concentration C_R under standard conditions according to the following equation:

$$C_R = C_M \cdot \frac{T_M}{T_{ref}} \cdot \frac{21\% - O_{ref}}{21\% - O_M} \cdot \frac{100\% - h_m}{100\% - h_{ref}}, \qquad mg / Nm^3$$

where:

- C_M - pollutant concentration measured;
- T_M – Measured temperature of the gas drawn;
- T_{ref} – absolute standard temperature;
- O_M – measured oxygen content, % vol;
- O_{ref} – reference oxygen content, % vol;
- h_{ref} standard content of water vapor (volume fraction, $h_{ref} = 0\%$ in dry conditions);
- h_m Measuring water vapor content of the sampled gas (volume fraction).
- C_R –C_M concentration at standard conditions;

As above, the following is a set of measured values spreadsheet for combustion gases and their normalisation:

Table 1. Measurement conditions

T_M =26,8 °C	O_M = 6,52 % vol	h_{ref} = 0 %
T_{ref} =273,15 °C	O_{ref} = 3,0 % vol	h_m = 38 %

Table 2. Value normalisation

Measured gas	mg/m^3	mg/Nm^3
CO	42,91	36,32
NO	10,18	8,62
NOx	14,36	19,61
SO_2	16,00	13,54

CONCLUSIONS

Currently, the share of solid fuels used for electricity production is still large thermal power plants are a major source of environmental pollution.

Through the chimneys, power plants emit into the atmosphere continuously and consistently huge volume of flue gas containing gaseous pollutants and particulate concentrations.

Monitoring of emissions from large combustion plants shall be in accordance with HG 541/2003 setting:

- evaluation criteria to monitoring;
- general requirements for monitoring continuously the large combustion plants;
- continuous measurement of the emission processes
- performance criteria and need for standardized measurement methods.

Concentrations in the effluent gases emitted aerosols must function normalized oxygen, temperature and humidity in accordance with the law.

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DEVELOPMENT OF METHOD FOR OBTAINING RECYCLED GLASS FIBERS FROM GRP COMPOSITE MATERIAL

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ABSTRACT

Composite materials, thanks to their good qualities, have a wider application, but the problem of composite waste is growing, because the composite material once used for certain purposes is disposed as a waste. The question of their recyclability and extension of their lifetime and today act as a method of recycling these materials are insufficiently used. Waste of composites, may represent an important raw material for the production of the same type of composite recycling process, in order to maximize their application. In this paper, a possibility of recycling composite material of glass fiber epoxy resin, and obtaining second glass fiber that can be used as reinforcement composites of the same kind is shown.

Key words: recycling, composite, glass fiber.

INTRODUCTION

There are three types of composite materials depending on the type of matrix, which are in wide use. Those are polymer matrix composites (PMC), metal matrix composites (MMC) and ceramic matrix composites (CMC). Depending on the type of reinforcement they can be divided into: composites with reinforcements in the form of particles, composites with reinforcements in the form of fibers and structural composites (laminates). Two types of classifications are illustrated in Figure 1. [1,2].

Composites with a polymer matrix dominate the market, of which the most common are those with thermostable polymer matrix, although in recent years we can see increased use of composites with a thermoplastic polymer matrix. Fibre reinforced polymers (FRPs) are increasingly being used in construction due to their light weight, easy installation, low maintenance, tailor made properties, and corrosion resistance. FRP production waste is generally disposed since the raw materials used in FRP manufacture are relatively inexpensive (Fig.2). [2,3,4]

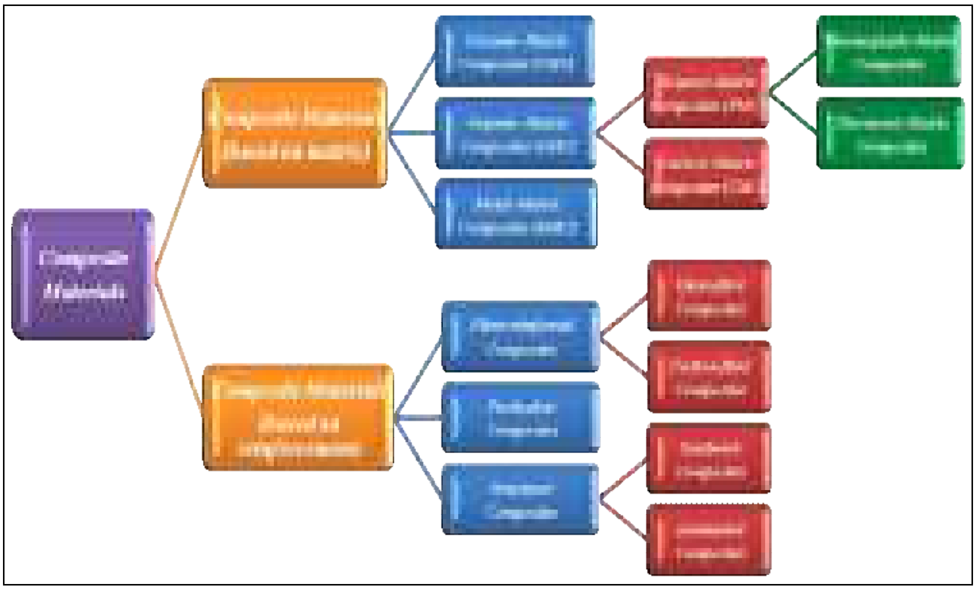

Figure 1. Classification of composite materials

Figure 2. Disposal of waste FRP

According to the waste hierarchy, the options for FRP waste management in order of preference are waste minimisation, reuse, recycling, incineration with energy recovery/composting, and lastly incineration without energy recovery/landfill (Fig.3).

Figure 3. The waste hierarchy

Recycling contributes to sustainable development of engineering materials. Today, materials such as metal, glass, plastic, are recycled widely, while the composite materials are still not recycled properly. The reason is their heterogeneous structure, and the recycling process is complex and difficult, and the resulting recyclates are of unsatisfactory quality, in particular, the case in a composite with a cured thermoset polymeric matrix. [5,6]

Methods for recycling composites are mechanical, thermal and chemical. Mechanical methods include the use of techniques of grinding and sanding of composite materials and separation of the two fractions of recycled materials, a fiber-rich and other rich matrix, which can be reused for different purposes. Recycling of composite by thermal processes involves the use of high temperatures (300-1000°C), at which the dissolution of the resin and fibers are separated from the composite. However, due to application of heat during execution of thermal recycling, damage occurs to the fibers. [7]

Chemical recycling is intended to be a chemical depolymerization or removal of the matrix and the release of fibers from the composite using the organic and inorganic solvents. When performing chemical recycling process we have formation of chemical waste, which affects the environmental pollution. There are many possibilities for application of recycled components from composite materials. Recycled components from composite materials are used as reinforcing for lumber (reinforced thermoplastics substituting even wood). Recycled fibers can be used as reinforcing for asphalt (i.e. asphalt for bridges), as interlayer between two pure glass layers in special casted boards and used in the process of stirring of volume casted mixtures which provides increased reinforcing due to the remaining recycled fibers.

The importance of recycling, because of the wide range of applications of recycled components made of composite materials is huge. In this study, composite glass fiber-reinforced epoxy resin is recycled by chemical method. After exposure the material nitric acid at an elevated temperature, and after neutralizing and washing, the obtained secondary are glass fibers which can be incorporated into new composite. [8,9,10,11]

EXPERIMENTAL

Fiber-reinforced composite material is formed by a manual method in a mold. The mold consists of two metal plates connected by screws. Once placed in the mold, the composition was held for 24 hours at room temperature in order to harden for the treatment and cure (Fig.4).

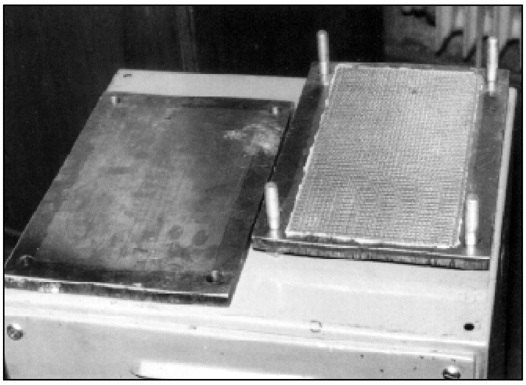

Figure 4. Mold

After 24 h mold was opened and hardened composite material (CM) without any significant defects was placed out of mold and left to cure completely in air during 7 days at room temperature. The specimens for mechanical testing were cut from prepared CM. The reinforcement for composite material preparation were 20 mm long „E“-glass-fibers based on low alkali silicate glass with surface density 550 g/m^2 and volume fraction 60%. E-glass-fibers have good mechanical, hydro-thermal and electrical properties (Table 1 and 2).

Table 1. Composition of „E“-glass

Structural component	**Fraction (wt%)**
SiO_2	52 – 56
Al_2O_3	12 – 16
B_2O_3	5 – 10
Na_2O and K_2O	0 – 2
MgO	0 – 5
CaO	16 – 25
TiO_2	0 – 1.5
Fe_2O_3	0 – 0.8
Fe	0 – 1

Table 2. Physical properties of "E"-glass

Property	**Value**
Specific weight, g/m^3	2.6
Tensile strength, MPa	2400
Modulus of elasticity, GPa	73
Elongation at break, %	3.3
Thermal elongation, 10^{-6} K^{-1}	5
Thermal conductivity, W/mK	1
Dielectric constant, ξ	6.7
Electrical resistivity, Ωcm	10^{14}
Moisture absorption, at 20°C $\rightarrow$ 65% wt	0.1

The polymer matrix used in this research was epoxy resin. The composite material was prepared by the procedure described above. Glass fibers were prepared in the form of a glass mat is of length 2 cm. Polymer matrix is synthesized from 2,2-bis(4-hydroxyphenyl) propane, bisphenol A and epichlorohydrin. 3-Aminomethyl-3,5,5-trimethylcyclohexylamine (modified cycloaliphatic amine) was used as a hardener. Shaped material has a 52.0% by weight of the glass mat.

The resulting composite material is recycled and the glass fibers were excracted. The epoxy resin was completely removed in such a way that material is first immersed in concentrated sulfuric acid (98 wt%), and thereafter immersed in 200 cm^3 of a solution of nitric acid (68,5 wt%), at 90 °C for 5 hours. After 5 hours in nitric acid epoxy resin is completely solved and secondary glass fibers were obtained. Fibers are separated from the nitric acid by filtration, rinsed with distilled water and neutralized with ammonium hydroxide solution (25 wt%), and again with distilled water until the pH value of 7 was reached. The neutralized and washed glass fibers were dried in an oven at 110°C, and thereafter cooled on a room temperature. Loss of glass fibers is 4,9%. The figure 5 shows the primary and recycled glass fibers.

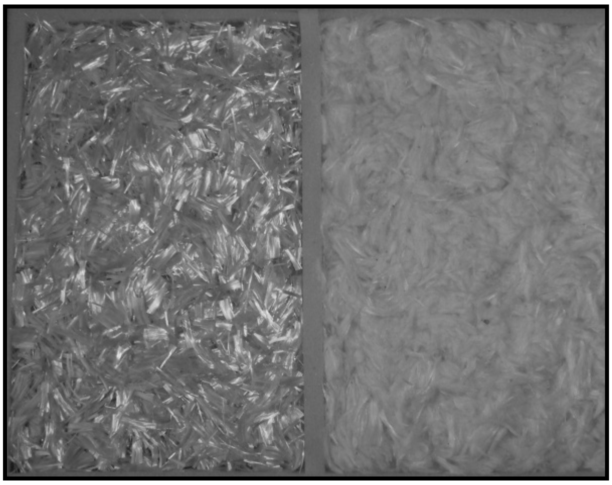

Figure 5. Appearance of non-recycled (left) and recycled (right) GFs

The resulting glass fibers may be used as reinforcement in the formation of the new composite material. We can make conclusions about the quality of recycled fibers and their potential reuse by measuring mechanical properties of composite materials with primary and composite materials with recycled glass fibers.

CONCLUSION

Composites have not been properly recycled, due to their inherent nature of heterogeneity, in particular for the thermoset-based polymer composites. The current and future waste management and environmental legislations require all engineered materials to be properly recovered and recycled from end-of-life (EOL) products. The aim of this study was to investigate the possibility of recycling composite material fiberglass-epoxy resin and obtaining second glass fiber as raw materials for new composites.

From the looks of the obtained glass fiber can be concluded that the method of recycling glass fiber reinforced resin by exposure to nitric acid may be applied to the recycling of small quantities of materials because of energy inefficiency, and that further research should be directed towards improving applied methods. The method should be developed for use of several different acids to shorten the exposure of composites in acids and increasing the efficiency of the recycling process at lower temperatures. In addition, it is necessary to obtain secondary fiber incorporated into a new composite, and determine the mechanical properties of the produced material, in order to make a conclusion about its quality. In any case, the recycling of composite materials and recycling in general can largely lead to savings of energy and raw materials, as well as to environmental protection.

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STUDY OF BETA ZEOLITE PHYSICAL-CHEMICAL CHARACTERISTICS BY OBSERVING ADSORPTION OF SOME ACID AND BASE COMPONENTS FROM AQUEOUS SOLUTIONS

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ABSTRACT

Thanks to their polyfunctional characteristics, nowadays zeolites are also significantly used in ecology, apart from their role of efficient catalysts in a series of industrial processes. Zeolites have distinct adsorption characteristics and therefore as surface-active materials they are more and more used in removing dissolved, chiefly organic matters and ammonia by adsorption as a simple and very efficient method. For the purpose of obtaining information on the character of active centers on the surface of BETA zeolite, the study examined physical-chemical characteristics of this zeolite by observing adsorption of ammonia and butyric acid from the aqueous solution, which are potential ecological environment polluters. BETA zeolite is of nanostructural dimensions and is produced in the American company *Zeolyst International* (index: CP814E) with a high Si/Al ratio, which makes it hydrophobic and thermally stable at high temperatures and as such it is applied in the adsorption processes in low-pollution technologies. Adsorption of ammonia and butyric acid from the aqueous solution was observed on NH_4BETA and its modified form, HBETA zeolite, in the temperature interval from 283 to 308 K. Characteristics of the adsorbent/adsorbate system are described by the Freundlich adsorption isotherm. The results proved that HBETA zeolite was a better adsorbent both for ammonia and butyric acid. With the adsorption temperature rise there was an insignificant fall of the quantity of adsorbed ammonia and also of butyric acid.

Key words: adsorption, BETA zeolite, ammonia, butyric acid.

INTRODUCTION

For a long time application of zeolites as catalysts have made significant results, which is a motivation for the new studies that have resulted in the discovery of a broad spectrum of new materials. By observing different aspects of the adsorption process in combination with kinetic results we get important information on the surface-active centers that are responsible for the adsorption phenomenon itself, but also for the catalysis, which is further significant since different chemical processes require active centers of different acidity. Activity and selectivity of zeolite catalysts depend on their physical and chemical characteristics and that is why knowing physical-chemical characteristics of zeolites is an unavoidable part of each study that aims at developing new or modifying and applying the existent materials (1-4). Zeolites, materials of nanoporous dimensions, produced by contemporary technologies, can be legitimately called precious materials, taking into account a broad spectrum of their use in almost all branches of industry, no matter whether they are used as adsorbents, catalysts or catalyst carriers. The porous structure of zeolite materials enables a high adsorption capacity, and different cavity openings also enable selective adsorption, known as the molecular sieve effect. The zeolite characteristics important for adsorption relate to the surface condition, and those are: chemical composition, structure, energetic relief of the surface, size and form of pores, whose inner surface also possesses potentially active centers of adsorption (5-8). The system composition in the border area between two phases is not the same as in the remaining part of the system due to the surface phenomena that occur in the contact area between the phases. The liquid surface is in the state of unsaturation, as well as the solid surface that has an unsaturated field of forces, so that there is a tendency of both surfaces on which we observe occurrences on the border of the phases to decrease their free energy, and as the consequence of that tendency there comes adsorption, i.e. increase or decrease of the concentration of individual components on the phase surface, which results in the decrease of free energy of the border surface. The connections established between adsorbents and adsorbates can be weaker Van der Waals or stronger chemical bonds with the participation of valence electrons, which depends on the nature of adsorbents, nature of adsorbates and temperature. If between active centers of the zeolite surface and molecules of adsorbates there exists chemical similarity, then physical adsorption is followed by chemisorption. Examining the character of active centers on the zeolite surface is very important for the purpose of their more efficient application (9-11). BETA zeolite crystal sieve is made of three-dimensional system of channels with twelve-member rings (12,13). Two mutually vertical flat channels, each with the diameter of 0.76 x 0.64 nm, strech in *a* and *b* direction, and sinusoidal channel with the diameter of 0.55 x 0.55 nm streches paralelly in *c* direction. Figure 1 gives a schemtic presentation of the BETA zeolite structure. This study tested active centers of BETA zeolite (NH_4BETA and HBETA) by observing adsorption of ammonia and butyric acid from the aqueous solution. The results showed that that zeolite possessed acid active centers suitable for ammonia adsorption, but also poor base ones that the molecules of butyric acid got bonded with.

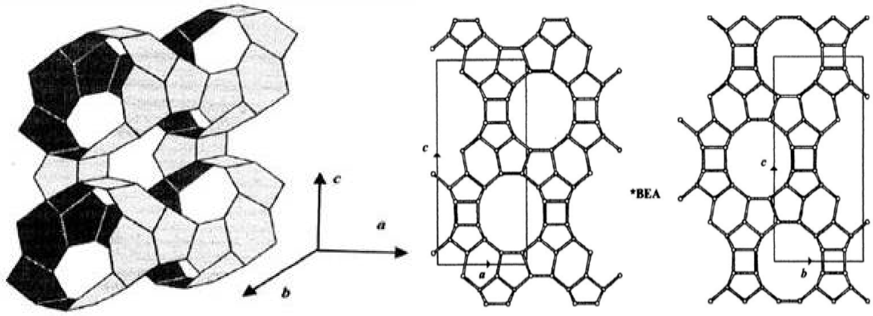

Figure 1. Schematic presentation of BETA zeolite

EXPERIMENTAL PART

Synthetic zeolite of BETA type is a product of the American company *Zeolyst International*. The original sample is NH_4BETA zeolite, while the modified H-form was obtained after the process of deamination at the high temperature of 673 K in the course of 4 hours. Table 1. states characteristics of these zeolite materials.

Table 1. Characterization of zeolite samples

Zeolite	Chemical formula	SiO_2/Al_2O_3	Na_2O (%)	Sp (m^2g^{-1})
NH_4BETA	$(NH_4, Na)_xO{\cdot}Al_2O_3{\cdot}25SiO_2{\cdot}4H_2O$	25.00	0.05	680.00
HBETA	$(H, Na)_xO{\cdot}Al_2O_3{\cdot}25SiO_2{\cdot}4H_2O$	25.00	0.05	650.00

Before making each round of experiments we established the optimal quantity of adsorbent, as well as the optimal time needed to reach a balance state. The zeolite mass was always correctly established (precise weighing ± 0.0001 g). The reaction admixture was thermostated. The optimal time for reaching the balance state between adsorbent and adsorbate was established and it amounted to three hours. Adsorption was observed in the temperature interval from 288 K to 308 K. The scope of concentrations of the ammonia aqueous solution was from 0.0180 mol/L to 0.2500 mol/L, and for the organic acids it was from 0.0200 mol/L to 0.2000 mol/L. The solutions of different concentrations were prepared by diluting the basic solution.The ammonia quantity was determined before and after the adsorption by the volumetric method, titration with the standard solution of hydrochloric acid, and the titrans used in determining the butyric acid quantity was sodium hydroxide. The quantity of ammonia, as well as of butyric acid, which was adsorbed on the zeolite surface, was calculated from the difference and marked as **x**, and by the unit of adsorbent mass as **x/m**. The initial concentration of the adsorbate was marked as $\mathbf{c}_0$, and the balance with **c**. We drew a curve of functional reliability **x/m** on the balance concentration (Freundlich adsorption isotherm) from which we read plateaus (plateau represents the adsorbate quantity that gets bonded with one adsorption monolayer). For obtaining data on the size, morphology and texture of zeolite material particles we used the method of scanning electron microscopy (Scanning Electron Microscopy) and figure 2 (from A to F) shows SEM morphologies of BETA zeolite, where the nanodimension particles are visible when 200 000 and 300 000 times enlarged.

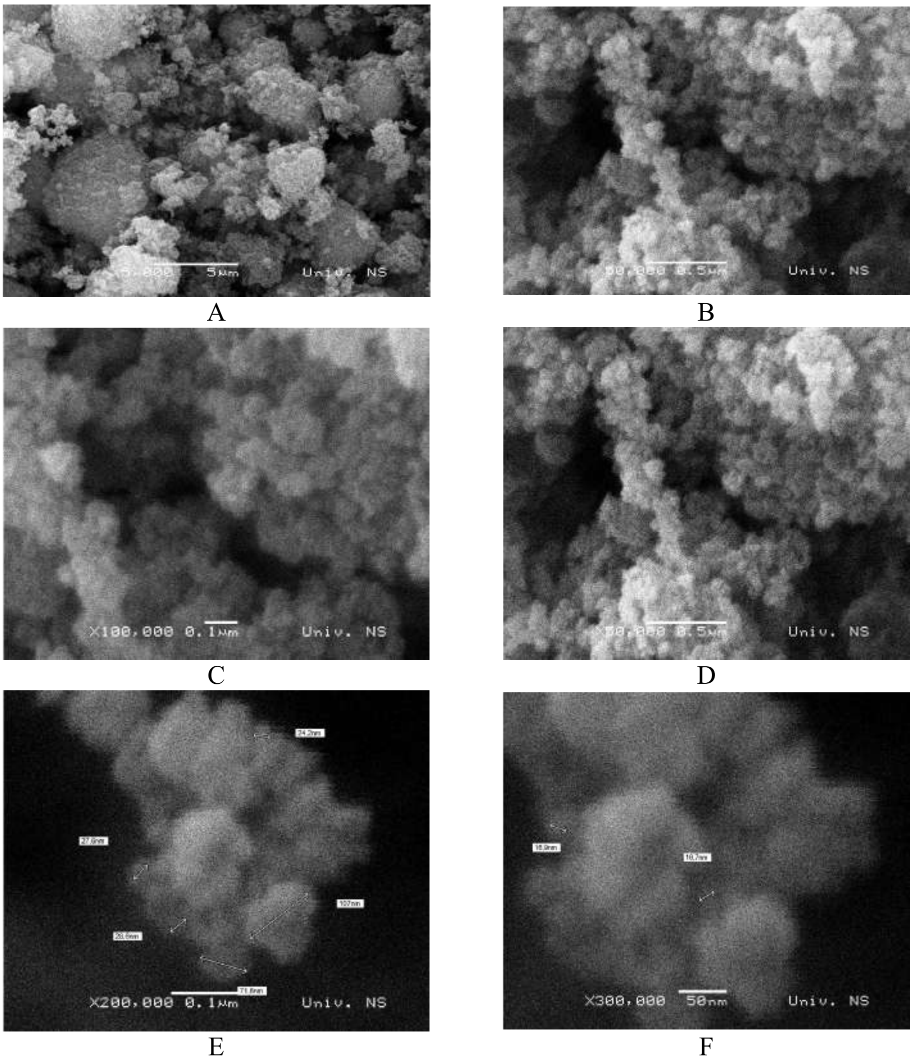

Figure 2. (A-F). Electronic photos of BETA zeolite from 5000 to 300 000 times enlarged

RESULTS AND DISCUSSION

Figures from 3 to 5 show Freundlich adsorption isotherms for the systems of ammonia-NH_4BETA and ammonia-HBETA at 283, 288, 298 and 308 K.

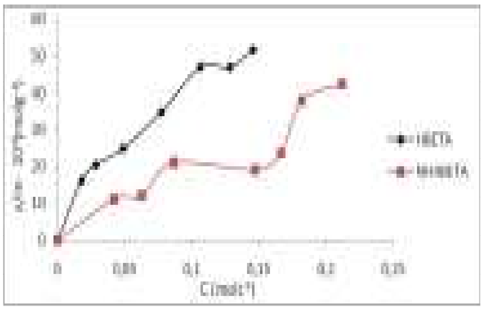

Figure 3. Adsorption of ammonia on BETA zeolites at 283 K

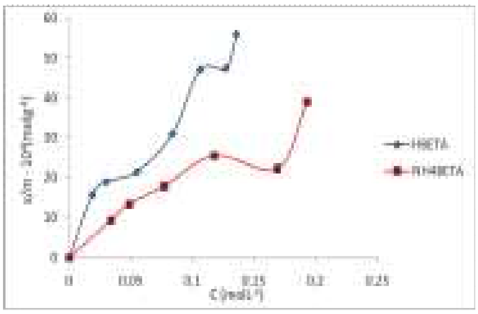

Figure 4. Adsorption of ammonia on BETA zeolites at 298K

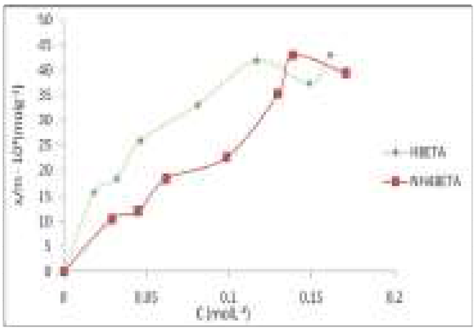

Figure 5. Adsorption of ammonia on BETA zeolites at 308 K

The survey of parameters, like temperature of adsorption and values of plateaus read from the adsorption isotherms (x/m), as well as the number of adsorbed molecules of ammonia on individual plateaus, has been presented in table 2.

Table 2. Survey of parameters of ammonia adsorption on BETA zeolite as adsorbent

Zeolite	Adsorbate	$T_{adsor.}$ (K)	Plateau height $x/m \cdot 10^3$ (mol/g)	No. of adsor. molec. $\cdot 10^{-20}$	Surface of adsorb. molec. S (m^2)	Q (%) S/S_p
NH_4BETA	Ammonia	283	I=1.20 II=2.10 III=4.20	I=7.23 II=12.65 III=25.29	23.35 40.86 81.69	3.43 6.01 12.01
NH_4BETA	Ammonia	298	I=2.50	I=15.06	48.64	7.15
NH_4BETA	Ammonia	308	I=1.20 II=2.00 III=4.30	I=7.23 II=12.04 III=25.89	23.35 38.89 83.62	3.43 5.70 12.29
HBETA	Ammonia	283	I=2.10 II=4.70	I=12.65 II=28.30	40.86 91.41	6.20 14.06
HBETA	Ammonia	298	I=2.00 II=4.70	I=12.04 II=28.30	38.89 91.41	5.98 14.06
HBETA	Ammonia	308	I=1.60 II=4.20	I=9.60 II=25.29	31.01 81.69	4.70 12.57

Results of the observation of ammonia adsorption on NH_4BETA and HBETA zeolite show that the modified H-form of zeolite has a bigger affinity towards this adsorbate at all temperatures, which was expected, since HBETA zeolite possesses more active centers of Brönsted acidity compared with the original form (14-16). For the system of NH_4BETA zeolite – ammonia, adsorption curves go through several plateaus, while the plateaus for the system of HBETA zeolite-ammonia are less distinct and adsorption curves are of Langmuir type. According to the form of curves we can conclude that the adsorption in case is a physical multilayer adsorption. For the purpose of examining adsorption capacity of the samples of BETA zeolite, i.e. their active surface and affinity towards some acid adsorbate, we chose butyric acid. Results of the experimental observation of adsorption of butyric acid (BA) from the aqueous solution on NH_4BETA zeolite are presented in figures from 6 to 10. Figure 6 presents Freundlich adsorption isotherms for the system NH_4BETA zeolite – BA at 283, 293 and 303 K. Summary of adsorption parameters for adsorption of butyric acid on BETA zeolites has been presented in table 3.

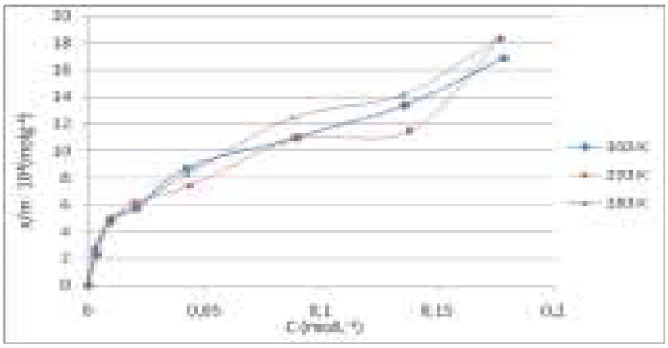

Figure 6. Adsorption of BA on NH_4BETA zeolite

Adsorption of butyric acid from the aqueous solution was also observed on the modified form of BETA zeolite (HBETA) in the same conditions. Figure 7 presents Freundlich adsorption isotherms for the system HBETA zeolite –BA at 283, 293 and 303 K.

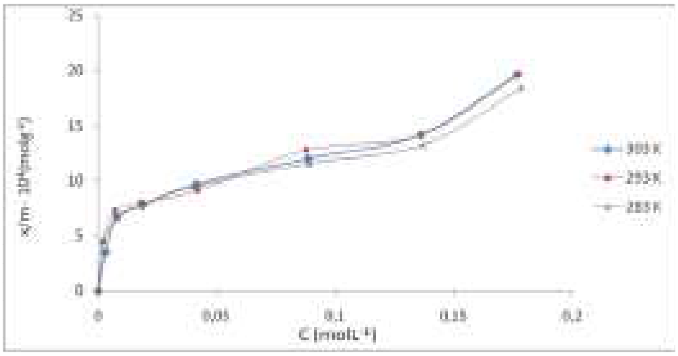

Figure 7. Adsorption of BA on HBETA zeolite

Figures from 8 to 10 show Freundlich adsorption isotherms for the systems of butyric acid-NH_4BETA and butyric acid-HBETA at 283, 293 and 303 K.

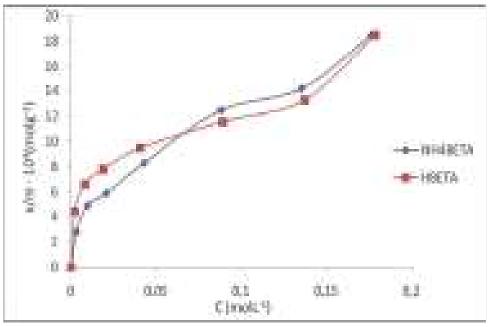

Figure 8. Adsorption of BA on BETA (283 K)

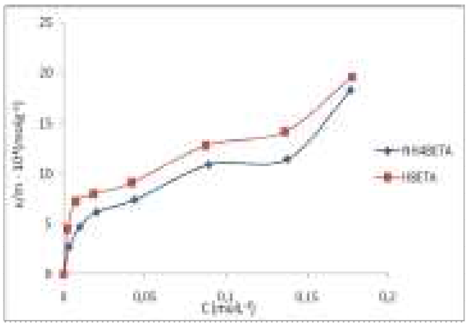

Figure 9. Adsorption of BA on BETA (298 K)

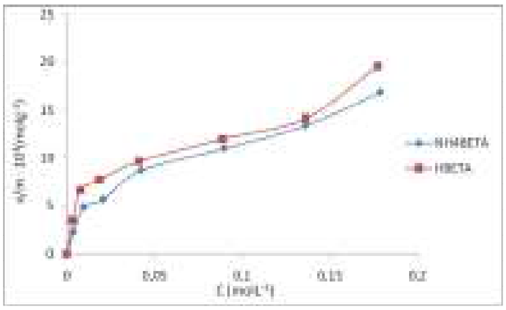

Figure 10. Adsorption of BA on BETA (303 K)

Table 3. Survey of parameters of butyric acid adsorption on BETA zeolite as adsorbent

Zeolite	Adsorbate	$T_{adsor.}$ (K)	Plateau height $x/m \cdot 10^3$ (mol/g)	No. of adsor. molec. · 10^{-20}	Surface of adsorb. molec. S (m^2)	Q (%) S/S_p
NH_4BETA	Butyric acid	283	I=0.50 II=1.24	I=3.92 II=6.99	65.93 117.57	9.70 17.29
NH_4BETA	Butyric acid	293	I=0.61 II=1.09	I=4.40 II=7.53	74.01 126.65	10.88 18.63
NH_4BETA	Butyric acid	303	I=0.50 II=1.00	I=3.92 II=6.02	65.93 101.26	9.70 14.89
HBETA	Butyric acid	283	I=1.16	I=7.47	125.65	19.30
HBETA	Butyric acid	293	I=0.73 II=1.25	I=3.67 II=6.57	61.73 110.51	9.48 17.00
HBETA	Butyric acid	303	I=0.65 II=1.00	I=3.01 II=6.02	50.63 101.26	7.79 15.58

Results show that the increase of adsorption temperature by 10 and 20 K slightly affects the quantity of adsorbed molecules of butyric acid on H_4BETA (first part of isotherms and I plateau coincide), and the adsorption isotherms on HBETA zeolite have the same form and coincide almost completely (figure 7). Since the change of the reaction temperature here did not significantly affect the factors that determine the power of acidity of active centers responsible for adsorption, we can conclude that the adsorption of butyric acid took place only on the centers on the outer surface of zeolite (14,16). Results show that the adsorption of butyric acid is more distinct on the modified zeolite, which was expected, since it is probable that HBETA possesses a bigger number of active centers on the surface, responsible for the butyric acid adsorption.

CONCLUSIONS

- The study examined adsorption possibilities of NH_4BETA and HBETA zeolites of a high quality, a product of the American company *Zeolyst International*.
- The adsorbates used were, a base one – aqueous solution and an acid one – aqueous solution of butyric acid.
- Obtained adsorption curves for the system of ammonia-NH_4BETA go chiefly through three plateaus, while with butyric acid on NH_4BETA there are two plateaus registered. By the form, according to Giles classification, adsorption isotherms belong to S4 group, which indicates a multilayer physical adsorption.
- Adsorption of ammonia and butyric acid from the aqueous solution was also observed on the modified HBETA zeolite for the purpose of obtaining information on acidity of active centers on the surface of this adsorbent.
- Results show that adsorption occurs faster and that a bigger number of adsorbed adsorbate molecules (for ammonia at 283 K: at I plateau the number of adsorbed molecules on NH_4BETA is $7.23 \cdot 10^{20}$, and on I plateau HBETA $12.65 \cdot 10^{20}$, namely 57 % more; for butyric acid at 283 K: at I plateau the number of adsorbed molecules on NH_4BETA is $3.92 \cdot 10^{20}$, and on I plateau HBETA $7.47 \cdot 10^{20}$, namely 54 % more).
- NH_4BETA and HBETA zeolites are somewhat better adsorbents for ammonia, which probably means that they have more acid active places that are accessible for this adsorbate.
- Adsorption of butyric acid on NH_4BETA and HBETA zeolite is also realized, which indicates that on the surface of these zeolites there are also weak base active centers, suitable for this adsorbate.

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SENSORLESS FAULT DIAGNOSTIC TECHNIQUES FOR INDUCTION MACHINES – PART II

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ABSTRACT

For maintaining optimal working condition of electrical machines (including induction machines), reducing the number of failures and build the optimal system for repair and maintenance work, it is important to have in place a system for monitoring the state, combined with faults identification techniques. In recent years in the field of diagnostics of electrical machines aim is to simple, reliable and non-contact techniques for monitoring the current electrical and mechanical condition. Paper deals with the most common techniques related to monitoring of the stator currents and voltages.

Key words: induction machine diagnostic, sensorless fault diagnostic techniques, fault detection.

INTRODUCTION

To assess the functional status of an induction machine, an algorithm based on engineering and modeling have been used: in the lab studies of dynamic monitoring system for generator operation have been carried out. Contactless monitoring techniques by analyzing real-time instantaneous values of currents, voltages and power capacities have been chosen. When building a system for monitoring and diagnostics aim is to lower costs, effectively applied techniques for monitoring and diagnostics, implemented with relatively simple measurements. The aim is to establish reliability and authenticity of the data acquired and the adequacy of the system for diagnostics and monitoring.
The system for measuring and collecting data comprises:

- Induction motor AD I with technical data:

$P_{2N} = 1{,}5\ kW;\ n_N = 2830\ min^{-1};\ U_{1N} = 380V;\ I_{1N} = 3{,}3A;$ Class of insulation F;

- Induction motor AD II with technical data:

$P_{2N} = 0{,}6\ kW;\ n_N = 1350\ min^{-1};\ U_{1N} = 380V;\ I_{1N} = 1{,}7A,$ Class of insulation B;

- Energy quality analyzer type MI 2092 (METREL);
- The dynamic analysis device described in [5];
- frequency regulator OMRON SysDrive 3G3EV.

The observed operating parameters are: current and voltage in each phase, active and reactive power for each phase, frequency of generated voltage, temperature. System, with multiple load imitate various operational errors of induction generator (unbalance of voltages and currents, low voltage overshoot frequency). From all existing algorithms described in [4, 5, 6, 7], the implemented diagnostic system function by using an algorithm based on the detection and isolation of the fault. As an indicator of damage the difference between the actual and reference value of the observed values has been used. When the difference is zero - no damage that would affect the wind turbine. When the difference is above a defined threshold value, it is a fault signal. This signal is not a simple comparison between the measured value and prediction model, because it is first filtered.

MONITORING OF ELECTRICAL QUANTITIES

It examined the operation of the generator for the four different cases, as described herein two of them. For clarity of the results the concept degree of load of generator β has been introdiced, in which case $\beta = P_2/P_{2H}$. During the experiments the data observed and visualized for the three phases are: waveform currents, active power, reactive power, apparent power, power factor, percentage of the manifested harmonics in voltage and current curves, frequency of the generated voltage.

- **Studies in case of active load and β=0,4**

In this case the generator feed resistive load with power 80W per phase and $Z_T = R_T = 312\Omega$. Figure 1 presents data for the values observed. *Figure 2* presents the harmonic analysis of voltages and currents for the three phases. The frequency of the generated voltage is 44,44 Hz.

In the curves of voltages for each phase stand out harmonics with serial numbers ν=3 (9,74% - 10,26%) and ν=9 (≈2%). In the curves of the currents observed occurrence of harmonics with serial numbers ν=3, and less appearance harmonic numbers ν=16, 32 and 48.

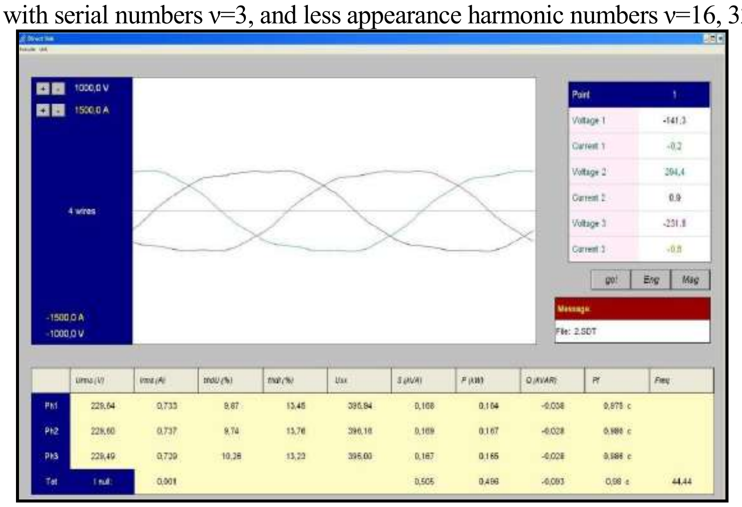

Figure 1. Data from generator study with active load and β=0,4

- **Studies in case of active - inductive load and β=0,62**

In this case, the generator supplies an active-inductive load $Z_T = 60{,}47 + j91{,}2\ \Omega$. As load a small induction motor with rated power 90 W has been used, idling, which explains the low values of power factor. *Figure 3* presents data for the values observed. *Figure 4* presents the harmonic analysis.

In fact, in an unsaturated induction machine there are numerous spatial harmonics determined by non-sinusoidal distribution of magnetization forces and non-uniform air gap (presence of stator and rotor channels, availability of eccentricity). In saturated magnetic system of the machine appear more and spectra of harmonics due nonlinearity of inductances and mutual inductances. Only a small part of harmonics influence the operation of the machine, because most of them have very small amplitudes and practically can be ignored.

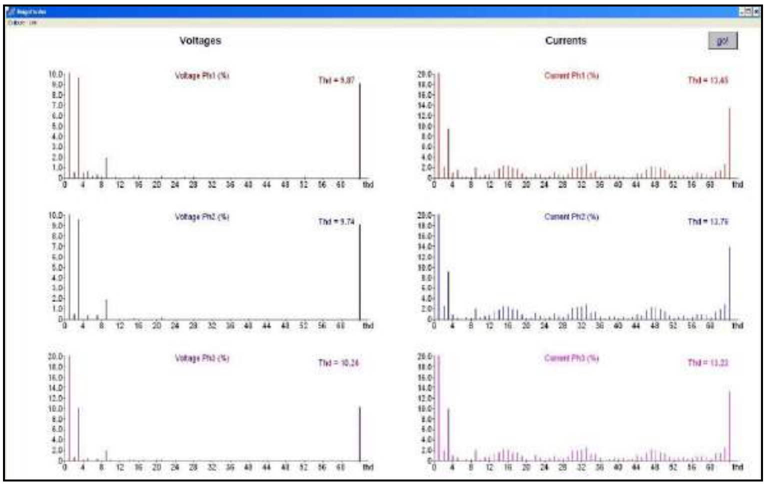

Figure 2. Harmonic analysis of the phase currents and voltages at β=0,4

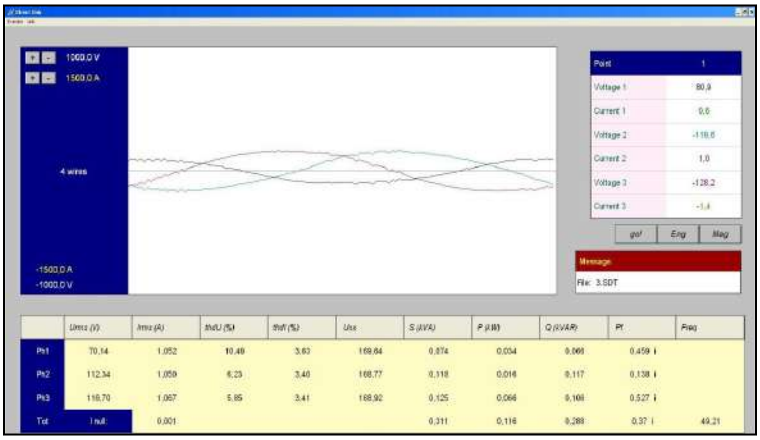

Figure 3. Data when testing the generator with active - inductive load and β=0,62

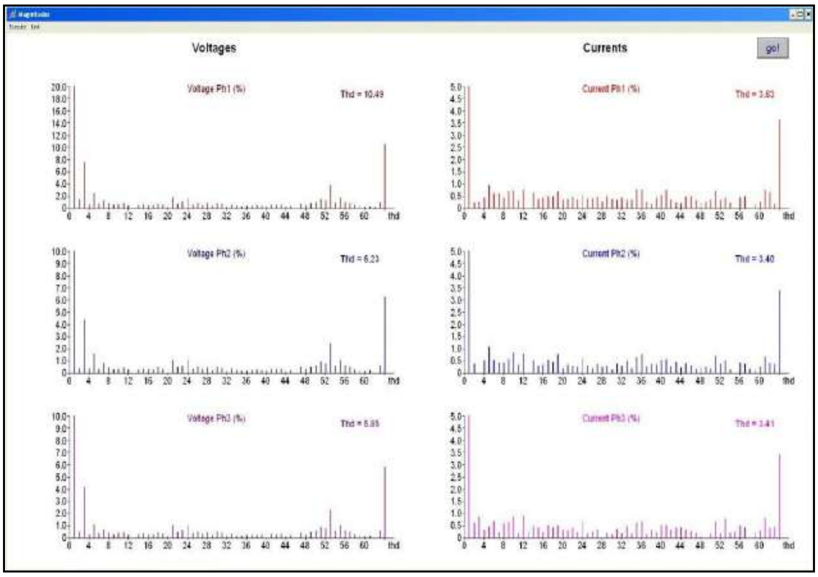

Figure 4. Harmonic analysis of generator currents and voltages for active-inductive load and β=0,62

In [1, 2] shall be considered a simple and reliable technique for the diagnosis of the current electrical and mechanical condition of the induction generator using ratios between primary and third harmonic voltage. It is known that the magnetization curve of the steel of the stator is highly nonlinear. In sinusoidal shape of current the magnetic flux curve is non-sinusoidal due to the nonlinearity of inductance and mutual inductance. The composition of the magnetic flux most prominent is the third harmonic. Connecting the stator winding in star, as in the case of us in each phase is induced corresponding harmonic of e.m.f.. The induced harmonics can be measured between the star center and artificial point with zero potential, which is formed by a load connected in star, and connected to the induction generator. Experimental data acquired at different voltages of the stator are shown in *Table 1* as the base voltage value is considered rated one.

Table 1. Experimental data acquired at different voltages

		$U_{3,\%}$		
		A	**B**	**C**
U^*	0,5	10,49	6,23	5,85
	0,97	9,54	9,55	9,0
	1,03	9,65	8,99	9,64
	1,04	9,87	9,74	10,26

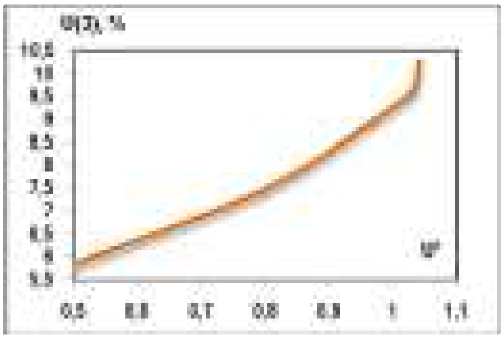

Figure 5. Depending on the percentage of third harmonic $U_{(3)}$ the relative value of the voltage U*

Determining the size of the third harmonic is the degree of saturation of steel and the position of the operating point of the magnetization curve, ie the value of magnetic induction. When operating under load position setpoint changes. With increasing load, the operating point comes down the B (H) curve, following an increase in pad $I_1.r_1$ and $I_1.x_1$ and inductive reactance of the winding dissipation and reduces the degree of saturation of the steel. Reduces inducted e.m.f. and the corresponding harmonics. When load reduction observed phenomenon back described - increasing inducted e.m.f. and harmonics. So in case the change setpoint e.m.f. inducted and third harmonic be amended simultaneously. The relationship between voltage and its third harmonic is as follows (*Figure 5*):

$$U_{(3)} = c.U^3 \quad (1)$$

where the coefficient *c* depends on the type of winding, type of the magnetization curve, the coefficient of the coil and the frequency of the voltage. With approximation is obtain:

$$\frac{\Delta U_{(3)}}{U_{(3)уст}} = 3.\frac{\Delta U}{U_{уст}}, \quad (2)$$

where $U_{(3)_{уст}}$ and $U_{уст}$ are established mode values, $\Delta U_{(3)}$ and ΔU are changes in deviation from the operating condition. Obviously voltage deviation from the established value causes 3 times greater deviation of the third harmonic of its established value. In voltages close to rated ones the third harmonic constitutes 8,99 ÷ 10,26% by the phase voltages. Based on the data acquired, if necessary, can be traced level of saturation of steel at different loads.

The spectral analysis of the stator current is an established and popular technique for diagnosis. There are mainly two approaches [2], [3]: monitoring the stator current and its harmonious composition and monitoring of generalized stator current. In [3] contactless sensorless technique for determining the speed of the induction motor in the spectral composition of the stator current is presented.

In monitoring the instantaneous values of the stator current is detectable a presence of components having as well as mains frequency *(f)*, and higher *(f_H)* and lower *(f_L)* thereof. Arrays with data for instantaneous currents are used in harmonic analysis by Fourier transformation (FFT) and on that basis has built an amplitude-frequency characteristic of the stator current i_c.

For the generator investigated in case of supply resistive load (β = 0,4) the stator current waveform is presented and amplitude-frequency characteristic is drawn – Figure 6.

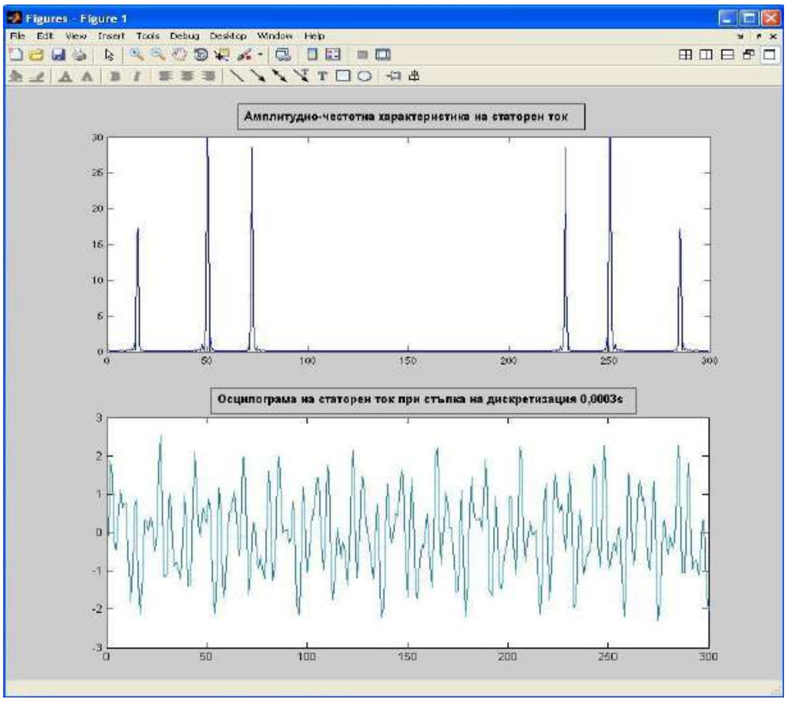

Figure 6. Stator current waveform and amplitude-frequency response

The rotor rotational frequency and slip can be determined by known expressions:

$$s = {}^{f_p}\!/_{f} \quad \text{and} \quad n = n_1.(1-s),$$

where: f_p - frequency of the main component of the rotor current, f - feed mains frequency, n - rotor rotational frequency, n_1 - rotational frequency of the stator magnetic field.

The direct measurement of the frequency of the rotor current in a short-circuited rotor winding is impossible. It is therefore convenient application of contactless sensorless technique for determining the rotational speed of the rotor in the spectral composition of the stator current.

Once applied Fourier (FFT) for the data set with instantaneous values of the stator current in this mode the presence of components has been established as well as mains frequency *(f)*, and higher (f_H) and lower (f_L), then use the established relationships between them to determine the rotational frequency only in the spectral analysis of the stator current.

$$f_{p_1} = f - 2.(f_в - f) \quad \text{and} \quad f_{p_2} = f - 2.(f - f_н) \tag{3}$$

$$s_1 = 3 - 2.\frac{f_в}{f} \quad \text{and} \quad s_2 = 2.\frac{f_н}{f} - 1 \tag{4}$$

$$n_{p_1} = n_1.(1 - s_1) \quad \text{and} \quad n_{p_2} = n_1.(1 - s_2) \tag{5}$$

where: f_{p_1}, s_1, n_{p_1} are respectively frequency of rotor current, slip and rotational frequency of the rotor determined using a frequency component of the stator current f_H; f_{p_2}, s_2, n_{p_2} are respectively frequency of rotor current, slip and rotational frequency of the rotor determined using a frequency component of the stator current f_L.

For purposes of the study in this mode of operation of the generator at the specified frequency $f_в = 74{,}8\ Hz$, *Figure 6*, we determine $f_{p_1} = 0{,}4\ Hz$, $s_1 = 0{,}0067$ and $n_{p_1} = 1524\ min^{-1}$.

CONCLUSION

Direct introduction of monitoring systems for all modes of operation of induction machines has its drawbacks. Physical measurement and identification of partial discharges, high levels of noise at work and raised temperature, are widely used techniques for monitoring of induction machines. They are simple, relatively inexpensive, but they can be used for fault diagnosis. The spectral analysis of signals from vibration sensors and sensors for the stator current is also an established and popular technique for monitoring. Its disadvantage is that it requires expertise to interpret these signals as well as very good knowledge on the working conditions of the machine and its components. The techniques used must be sufficiently informative and allow the diagnosis of electrical and mechanical faults in the stator and rotor. Datasets instantaneous values we use are stored in (* .txt) format and, if necessary, can be converted into software like Excel, Matlab, etc. for visualization and other studies, as was done, Figure 6. Thus by collecting these signals and create a database with them, it is possible to automate and computerize the diagnostics system, as its structure, functions and operation be tailored to a particular machine.

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PHASE COMPOSITION AND RECYCLING OF BY-PRODUCTS FROM STEEL PRODUCTION

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ABSTRACT

We live in the age of civilization where different materials are produced and used. For the production of such materials raw materials are used**.** At the exploitation of raw materials and production of different materials by-products are generated which can be used as the secondary raw materials. Iron scrap is also regarded as by-product from which in electric arc furnace (EAF)a new steel grade is produced.

In recent years we have reported about the formation and recycling of by-products from production of alloying steels.

In this work the phase composition of by-products from the production of alloying steels is described. By-products presented in this paper are: EAF slags, EAF dust, refractory and insulation materials; and mold powders.

INTRODUCTION

Steel is the most used metal material. Solid and gaseous by-products are formed at the preparation of raw materials and its production. At the production of steel the dominant by-product is slag, either oxidizing or refining slag.

Slag from oxidation in EAF (black slag) is used as a secondary raw material in building industry. EAF dust is secondary raw materials at the production of zinc, etc[1-5]. In this work the phase composition of by-products arising from production of stainless steel and steel casting are presented. For the evaluation chemical and phase composition is required.

SLAGS FROM PRODUCTION OF STAINLESS STEELS

During melting of alloyed steel scrap in EAF and the oxidation of carbon, also chromium oxide is formed In the slag we get spinnels with high melting point and very complex composition (FeO,MnO,MgO) (Cr_2O_3 Al_2O_3). In the EAF also a slag containing calcium silica and iron oxide (olivine slags) arises.

Their melting point is lower than melting point of spinnels. On Figure 1 is the microstructure of slag originated from the production of stainless steel. Slag has a heterogeneous composition. »Spaces« between spinnels are filled up with slag with the composition of calcium silicates. In the basic slag a calcium chromite is formed.

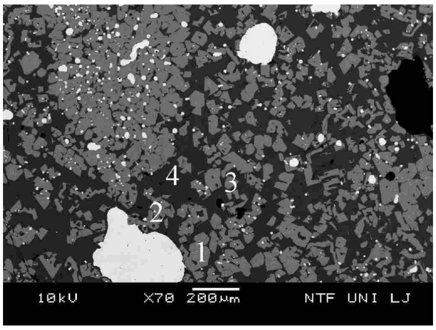

Figure 1. Spinnels with composition (Fe,Mn,Mg).(Cr2.Al)O3 in calcium silicate slag[6]

During the production of stainless steel 10 to 25 kg of chromium per tone is oxidized from steel melt and between 15 and 37 kg Cr_2O_3 is formed.

After the oxidation of carbon the reduction of the chromium oxide with aluminum, silicon or calcium-silicon (CaSi) occurs. These elements have namely more stable oxides as a chromium oxide.

Reduction level of slag is influenced from the composition of chromites. At increased concentration of magnesium oxide in the slag $MgO \cdot Cr_2O_3$ is generated. Even after the reduction of the slag remains picrochromite (Fig. 2).

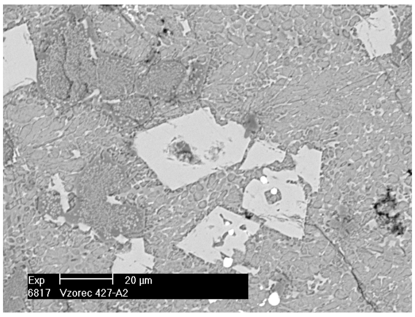

Figure 2. Picrochromite in slag after the process of reduction[7]

EAF DUST

At the melting of steel scrap and at the refining EAF dust is generated.

Gases are cleaned in cleaner devices. EAF dust contains from 10 to 20 mass % of zinc oxide which is a secondary raw material for the production of zinc.

For the production of zinc pyrometallurgical processes or electrolysis can be used. In EAF dust zinc oxide can be »free« or it is in a shape of spinnels. On Figures from 3 to 5 the »shape« of EAF dust and its phase composition is presented.

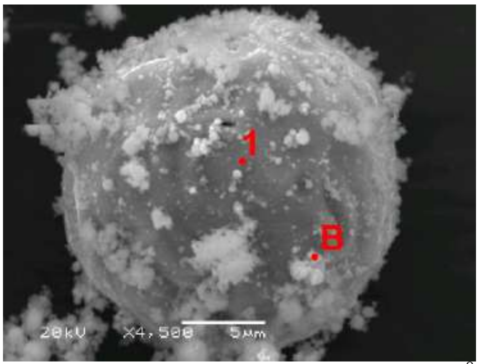

Figure 3. The size of particles of EAF dust[8]

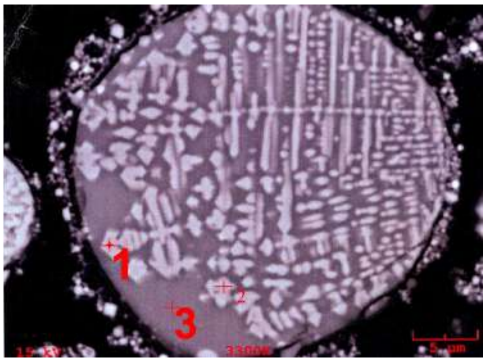

Figure 4. Phase composition of EAF dust, chromite $(Fe,Mg,Mn,Zn)O\cdot(Cr,Al,Fe)_2O_3$ in matrix (olivine slag)[8]

Between the reduction of steel zinc evaporates and then oxides with very characteristic shapes similar to nano tubes are formed (Figure 5),

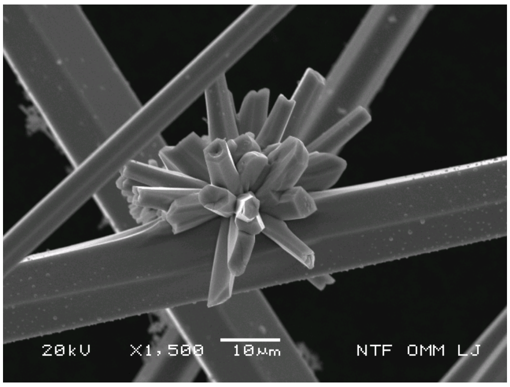

Figure 5. Zinc oxide after the oxidation from Zn vapor[8]

CASTING OF STEEL - TUNDISH SLAGS

At the continuous casting of steel the melt flows from refining ladle into a tundish and from there into a crystallisator (mould). In tundish the melt surface is covered with thermo isolation flux.

On the Figure 6a microstructure of tundich slag is presented – (1) chromite, (2) olivine $(MgO,FeO)\cdot SiO_2$ and (3) monticellite $CaO\cdot MgO\cdot SiO_2$ (3). At Figure 6b chromite in tundish slag is presented.[8]

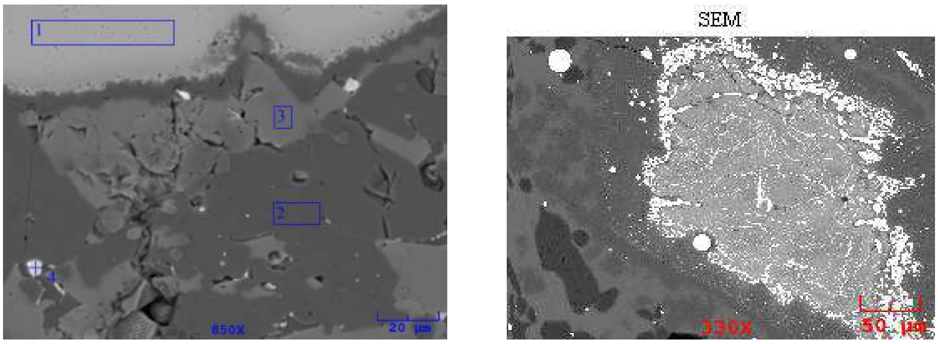

Figure 6a and 6b: Microstructure of the slag from tindish[9].

PHASE COMPOSITION OF CASTING FLUX AND SLAGS

Casting fluxes are used for casting of steel on the continuous casting machines or in moulds. In the mould the casting fluxes are melted on the surface of liquid steel. Slag from mould contains silica and solidified in form similar to glass. Melting points of these fluxes are between 1050 and 1150 °C.

At casting of bigger ingots with high weights casting flux that floats on the melt and fills the mold are used. When the mold is complete filled exothermic flux and isolation refractory materials are added. Metals in exothermic fluxes oxidise and heat the surface of the melt. On Figure 7 the microstructures of solidified casting flux and isolation refractory material is presented. In $2CaO\cdot SiO_2\cdot Al_2O_3$ among slag phases also steel granule can be observed.

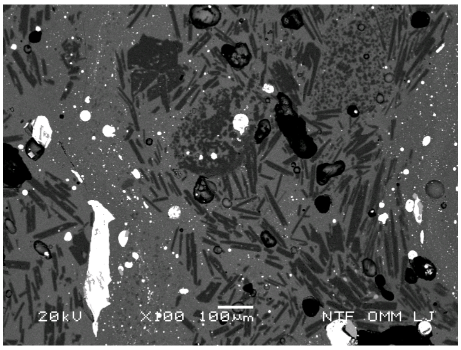

Figure 7. Phase composition of slag from the head of ingot

ARCHEOMETALLURGICAL SLAGS

Slags from modern iron- and steelmaking technologies have very different composition regarding to those from production of wrought iron. Those slags are mainly produced from fayalite (olivin) and wüstite and are now for centuries in the earth.
In natural environment there are for thousand year's deposits of slags, as a by-product of metallurgical activity.

On Figure 8 is the microstructure of slag originated from the production of wrought iron at »bloomery«.

Figure 8. Fayalite and Wüstite

CONCLUSION

During production of materials that are used in everyday life various by-products are formed. Their composition is in most cases different from the natural materials[10].

Various synthetically compounds are formed during steelmaking: $2CaO\ SiO_2$, $3CaO\ SiO_2$, $3CaO\ Al_2O_3$, $2CaO\ Al2O_3\ SiO_2$, $(FeO,MnO,MgO)\ (Cr_2O_3,Al_2O3)$, ZnO, Fe_2O_3 $MgO\ Al2O_3$, $MgO\ Cr_2O_3$ etc. It can be treated as secondary raw materials from which chromium and zinc can be obtained by metallurgical extraction.

The attention must be paid at using secondary raw materials because hazardous elements or compounds which would pollute the natural environment (water, air and earth) can arise.

In future development of metallurgical technological processes is directed to the production of metals and alloys with production of secondary raw materials instead of waste materials.

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REMOVAL OF ARSENIC FROM WASTE METALLURGICAL WATER FIXING ARSENIC AS CRYSTALLINE SCORODITE

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ABSTRACT

Stringent environmental standards require improvement of the existing and development of new copper production technologies. Autogeneous copper smelting processes in flash furnace are one of the best available technologies. Metallurgical waste water are rich in arsenic and heavy metals and require treatment before discharge into recipient or re-cycling into the production process. The paper includes an analysis of the content of arsenic in the smelter's outlet effluent and copper electrolysis outlet effluen, as well as the possibility to remove it by precipitation with iron sulfate ($FeSO_4x7H_2O$) with fixing crystalline scorodite ($FeAsO_4\times2H_2O$).

Key words: metallurgical waste water, arsenic, treatment, scorodite.

INTRODUCTION

There are different methods for removal of arsenic in non-ferrous metal industry [1-5]. Many authors have been dealing with the topic of fixing arsenic as crystalline Scorodite [6-10], as well as investigating scorodite solubility and long-term stability [11]. The leaching characteristics of scorodite particles synthesized from Fe(II) under different conditionns, such as reaction time and temperature, were invetigated [12] as well as the effect of pH on atmospheric scorodite synthesis by oxidation of ferrous ions [13].

By fixing of arsenic from waste industrial water we obtain treated waster which satisfies the criteria for discharge into water recipient [14-16]. The U.S. EPA recently descreased the maximum concentration level (MCL) of arsenic in drinking water from 50 to 10 µg/l [17].

MATERIAL AND METODS

By introducing new copper smelting technologies in flash surnaces, waste water is generated from flash furnace gas scrubbers, converter gas scrubbers, wet electrostatic percipitators in the sulphuric acid plant and copper electrolytic refinery.

Based on the composition of different types of concentrate and design process data for fuel gas, generated in the flash furnace and the convertor, the quality of water that requires treatment in the Effluent Treatment Plant is given [18].

The Institute of Mining and Metallurgy in Bor has conducted analysis of water, quantities and the content of effluent from the copper electrolysis process from three technological units: cathode production, copper sulfate production and precious metals production.

The cause of effluents have been analysed by AAS method. This analysis presented the current and real arsenic concentrations in waste water from the technologicla copper production procedure.

For the treatment of waste water from the copper smelter, a modified HighDensitySludge (HDS) process is envisaged where acid is neutralized and heavy metal hydroxides precipitated. The process is conducted in two stages, in four roasters with insertion of calcium(II)hydroxide (slaked lime) as percipitation media.

The aim of the paper is to discover proper solutions for waste water treatment and fixing of arsenic.

Percipitation of arsenic (As^{5+}) with ferrous ion (Fe^{3+}) presents a practical and the most efficient method for fixing arsenic, especially in metallurgy where big quantities of iron and arsenic are side products of the process. Depending on conditions of precipitation crystalline scorodite is created as residue ($FeAsO_4 \times 2H_2O$). With the stoichiometric Fe:As ratio and controlled precipitation conditions, complete oxidation of As^{3+} into As^{5+} use of hydrogen peroxide (H_2O_2), precipitation of scorodite is done gradually from over saturated solution in a series of roasters with controlled pH value.

The process of arsenic fixation from high As-bearing intermediates is conducted in 3 stages:

1. Leaching
   - Blending and repulping for efficient leaching
   - Leaching of As and recovering Cu into residue

     $Cu_3As + 6H^+ + 9/4O_2 \longrightarrow HAsO_2 + 3Cu^{2+} + 5/2H_2O$

     $3Cu^{2+} + As_2S_3 + 4H_2O \longrightarrow 2HAsO_2 + 3CuS + 6H^+$

     $Cu_3As + As_2S_3 + 9/4O_2 + 3/2H_2O \longrightarrow 3HAsO_2 + 3CuS$

     $(HAsO_2 + 1/2O_2 + H_2O \longrightarrow H_3AsO_4)$
2. Oxidation
   - Oxidiying leached As(III) to As(V)

     $HAsO_2 + H_2O_2 \longrightarrow H_3AsO_4$
3. Crystallization
   - Adding $FeSO_4x7H_2O$ as Fe(II) source
   - Atmospheric pressure at 95°C
   - Fixing As as crystalline Scorodite (97%)

     $2H_3AsO_4 + 2FeSO_4 + 1/2O_2 + 3H_2O \longrightarrow 2FeAsO_4x2H_2O + 2H_2SO_4$
   - Filtering and washing Scorodite ($FeAsO_4x2H_2O$)

RESULTS AND DISCUSSION

Tables 1 and 2 present As concentrations and quantities of effluents from the copper smelter and electrolysis.

Table 1. Waste water from the smelting complex – copper smelter [18].

Type	Quantity, m^3/h	As, g/l	H_2SO_4, g/l	pH
Waste water from the flash furnace scrubber and converter gas scrubber:	8,66	1,467	140,9	-0,4
• from the flash furnace gas scrubber	4,8	1,463	210	-0,6
• from the converter gas scrubber (during slag blows)	1,9	2,669	62,5	-0,1
• from converter gas scrubber (during copper blows)	2,0	0,457	62,5	-0,1

Table 2. Waste water from the smelting complex – copper electrolysis process [18].

Type	Quantity, m^3/h	As, g/l	H_2SO_4, g/l	pH
Waste water from copper electrolysis process:	7,45	0,1	38,9	0,1
• Copper electrolytic refinery	3,125	0,013	11,52	0,6
• Electrolytic regeneration	2,250	0,280	75,0	-0,2
• Gold production plant	2,083	0,028	41,10	0,1

Image 1 shows the technological scheme for removal of arsenic from the outlet effluent from the copper smelter plant, sulphuric acid plant and copper electrolysis.

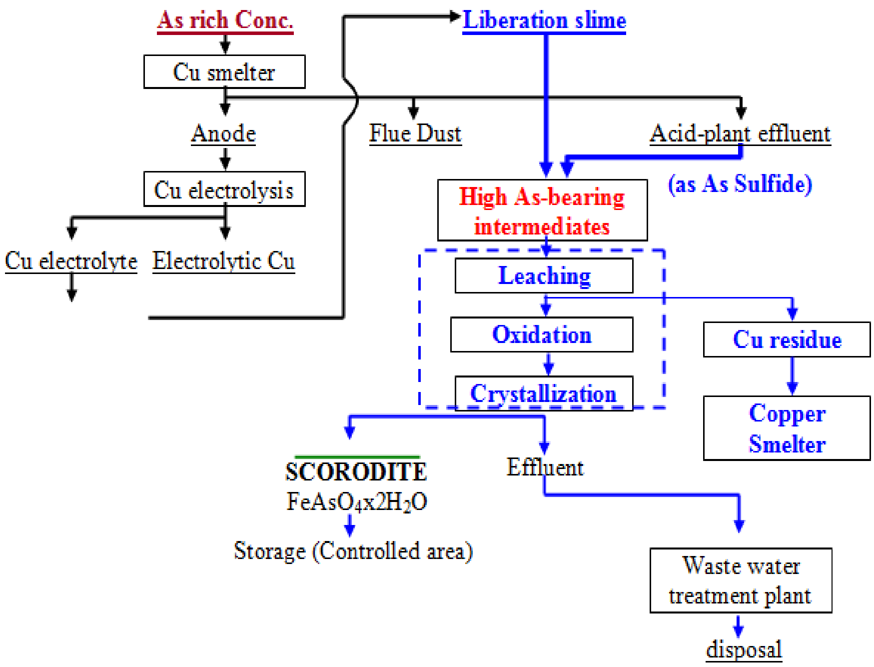

Figure 1. Technological scheme of removal of arsenic from high As-bearing intermediates with formation of scorodite

The products of leaching, oxidation and crystallization are: Scorodite ($FeAsO_4x2H_2O$), where 97% arsenic is fixed and the effluent which is further conducted for treatment in the effluent treatment plant. Arsenic leaching ratio is 93% at optimum condition. Also, copper in sulfide form is separated during leaching and it is sent for treatment in the copper smelter plant. Scorodite contains from 10-15% H_2O, 30-32% As and 23-25% Fe.

CONCLUSION

Treatment of waste metallurgical water which contains heavy metals and arsenic is required with the aim of protecting the environment. By applying the method which implies fixation of arsenic into scorodite it is possible to achieve a high level of cleaning of waste water from arsenic. Moreover, it is possible to separate and valorize copper from electrolysis waste water. The obtained scorodite is stable and as such it can be disposed into a dump without endangering the environment.

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BROWN COAL DEPOSITS OF "SOKO" MINE – USABLE VALUE OF NATURAL CAPITAL

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ABSTRACT

Coal is a non-renewable natural resource and a strategic mineral raw material in the Republic of Serbia and now is the main energy source for electrical energy production.

Existing available forms of energy in terms of fuels are renewable (biomass, wind energy, hydro-potentials) or non-renewable (fossil fuels) resources that are located on or under the surface of the Earth. In geological terms, fossil fuels are non-renewable energy resources. Fossil fuels deposits (oil, coal, natural gas) and other fossil fuels make most of the energy potential of majority states in the world. Modern trends of technological and industrial development demands permanent increase of spending as well as fossil fuel exploitation.

Consumption and use of abovementioned energy resources has to be planned and rational with continuous additional research of existing and discovering of new energy sources for decreasing disproportion between spending and production. The Republic of Serbia has significant deposits of fossil fuels mostly lignite and brown coal deposits, with significant potential found in brown coal deposit "Soko" – Sokobanja.

Key words: coal, mine, underground exploitation, coal value.

INTRODUCTION

In terms of traditional approach of economic theory, the term "capital" is classified to factors of production: capital, work, land and raw material.

Within natural capital there are:

- natural resources;
- renewable and non-renewable resources;
- the environment, and
- land in terms of production factor for different purposes.

In the most extensive definition resources are defined as natural activity, heritage of material goods from the human standpoint of the environment, biological, climate, ore, mineral, forest and hydrological character. Technological, economic and noetic development of human community does differentiation of natural capital to economic resources and reserves as potential of natural goods suitable for transfer into manufactured goods.

"Resources" are a broader term than the term "reserves", i.e. they are natural activity of goods of animate and inanimate nature. The term "reserves" is defined as a stock of experientially usable materials and their function, indirectly or directly usable for human economic activity.

In economic sense, reserves mostly refer to a term of raw materials and they include economically cost-efficient for exploitation of part of resources. The achievement of a transfer of resources into reserves depends on technological development of the specific activities and the price of a resource on market.

In the Republic of Serbia there is institutionalized system of measures for natural goods protection, especially for their use. It is based on a complex of normative measures, prescribed standards, fees, taxes, technical conditions, allowed levels and rules.

The subject of research for the needs of this paper has an emphasis on a brown coal deposits "Soko", which represents a narrow field i.e. frame of research.

The paper connects the significance of coal as a non-renewable resource and its value in form of usable value.

Basic goals of the research are included in the need to, based on available information on deposits and direct insight in their location, communication opportunities and existing infrastructural facilities, develop current analysis of possibilities of activation for underground perspective development of coal mine and to evaluate usable values of balance reserves.

GENERAL CHARACTERISTICS OF "SOKO" COAL MINE DEPOSITS

Brown coal mine "Soko" is located in the area of Čitluk village, 12 km away from the regional motorway Sokobanja – Knjazevac, in the southeast part of Sokobanja tertiary basin. In the "Soko" mine there is exploitation of high-quality brown coal for over 70 years.

Sokobanja tertiary basin has an area of around 220 km2, and it belongs to Sokobanja municipality.

Communication connections of the mine with other centers are very good. Through the asphalt road Sokobanja-Aleksinac, the mine is connected with the highway Beograd-Niš-Skoplje, and over Mountain Rtanj with Paraćin-Zaječar road, which enables uninterrupted transport of coal to all areas in Serbia.

The oldest rocks in the area of Sokobanja basin from Proterozoic and Devonian period are made of terrigenous sediments (schists, sandstones, clay with thin layers of coal). Next younger rocks are dolomites, limestones and other calcareous clastic rocks from upper Jurassic period, and lower and upper Cretaceous period. The youngest (tertiary) part of the basin is made of lake sediments with thickness around 1000 m that are separated into four series (Fig. 1.): old Paleogene; Citluk coal-bearing series; Vrmdzan coal-bearing series and clastic series.

Characteristics of coal layer: The average thickness of coal layer is 23 m. Coal layer depth starts from 50-1000 m. Coal layer inclination: towards north at an angle of 25^0-45^0**.**

Geological age: middle Miocene M_2.

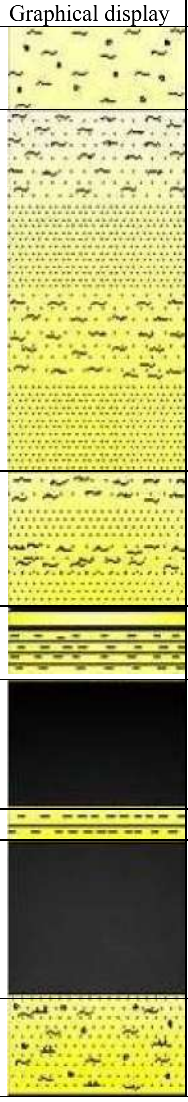
Geological age		Graphical display	Thickness (m)	Lithological description
NEOGENE	Uppermiocene		30	Clay with pebbles limestone
			150	Sandy clay and clay's sandstone in alternately rotation
			35	Heavy clay and sandstone in alternately rotation
			10	Interbed of coal
			10-15	Coal
			1	Layerd marl
			15-10	Coal
				Sandy clay, limestone breccias, conglomerates

Figure 1. Geological pillar of productive series of deposit „Soko“

COAL RESERVE AND QUALITY BALANSE

Coal from the main coal layer of the "Soko" deposits is in the group of brown coals with the average degree of carbonation. The coal is dark-brown color, with flat to mild shelly faults with very sharp edges. In some places there is a clear woody structure. Macro and micro petrographic research of coal samples showed presence of humus detritus of lower and higher level, gelificated wood tissue, humus gas and fuziniteta.

Present microlithotypes and macerals have a high level of gelification between which there are thin layers of carbonaceous clay with thickness under 1m.

The most significant lithotypes in the layer are: densinite, ulminite, attrinite, textinite, etc. In terms of barren materials there are mostly clay, and rarely carbonate and pyrites.

For monitoring of basic elements of "quality" features of coal in the deposits there are frequent chemical and technical analyses on samples taken in the process of exploitation and during research drilling.

Average values for commercial types of coal are:

- Moisture%..19.22
- Ashe%.. 11.83
- Volatile... 35.80
- C-fix %.. 34.47
- Combustible%... 70.62
- Coke%... 45.71
- S-total% 1.70
- TEGKJ/kg 19.506
- TED on a total moisture KJ/kg............ 18.239

Overview of activities of research, opening and digging out the deposits and elaborates on reserves shows the state of geological reserves in the "Soko" mine on the day **01.10.2011** in the following chart:

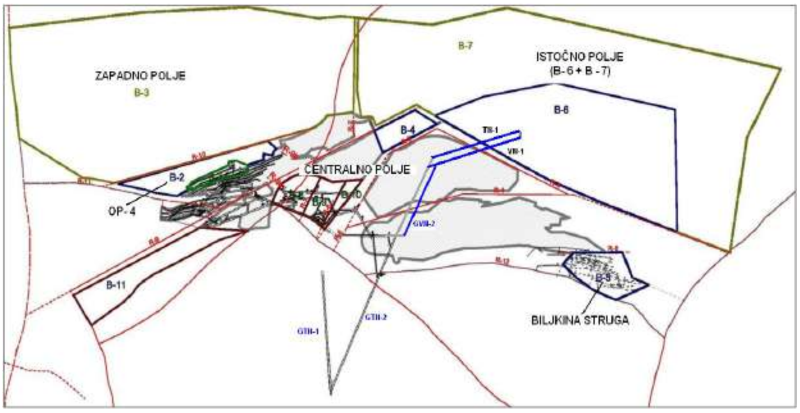
CATEGORY	GEOLOGICAL RESERVES	
	BALANS (t)	**NON-BALANS(t)**
A	284 447	2 062 204
B	15 309 063	701 068
C_1	41 887 592	
A+B+C_1	57 481 102	2 763 272
TOTAL	**60 244 374**	

Category "A" reserves – non-balanced – are mostly in a protective pillar I.O. of exporting shaft and main chambers of pit opening (IN-1, VN-2). Balance category A reserves are in central excavation field (OP-4 and OP-1) – northwest part of it, excavation level: EH-(-69i), EH-(-78i), EH.-(-87) and EH-(-96).

Excavation of category A reserves in excavation parts OP-4 and OP-1 was enabled by opening chambers TN-1z, ETN-12, TN-2z, TN-3z, VN-1z, EVH-39, VN-2z and VN-3z.

Category "B" reserves located in northwest part of the Central field (OP-4, OP-5, OP-6) between cleavages R-10b in south, R-10 in north, R-11 in west and R-4 in east; and mostly in the East field. The end of B reserves towards north and especially towards east is not clearly defined, so with the additional research activities in the future the amount can be significantly increased (image 3).

Category "C_1" reserves are mostly located in the West field, north from the cleavage R-10 and the part of East field where should be emphasized that research activities in the future can discover significant increase of these reserves, especially towards north, west and east (currently known as C_2 category reserves and are around 135.8 million tons).



POTENTIAL RESOURCES OF "SOKO" COAL DEPOSITS

Sokobanja basin includes almost a half of Sokobanja municipality area. However, from around 200 km^2 under Neogene sediments, only small part of it is researched, around 10 km^2 with balanced reserves of 60 million tons in the area of Citluk village, far east part of the basin. When we speak of potentials of Sokobanja basin, it should be emphasized that it is based only on creation of "Citluk coal-bearing series" – middle Miocene $M_{2,}$ with the major coal layer that has been exploited for years in the far east part of mine basin "Soko". Younger Vrmdzan series is also widely spreader, with locally developed layer of lignite (thickness 3.0-8.0m in the area of Vrmdze-west part of the basin), that in this phase from the aspect of potential evaluation is put it the further priorities.

Considering that active mine "Soko" is located in the far east of the basin so it is partly researched or at least included in the research which confirms the potential of that part of the basin. In the previous text it is emphasized that Citluk coal-bearing series spreads through the whole area of Sokobanja basin so this paper emphasizes the potentials of two conditionally separated parts of the basin:

- **East part** in which in the wider area there is presence of coal and
- **West part** that is not researched and in which there is no known coal-bearing capabilities.

Coal-bearing area of I priority – East part

This part of the basin is marked as an area of the first priority from the aspect and includes the area of around 80 km^2.

Considering the presence of coal-bearing layer and thickness of Neogene and level of exploiration of this area of first priority is divided into two smaller parts:

a) East part including the area around 30km^2, east from Sesalacka river from Lovorik. In this area there is active mine "Soko". In the same area there balanced reserves of around 60 million (A+B+ C_1) and reserves C_2 category of around 140 million tons (drilling KM-208, area of the village Bogdinac) in north.

b) West part includes the area west from Seselacka river (around 50km^2) from form Sokobanja. Our belief that the presence of the major coal layer in the east part of basin on the depth of 50-1000m that we separated as the first priority (potential) from the aspect of further research and development and production increase, can be considered completely feasible and real on the whole area.

Coal-bearing area of II priority (west part)

The potential area of II priority–west part of the basin covers the area of over 100km^2 form Sokobanja to Bovansko lake is not significantly researched so there is not enough data for it on the right and real potential evaluation.

The fact remains that in more locations in this area there is discovered and registered existence of "younger Vrmdzn series" with layers of lignite and in some (small number) excavation site and a part of the "older Citluk series" which points out to conclusion that in this area it the presence of the major coal layer could be expected.

DETERMINING USABLE VALUE OF BILANCED RESOURCES

Explotation of coal in the mine "Soko" is now done by classic systems, while for digging pillar-chamber method is used with the technology of getting coal with mine blasting. Also, the development of mining chambers is done by drilling-mine blasting technology, while the transport is organized through systems of scraper and belt conveyor, and the export is done through the shaft. Coal treatment is done on two levels, through classification in the classification room and wet separation in Parnaby facility which significantly influences the quality of available coal. Production capacity with the current conditions is from 100 000 to 130 000 t/year, and with planned introduction of short mechanized mines and wide forehead method, the capacities could be multiplied many times. For calculation of usable value of natural capital of a specific basin, transitory data is the amount of reserves of A, B and C_1 category in the active part that is 60.2 million tons and usage of coal with current methods of 80%.

Usable value of coal includes total value that can be acquired by exploitation of balanced reserves of coal of specific quality.

Coal quality is adopted from the elaborate on reserves in the size of 18.239kJ/kg and with the average price of coal of 3.0 EU/GJ currently on our market, the price is 54.72EU/ton.

The market value of coal is received from the following formula:

Tcu = Evu x Jcu

with:

Evu – Energy value of coal
Jcu – Unit coal price

Tcu =18.239 GJ/ton x 3.0 EU/GJ

Tcu = 54.72 EU/ton

Usable value of natural capital of coal basin "Soko" is:

Viu = Rb x Ki x Tcu
meaning:

Rb – balanced coal reserves
Ki - coefficient usage through exploitation
Tcu – market value of coal

Viu = 60.244374 tons x 0.80 x 54.72 EU/GJ

Viu = 2,637 billion EU

Calculated values show the necessity for the development of study for coal exploitation feasibility from these deposits, with the goal of defining values of coal deposits as a result of difference of usable value of coal deposits and cost of exploitation. High usable value of "Soko" coal deposits presents ultimate engineering challenge for establishing profitable coal production and organizing production of coal through technology of underground exploitation without state grants.

CONCLUSION

The abovementioned research determines usable value of natural capital of the brown coal deposits of "Soko" mine, that for the balanced coal deposits in the currently active part – the pit is 2.637 billion Euros.

As this is only a small part of the deposits, it is necessary to give these deposits more importance, while the mechanization and modernization of technological process significantly increases production capacities. At the same time, the influence of exploitation on the environment in the "Soko" deposits is very low, and exploitation contributes to wellbeing of the community through creating new values and new jobs, directly at the mine as well as indirectly through third party services. The abovementioned steps in research should be directed towards definition of total value of deposits.

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OBTAINING AND CHARACTERIZATION OF MODIFIED NANOCELLULOSE BY FTIR SPECTROSCOPY AND TGA

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ABSTRACT

Nanocelluloses or nanofibrillated celluloses (NFCs) have attracted increasing attention as new, biobased, and highly crystalline nanofibers because NFCs are not only environmentally compatible but also have unique characteristics as nanomaterials. The process for isolating the nano-crystalline cellulose from cellulose fibers is based on acid hydrolysis. This paper presents the results of characterization nanocellulose (obtained from cotton, acid hydrolysis using sulfuric acid mass fraction of 64%) modified with maleic anhydride, recording FTIR spectra and TGA analysis. FTIR spectroscopy shows that samples which are modified nanocellulose anhydrides show typical strip to a carbonyl group from maleic anhydride ester, and ester C-O vibration. For samples of modified nanocellulose, the intensity of the tape due to O-H vibrations is noticeably decreasing. Based on the obtained results and TGA curves for unmodified and modified nanocellulose conclude that shown great similarity, which also reveals that thermal degradation takes place in three stages.

Key words: nanocellulose, acid hydrolysis, maleic acid, FTIR, TGA.

INTRODUCTION

There is growing interest in using agriculture and food industry byproducts to develop biodegradable materials to replace petroleum-based polymers in packaging applications. Furthermore, the use of nanotechnology in food packaging is expected to grow rapidly over the next few years as further globalization increases demand for shelf life-enhancing packaging. Applications of nanotechnology include improved barrier, mechanical, and antimicrobial properties as well as the incorporation of nanosensors for traceability and the monitoring of the condition of foodstuffs during transport. In recent years, a lot of effort has been aimed at developing new biobased polymer containing films and nanocomposites which can act as barrier materials in packaging. Unlike synthetic plastics, under dry conditions the films of natural polymers exhibit good barrier properties against oxygen and grease due to their high cohesive energy density. However, natural polymers are hydrophilic in nature, and films produced from these materials are often hygroscopic, resulting in the partial loss of their barrier properties at high humidity levels. The gas permeability of polysaccharide materials can increase by orders of magnitude as humidity increases. [1,2,3]

Since most food applications demand materials that are resistant to moisture as well, the major challenge is to overcome the inherent hydrophilic behaviour of these biomaterials. Nanocellulose (NC) forms a remarkable emerging class of nature-derived nanomaterials because of its extraordinary mechanical properties, combining high stiffness of up to ca. 140 GPa and its expected strength in the GPa range with a lightweight character (density ca. 1.5 g/cm^3). Since NC is derived from wood or plant sources, it is globally abundant and renewable and, which is more important, represents a resource that does not interfere with the food chain or require petrochemical components. Consequently, NC is emerging as one of the most promising sustainable building blocks for future advanced materials. In order to expand the use of nanocellulose as a gas barrier in large-volume packaging applications for high-moisture environments, the hydrophilicity of the nanofibers must be decreased by surface chemical modification. [2,4]

Nanocellulose, including nanocrystalline cellulose, cellulose nanofibril and bacterial cellulose nanofibers are building blocks for creating new biopolymers. The process for isolating the nano-crystalline cellulose from cellulose fibers is based on acid hydrolysis. In this paper, the process of obtaining nanocellulose using sulfuric acid mass fraction of 64% with the ratio of acid to cellulose of 8.75 to 17.5 ml / g. Hydrolysis occurred at a temperature of 45°C, for a time period of 25-45 min. The resulting nanocellulose been modified with maleic anhydride. The paper presents the results of the characterization modified nanocellulose, recording FTIR spectra and TGA analysis. Nanocellulose is applied to a metal carrier and then recorded. [4,5]

EXPERIMENTAL

Cellulose is macromolecular product that corresponds to the empirical formula $(C_6H_{10}O_5)_n$, and its hydrolysis formed almost theoretical yield of *D*-glucose.
Cellulose fibers can be divided transversely along their axis, giving the amorphous regions nanometric and highly crystalline rod-shaped parts without defects-cellulose nanocrystals (CNCs). Through mechanical friction, cellulose fibers can be laterally separated into their substructural parts which measures with nanosizes (nanofibers)-nanofibril cellulose (NFC). This second biomaterial can be synthetized by microorganisms-bacterial nanocellulose (BNC). [5,6,7,8]

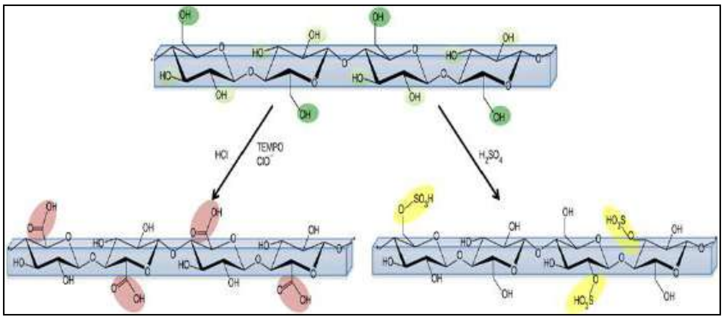

Figure 1. Chemical methods of obtaining nanocellulose

Acid hydrolysis of cotton

Nanocellulose nanocrystals were obtained from cotton by acid hydrolysis (fig.1). About 20 g microcrystalline cellulose (MCC) was mixed with 200 mL sulfuric acid (64 wt%), the mixture was hydrolyzed at 40ºC for 60 min with continuous stirring. The hydrolysis was quenched by adding 1000 mL of water to the reaction mixture and then the slurry was washed with deionized water for 20 min at 5000 rpm, using repeated sonification and centrifugation. The supernatant was removed from the sediment and replaced by new deionized water and mixed, the centrifugation step continued until the pH of the supernatant became 4. The last wash was conducted using dialysis with deionized water until the wash water maintained a constant pH of 7. [6,8,9]

Chemical modification of nanocellulose with maleic anhydride (NC-MA)

The sample of 20 g nanocellulose was prepared for modification with maleic anhydride by washing and centrifugating with acetic acid in order to exchange solvent. The sample was placed in a stoppered glass bottle containing a mixture of 160 mL of acetic acid and 200 ml of toluene and sonicated for 1 min. Afterwards, 0.8 mL of 60% perchloric acid was added, reaction mixture was sonificated for 1 min, and then 1 g of maleic anhydride was added. The mixture was allowed to stand for 1 h at room temperature. After the reaction the NC sample was thoroughly washed and centrifuged with methanol, then with dichloromethane. [10,11,12]

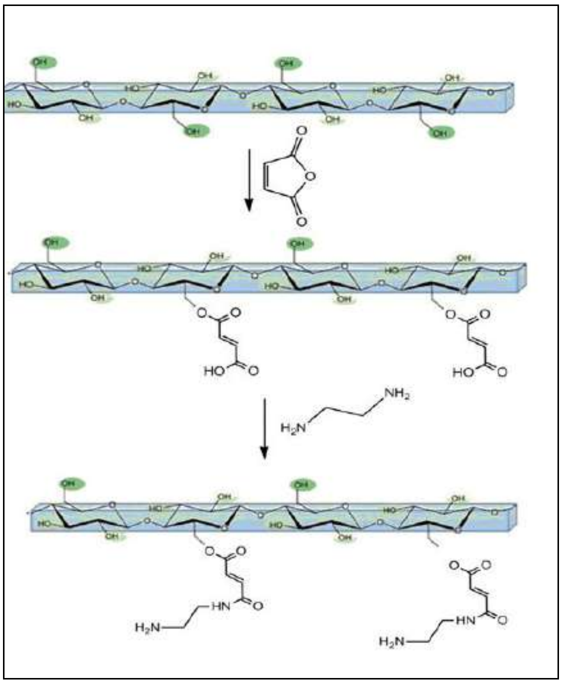

Figure 2. Nanocellulose reactions with maleic anhydride and ethylenediamine

Chemical modification of nanocellulose modified with maleic anhydride and ethylenediamine (NC-MA-EDA)

20 g of nanocelulose modified with maleic anhydride was placed in 500 ml three-necked flask and dispersed in ultrasonic bath. In the reaction mixture, 5.74 g of N,N-dicycloheksylcarbodiimid (DCC), 0.73 g of 4-dimethylaminopyridine were added, and 1.2 g of ethylenediamine disolved in 10 ml of dichloromethane (DCM) was added dropwise under nitrogen atmosphere at room temperature during 12 hours (fig.2). After the reaction completion, nanocellulose was washed with DCM three times (fig.3).

Figure 3. Nanocellulose

FTIR spectroscopy

Infrared spectroscopy is used to determine the structure of unknown molecules by passing infrared radiation through the sample. Infrared spectroscopy with Fourier transform (FTIR) provides the basis vibrational spectra of the same information as conventional IR spectrometer.

However, FTIR spectrometer has several advantages over conventional dispersion spectrometer, which are: significantly improved signal / noise ratio (S / N) in relation to the best dispersion infrared spectrometers, higher luminous flux, increased sensitivity, high accuracy of the wavelength, high power decomposition, significantly increased speed of recording spectra, facilitated operations with spectra because these instruments are associated with computers. [13]

Thermogravimetry

Thermogravimetry (from the Greek "therme" - the heat and the Latin "gravis" - weight) applies to all methods of thermal analysis, which is based on measuring changes in weight, which occurs due to the effect of heat on the subject.

Behavior unmodified and chemically modified nanocellulose when thermal degradation is determined using thermogravimetric analysis (TGA). TGA curves for the unmodified and modified nanocellulose are very similar, in which it can be seen that the thermal degradation takes place in three stages.

ANALYSIS OF RESULTS

Samples nanocellulose unmodified and modified nanocellulose were characterized by FTIR spectroscopy (fig.4) and thermal analysis (fig.5).

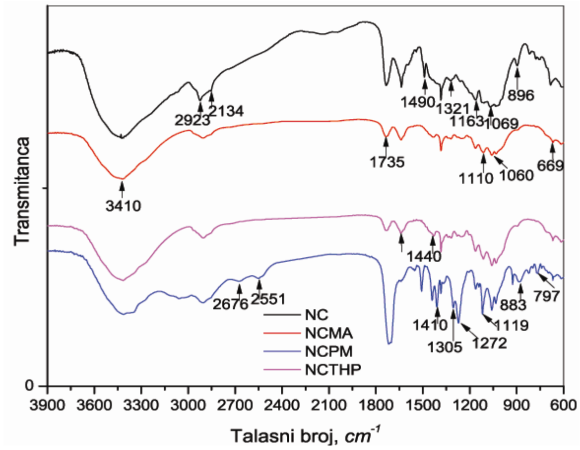

Figure 4. FT-IR spectra of NC , NC-MA and NC-MA-EDA

The tracks on the frequencies of 3410, 2923, 1640, 1490, 1321 and 1069 cm^{-1} derived from unmodified nanocellulose. The peaks between 750 cm^{-1} and 1000 cm^{-1}, as well as other peaks around 1350 cm^{-1} and 1175 cm^{-1} indicate the presence of the sulfonate in nanocellulose. FTIR spectroscopy shows that the samples that were modified nanocellulose anhydrides show the characteristic bands for the carbonyl ester groups at 1735 cm^{-1} of maleic anhydride, and an ester CO vibrations at approximately 1060 cm^{-1}. The signals around 1640 cm^{-1} originating from the symmetric deformation vibration of water molecules which are absorbed on the nanocellulose surface, although the FTIR samples are taken after drying at 105°C. In addition, samples of modified nanocellulose are noticeable and reducing the intensity of the band around 3400 cm^{-1} comes from OH vibration.

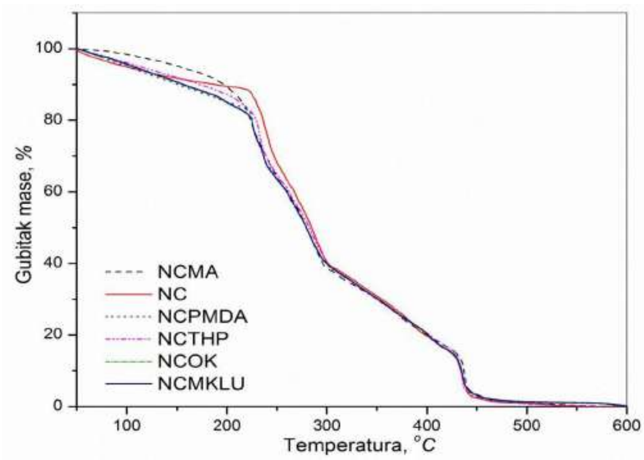

Figure 5. Thermogravimetric analysis

A sample of unmodified nanocellulose (NC) shows a weight loss from room temperature to 130ºC which is attributed to the moisture content, or residual solvent. Losing weight unmodified NC exists and after the temperature of 130ºC or less considerably reduced because a lot of moisture and solvent content compared to other samples of modified NC. This effect decreases for samples nanocellulose modified with anhydride.

From 230ºC begins destruction of crystalline regions nanocellulose and greater weight loss occurs in the range of about 250-350ºC. This peak with unmodified nanocellulose occurs at a temperature of 230ºC, and in chemically modified samples nanocellulose occurs at lower temperatures. In addition, previous studies have shown that in samples nanocellulose modified with fatty acids, with increasing length of the hydrocarbon chain the temperature thermal degradation is reduces due to the reduced number of hydrogen connection which significantly reduces the efficiency of the packing of nanocellulose molecules. At a temperature of about 430ºC occurs new weight loss which is probably a consequence of sulfonic groups present at the nanocellulose surface.

CONCLUSION

Nanocellulose, including nanocrystalline cellulose, cellulose nanofibril and bacterial cellulose nanofibers are building blocks for creating new biopolymers. The process for isolating the nano-crystalline cellulose from cellulose fibers is based on acid hydrolysis. The resulting nanocellulose has been modified with maleic anhydride and characterized by recording FTIR spectra and TGA analysis. On the basis of the FTIR spectra can be concluded that samples nanocellulose modified maleic acid anhydride show a band characteristic of the carbonyl group of the maleic acid ester, and ester CO vibration. For samples of modified nanocellulose band intensity of OH vibrations are noticeably reduced. Based on the results of TGA curves for unmodified and modified nanocellulose conclude that shown great similarity, which also reveals that thermal degradation takes place in three stages.

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THE SIMULATION OF THE BENCHES EXCAVATION IN THE OPEN PIT MINE IN ORDER TO DEFINE SLOPES' STABILITY

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ABSTRACT

The stability of slopes is one of the major factors for secure excavation of overburden and coal in open pits. On the other hand, the increase of inclination of a working or a temporary slope can have many economical benefits, because it can provide higher early income and the expenses of overburden excavation will be delayed for the future period of time. The use of numerical modeling by computer simulation make it possible to consider several variants, to change the inclination of a working or a temporary slope which helps to estimate the stability of slopes.

Key words: numerical modeling, simulation, the stability of slopes, stress, deformations.

INTRODUCTION

Numerical modeling is a very useful tool for engineering projecting and analysis. It is usually done in a few steps. First of all, it is necessary to make a certain phycical problem as simple as possible without compromising the basic laws of the problem. [1] After that a mathematical model for corresponding physical problems is built. A mathematical model is an abstract model [1, 2] which uses a mathematical language to describe a system behaviour. The next step is to construct a convenient numerical model or approximation of a mathematical model. A ready-made software package is used for solving complex systems, and these packages already contain certain numerical methods. When a mathematical model [3] is simulated on a computer by using numerical methods, an output consists reactions and behaviour similar to a physical situation under the same conditions. The obtained results must be analyzed and final conclusions must be given, which means that it is needed to convert mathematical data into a real language of the science which treats a specific physical model.

The use of numerical modeling [4] for the simulation of geotechnical structures' behavior makes a great step forward. It makes possible for engineers to simulate in details the process of building and working for the spectrum of problems including the slopes in open pits, bulks, deep excavations, tunnels and other static and dynamic activities of the ground structure, as well as numerous border problems. An engineer can use a wide range of available computer codes, as well as the library of material models for a simulation of constitutive ground or rock behavior.[1]

In this paper, for the analysis of slopes stability in the open pit Grivice we have used the numerical method of finite elements [2] which has been implemented in ADINA software. This programme has been chosen because of the possibility to simulate different conditions and inclinations of slopes through the period of time by using one geometrical model because it provides the option of restart analysis, as well as the option of death and birth of elements. The simulation of overburden or ore excavation is done by using the option of death elements and in this way, during the simulation, a slope changes its position through the time and space – the height of certain parts of a slope and its inclination are changed which leads to the change of load.

THE RESEARCH

In order to analyze the stability of slopes in the open pit Grivice, the typical profile with the current state of mining work is chosen. In this profile, the projected future state of work is also presented. On the basis of engineering geological profile 1, the geometric model of the current state of mining work is made, and on that model the geometry of projected [5] state of mining work. Each type of material has been treated in particular. The layers of these materials have been divided into triangles and rectangles. The surfaces positioned between the current and projected state are also treated in particular in order to simulate the process of excavation. The geometric model of profile 1 in its final form consists 3325 nodes and 3286 elements with defined six types of materials which include floor materials, coal materials and the roof of coal layer's materials. The roof materials are consisted of four types of marl – calcareous marl, grey marl, dark grey marl and clay marl. The option of death elements has been used for defining 58 time steps which represent the sequences of overburden and coal excavation to projected state. The duration of each time step is time needed for excavation of one dredge block. The surfaces are defined with the height of 12 m which corresponds the real bench height in the open pit and the width of two dredge blocks. During the simulation, from the first to the last step, the slope changes its position and the inclination. Figure 1 shows profile-1 geometric model in the current state of mining work, while figure 2 shows the last, 58^{th} time step and the projected state of the work. The calculation of the stress and the deformations has been done in two versions. The first version presupposes that there are no faults and it has been introduced in order to follow the changes of the model in more efficient way and to understand the influence of faults on slopes' stability in detail.

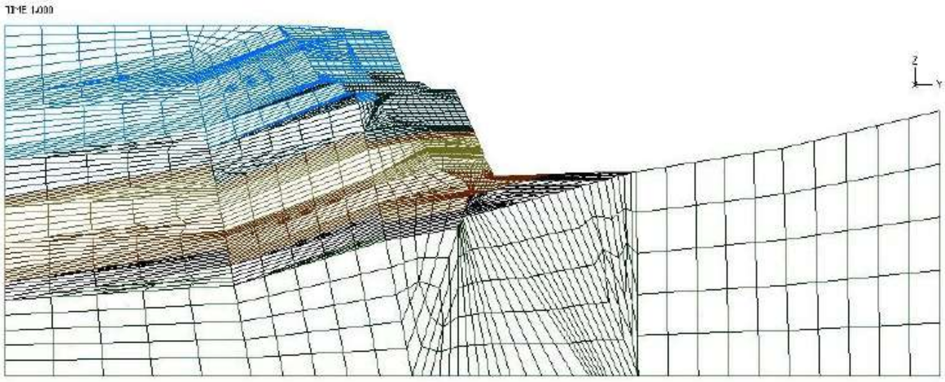

Figure 1. The model of the mesh of finite elements for profile-1 for the time step 1

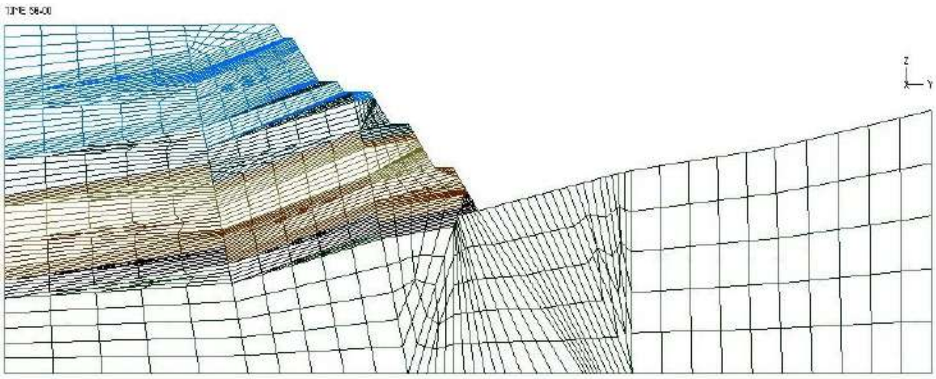

Figure 2. The model of the mesh of finite elements for profile-1 for the time step 5

Figures 3 and 4 show the changes of the stress yz for the first and last time steps.

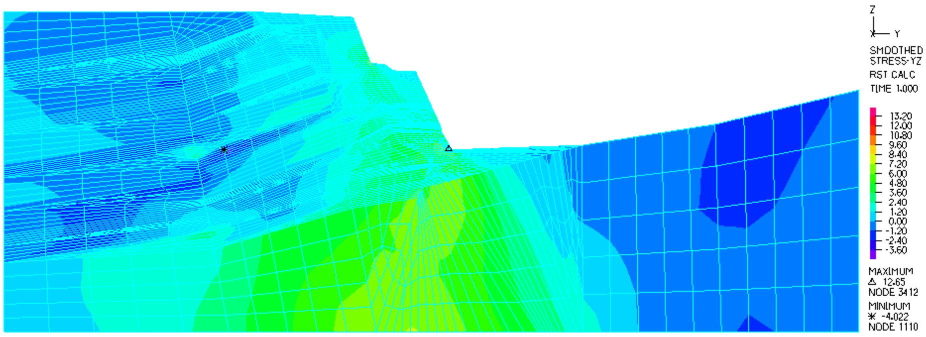

Figure 3. The stress yz for the profile-1, current state of mining work

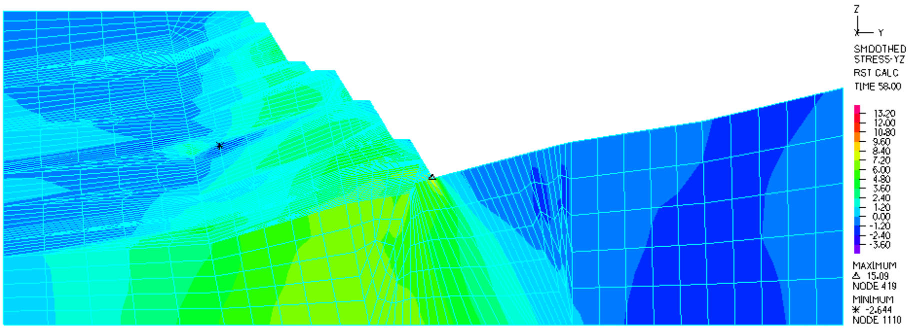

Figure 4. The stress yz for the profile-1, time step 58

The position of the maximal value is predominantly at the lowest bench, while the minimal value is positioned in the left half of the profile towards which the mining work moves on. Figures 5 and 6 show the plastic deformations on profile-1 which are caused by overburden and coal excavation. Figure 5 shows the time step 1 – the current state of mining work, while figure 6 shows time step 58 – the future, projected state of mining work.

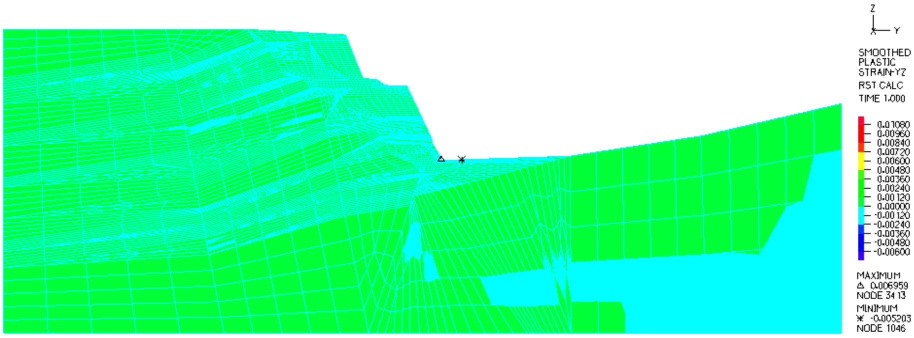

Figure 5. Plastic deformations for the profile 1, current state of mining work

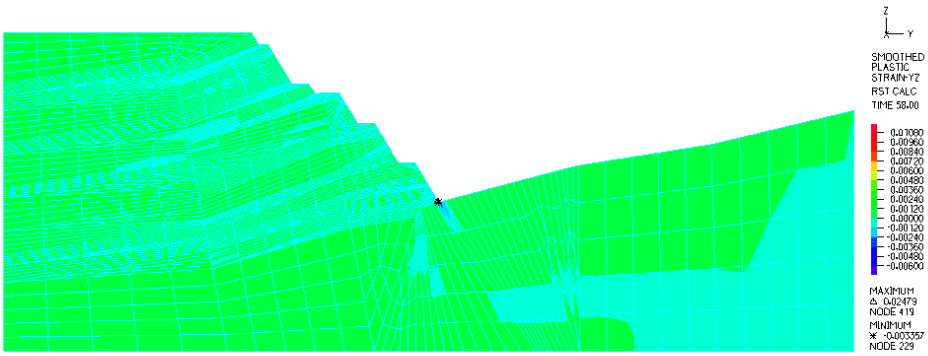

Figure 6. Plastic deformations for the profile 1, time step 58

It is visible from the figures that certain maximal and minimal values of deformations occur within the first time step and they are positioned at the lowest bench of the open pit.

The model of the second variant is almost identical to the model without faults. The geometric model in which faults are presented contains the additional mesh of finite elements [1] in the area of faults' lines. In order to consider the influence of faults in the lines of faults' zones, the materials are given up to 50% weaker characteristics. Figure 7 shows the distribution of the stress during the last, 58^{th} step – the future, projected state of work.

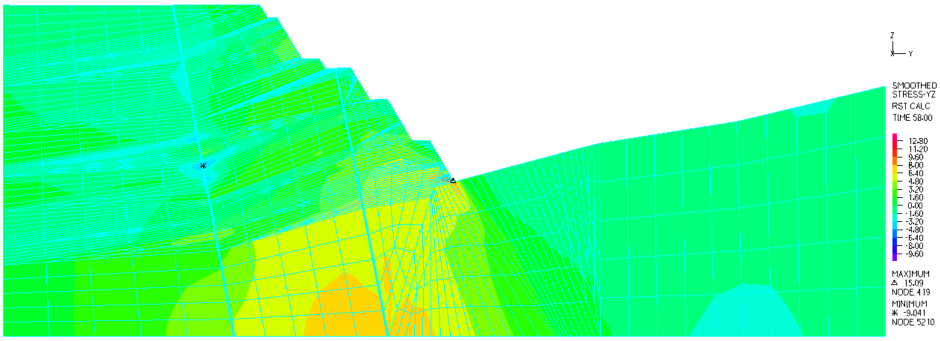

Figure 7. Stress yz for profile-1with faults for the time step 58

This, the second variant, just like the first one (without faults), shows that the maximal stress value occurs at the lowest bench. On the other hand, the position of minimal (negative) values has been changed, and it is positioned in the area of the second fault's line. Figures 8 and 9 show the plastic deformations in the first and the last time step.

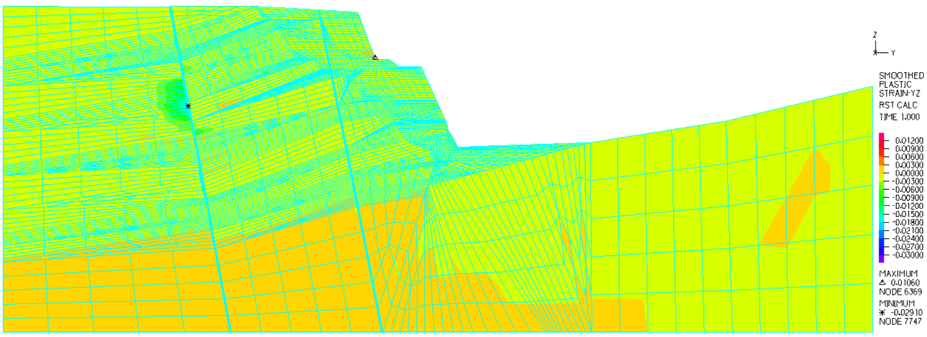

Figure 8. Plastic deformations on profile-1with faults for the current state

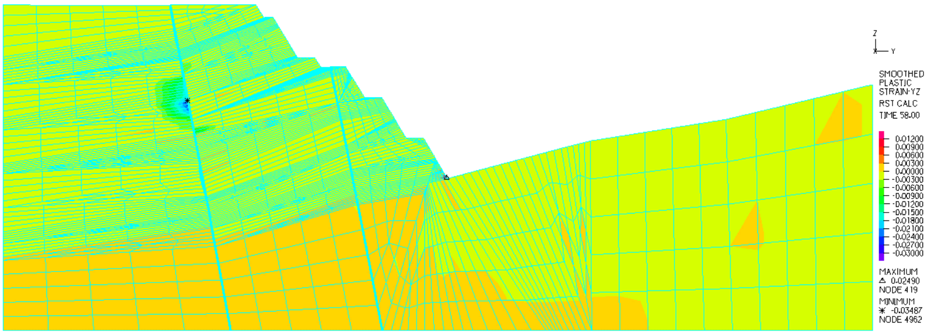

Figure 9. Plastic deformations on profile-1, with faults, time step 58

The maximal values of deformations firstly occurs in the foothill of the first part of a slope, and then at the lowest bench, and the position of the minimal (negative) values of deformations changedjust like the positions of the minimal stress values, and it occurson the line of the second fault.

DISCUSSION

In order to estimate the stability of slopes and the influence of the faults on their stability and also to make comparison, the changes of deformations by time steps compared to the first one are presented in the diagram. Figure 10 shows the diagram of the change of plastic deformations trough time step, without faults.

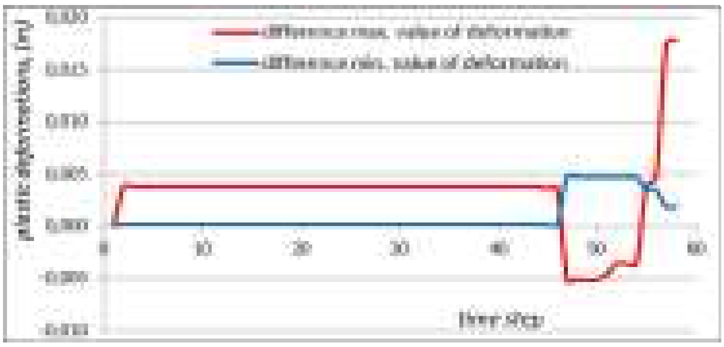

Figure 10. Diagram of the changes of plastic deformations trough time step, without faults

It is visible from the diagram that the certain changes of deformations occur during the first time step. More significant changes occur from the 47th to the last step when the lowest part of the open pit slope is formed. These changes occur in material 2 – the uncovered part of coal layer. More significant changes in the last time step occur where the coal and the foot of the coal layer meet. The values of these deformation do not reach critical values which means that materials do not break.

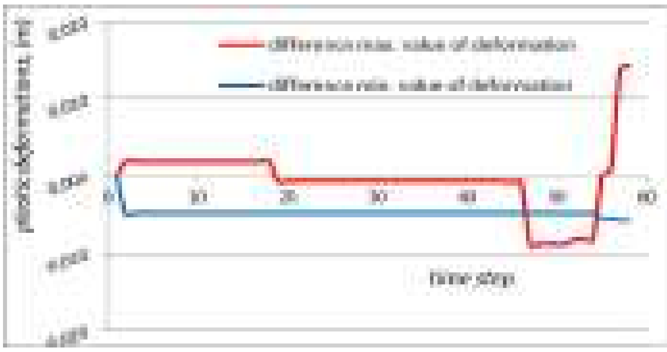

Figure 11. Diagram of the changes of plastic deformations trough time step, with faults

When the changes of plastic deformation are observed for the first time unit, it is obvious that the values of plastic deformation in the variant when faults are considered are noticeably larger than the values of these deformations in the variant when faults are not considered (figures 8 and 5). This fact is even more significant when it comes to minimal (negative) values of these deformations for variant with faults which differ for 0,024 m from the values in the variant withot faults. However the changes of the deformations are smaller with the progress of the excavation compared to the changes in the variant withot faults. In both cases, the values of plastic deformation are not critical and there is no breakage of the materials.

Maximal stress value yz goes down by unloading of masses and decreasing the slopes' inclanation during the first time steps. Increasing of the slopes' inclination during later time steps values of these stress grow. During the last steps the maximal values are bigger than at the beginning. The slope of the open pit in its projected state, even it has lesser inclination, has bigger stress yz than it has in the current state. Minimal stress values yz slightly grows during the first steps, and then untill the end of excavation are close to constant values.

CONCLUSION

The slope of the open pit at the current and at the projected state has required stability and safety for doing mining work. As analysis shows, smaller deformations of groundmass and coal layer occur which tells that the inclination of the slope is close to border line.It is economically acceptable because it delays the excavation of masses for the future. It can be arranged over several years which leads to economical benefits for the firm. The occurrence of deformation and stress growth during the excavation of the lowest benches is caused by bringing the part of the slope in steeper position and by the deepening of the open pit. From above it can be concluded that the analysis of stress and deformations should be done for the deeper sites of the open pit, because the projected inclination of the slope given in profile-1 do not have to be acceptable for other depths of the open pit.The comparative analysis of deformations shows significantly bigger start values of plastic deformations in variant which treats faults which means that faults have significant influence on the slopes' stability.

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DEFINITION OF CONTROLLED BLASTING ZONES AT JUZNI REVIR OPEN PIT COPPER MINE MAJDANPEK

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ABSTRACT

Open pit Južni revir operates under RBM Majdanpek, a part of the RTB Bor – Group. According to the new mine design suggested pit development will bring mining operations in a close proximity to residential structures of the Majdanpek town. Since technology applied utilizes drilling and blasting operations there is a high probability that the closest structures could be affected by ground vibrations generated by the blasts. In order to protect the buildings and prevent damage appearance it was necessary to predict the intensity of ground vibrations, define the safe magnitude of ground vibrations and finally define the maximum explosive charge weight per delay.

Key words: ground vibrations, PPV, controlled blasting, safety zone.

INTRODUCTION

Južni revir open pit copper mine is located in East Serbia, near Majdanpek. It operates under RBM (Rudnici bakra Majdanpek – Copper mines Majdanpek) as a part of RTB Bor – Group. Besides Južni revir RBM has one more copper mine, Severni revir, located to the North of Južni revir. The first mining operations on overburden removal at Južni revir open pit mine started back in 1958. Copper production begun in 1961 and the mine is in operation up to date. At the past 20 years due to various reasons the focus of mining operation shifted to Severni revir resulting in operations at Južni revir almost coming to a seize. However, significant amounts of ore reserves at Južni revir were a cause for introduction of the new mine design [1] prepared by the Institute for mining and metallurgy Bor in 2012.

According to this mine design, the planned development of the pit will bring mining operations into a close proximity of residential and other structures of Majdanpek town. Suggested technology considers drilling and blasting operations and there is a high probability that the structures closest to the pit could be affected by the ground vibrations. In order to protect the structures from damage appearance it was necessary to revise the mine design from the aspect of negative effects of blasting. A thorough study was performed by Technical faculty in Bor (TFB) and Faculty for mining and geology

Belgrade (RGF). The study was conducted in phases, first defining the intensity of ground vibrations and setting the propagation law. The second task was to perform initial investigation of the nearest buildings and record any existing damage in order to set the initial conditions and define the maximum allowed ground vibrations intensity. The next phase was to revise the blast design in order to calculate maximum explosive charge per delay upon the determined ground vibrations limits. Finally, a monitoring system was designed to monitor and collect data on ground vibrations once the mining operations start. All of these phases were finally presented through three different documents, Elaborate on seismic measurements during experimental blasts at Južni revir Majdanpek (RGF) [2], Elaborate on initial state of structures in the proximity of Južni revir Majdanpek (TFB) [3] and the Monitoring design for ground vibrations and their affect to humans and structures (TFB) [4]

This article will give the details on blast design revisions and reference to other phases of the Study.

DEFINITION OF MAXIMUM ALLOWED GROUND VIBRATION INTENSITY

Investigation of the initial condition of residential structures was necessary in order to define the maximum allowed ground vibrations intensity. It is commonly adopted that the best descriptor of the ground vibrations intensity is peak particle velocity or short PPV.

Various studies were performed during the last several decades in order to correlate PPV and damage to structures and the results are given in table 1

Table 1. Correlation between PPV of ground vibration and damage

PPV (mm/s)	Effect
254,0	Damage in reinforced concrete pillars and walls
114,3	Damage in walls
76,2	Damage in binding material and foundation/wall juncture
50,8	Limit damage level. Structural damage possible above this level
25,4	Appearance of new cracks in plaster and drywall
19,0	Development of existing cracks in plaster and drywall
12,7	The appearance of cosmetic damage in old plaster and development of existing cracks – damage threshold
1,0	No damage

Since Serbia does not have standard covering blast induced ground vibrations maximum allowed PPV was set in accordance with German DIN 4150 (table 2)

In accordance with DIN 4150, PPV/damage correlation in Tab. 1 and determined condition of the nearby structures maximum allowed PPV was set to 15 mm/s. The reason for this decision lies in the fact that the structures closest to the pit are built in accordance to seismic construction regulations and are hence resistant to vibrations. Additionally, due to proximity of structures to the pit it was expected that the frequency of ground vibrations will be higher allowing higher end PPV.

Table 2. DIN 4150-3:1999

Structure type	Frequency of vibrations Hz	PPV mm/s		Measurement location
		Short term vibrations	Continuous vibrations	
Industrial buildings and offices	<10	20	-	Foundation
Industrial buildings and offices	10÷50	20-40	-	Foundation
Industrial buildings and offices	50÷100	40-50	-	Foundation
Industrial buildings and offices	All frequencies	40	10	Highest floor, wall on a floor level*
Residential structures and similar objects	<10	5	-	Foundation
Residential structures and similar objects	10÷50	5-15	-	Foundation
Residential structures and similar objects	50÷100	15-20	-	Foundation
Residential structures and similar objects	All frequencies	15	5	Highest floor, wall on a floor level*
Structures that cannot be classified into previous categories and structures sensitive to vibrations	<10	3	-	Foundation
Structures that cannot be classified into previous categories and structures sensitive to vibrations	10÷50	3-8	-	Foundation
Structures that cannot be classified into previous categories and structures sensitive to vibrations	50÷100	8-10	-	Foundation
Structures that cannot be classified into previous categories and structures sensitive to vibrations	All frequencies	8	2,5	Highest floor, wall on a floor level*

* Horizontal component of measured velocity

DEFINITION OF THE PROPAGATION LAW

In order to be able to predict the intensity of future ground vibrations it was necessary to define the propagation law. Propagation law is in fact a dependency of ground vibrations of the explosive charge per delay and distance from the blast. In order to define the propagation law it was necessary to perform test blasts and measure the intensity of generated ground vibrations. The measurements were performed by RGF and the results are presented in a form of Elaborate [2]. The final result of the measurements was the propagation law in the form

$$PPV = K\left(\frac{d}{\sqrt{Q}}\right)^{-n} = 3321\left(\frac{d}{\sqrt{Q}}\right)^{-1.9}, \text{ mm/s} \tag{1}$$

Where ***d*** is the distance to the blast and ***Q*** is explosive charge per delay.

DEFINITION OF CONTROLLED BLASTING ZONES

According to the blast design from the mine design the blasting would be performed on the 15 m high benches, using 460 kg of ANFO charged into 250 mm diameter blastholes. Based on these data and the propagation law it was possible to calculate the distance from the pit to which the structures will be affected by ground vibrations with PPV higher than 15 mm/s. The distance was calculated as

$$d = \sqrt{Q} \cdot \left(\frac{K}{PPV} \right)^{\frac{1}{n}}, \text{ m} \tag{2}$$

Once the appropriate values were introduced to equation (PPV=15 mm/s, Q=460 kg, K=3321 and n=1.9) the affected distance was 367 m. it became obvious that this affected zone cover more than half of the town center (Fig. 1)

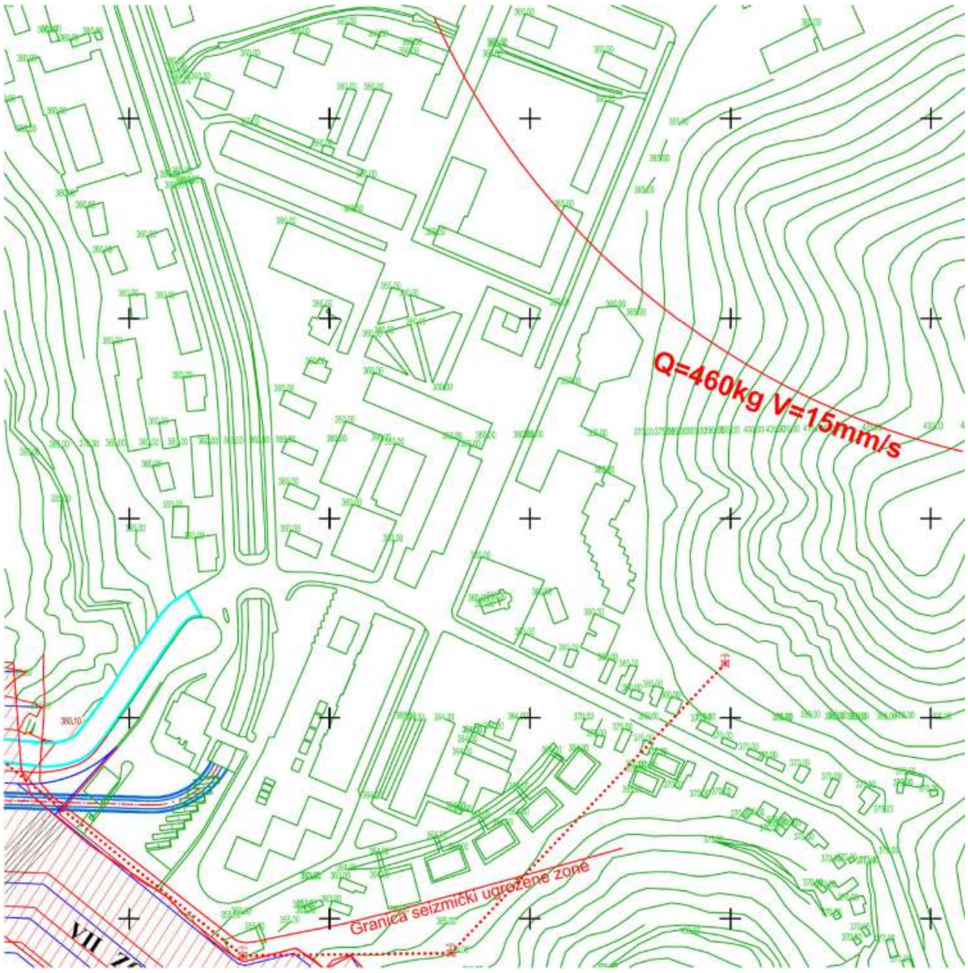

Figure 1. Affected zone for non controlled blasting

Because of that the mine management decided to set the safe zone limit in such way that no structures could be affected, meaning that affected zone can spread to a maximum of 30 m from the pit outline (Fig.2).

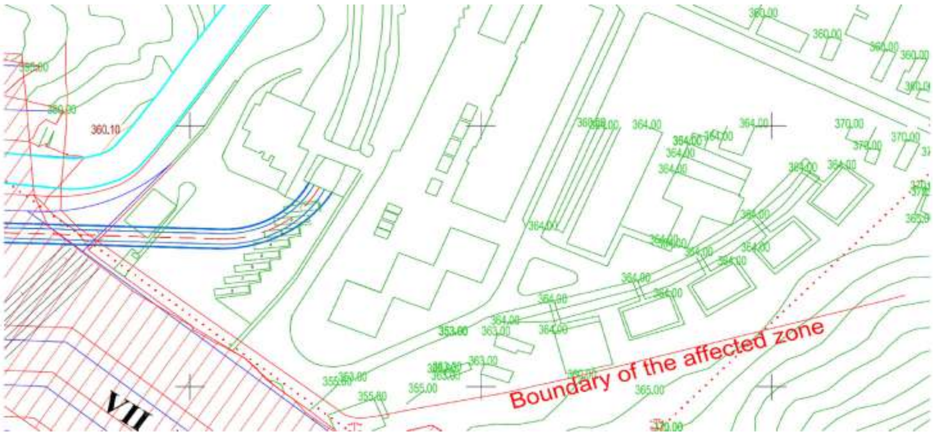

Figure 2. Boundary of the affected zone set by the mine management

Since the affected zone limit was fixed it was necessary to define controlled blasting, that is to revise the blast design and calculate maximum explosive charge per delay in a way that generated ground vibrations do not exceed 15 mm/s beyond the affected zone limit.

Drilling equipment at Juzni revir is capable of drilling with diameters of 250, 130 and 85 mm and these diameters were considered in blast design revision. Besides the diameter reduction the controlled blasting design considered reduction of the charge per delay through the introduction of split column charges and possible variations of three possible diameters and a maximum of four split deck charges are given in table 3.

Table 3. Possible configuration of explosive charges

Diameter mm	**Total charge length m**	**Explosive charge per 1 m kg**	**Charge weight per deck for decked charges kg**			
			1	2	3	4
85	13	5.38	70.04	32.32	19.75	13.47
130	12	12.60	151.23	69.31	42.01	28.35
250	10	46.60	466.09	209.74	124.29	81.56

Based on the results from Tab. 3 seven possible configurations were accepted for further consideration: 460 mm single charge, 460 mm two decks, 130 mm single charge and 85 mm single charge, two, three and four decks (Tab.4)

Table 4. Finally accepted controlled blasting parameters

Diameter mm	**Charge weight per deck for decked charges kg**			
	1	2	3	4
85	70	32	20	13
130	150	-	-	-
250	460	210	-	-

Once the parameters of controlled blasting were defined it was necessary to define the zones within which these parameters will be used i.e. controlled blasting zones. The calculations were performed utilizing Eq. 2 and the results are 7 zones of controlled blasting with blasting being fully prohibited in zone 7. The distance of the specific zone from the pit outline is given in Tab. 5 and the zones are presented in Fig. 3.

Table 5. Controlled blasting zone distances

Zone	Charge weight kg	Distance from the pit outline m
0	460	Beyond 367
I	210	248 – 367
II	150	210 – 248
III	70	143 – 210
IV	32	97 – 143
V	20	77 – 97
VI	13	62 – 77
VII	No blasting	0 – 62

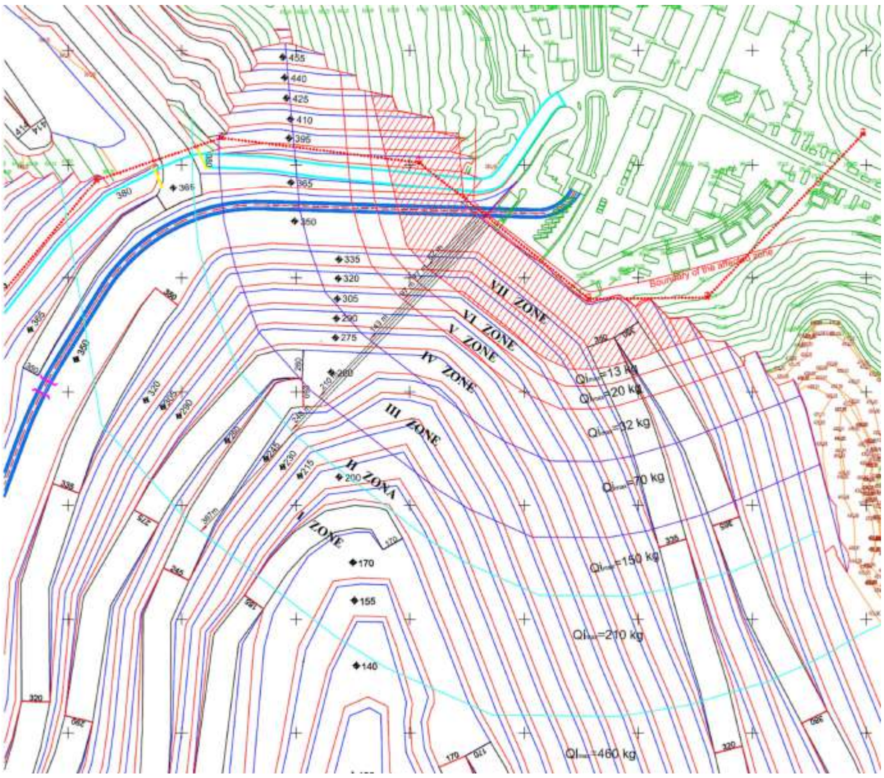

Figure 3. Controlled blasting zones

CONCLUSION

Due to concerns that blasting generated ground vibrations could cause damage to the structures in Majdanpek it was necessary to revise the blast design and define controlled blasting parameters. After taking into consideration all of the influential factors, primarily the condition and the type of the affected structures seven zones with corresponding blasting parameters were defined. In addition, a monitoring system is designed in order to monitor the intensity of ground vibrations for further actions in terms of blasting parameters adjustments.

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THE CONTENT OF MANGANESE IN SOILS AND PLANTS OF BOR MINE OVERBURDEN SITE (SERBIA, SE EUROPE)

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ABSTRACT

Manganese is ubiquitous element in nature, being abundant constituent of soils and having essential role as micronutrient in plants. However, some interactions of manganese in diverse natural processes are not yet fully understood. This paper analyses the results of manganese content screening for frequent wild plants of Bor mine waste overburden, defines main relations with characteristics of overburden mine soils and presents the extent of its transfer in wild plants of this area.

Key words: manganese, overburden soil, wild plants.

INTRODUCTION

Manganese is a common metal in the Earth's crust and its presence in soils mainly results from Mn in the parent material. Manganese mobility in soil is sensitive to conditions such as acidity, oxido-reduction processes, organic matter content, biological activity and moisture [1]. The solubility of soil manganese is mainly controlled by redox potential and soil pH, where low pH or low redox potential favor the reduction of insoluble manganese oxides which increase the solubility of Mn^{2+} [2]. Manganese oxides have high adsorption activity for heavy metals. This is especially important for mine soil environments prone to acidification and leaching, where these oxides exhibits strong control on the mobility and bioavailability of many bio-essential and toxic heavy metals [3].

Manganese is also essential microelement for plants, taking role in photosynthesis process, lipid biosynthesis, protecting cells against reactive oxygen species and being cofactor of certain enzymatic activities in plants [4]. The critical deficiency levels of Mn in plants are similar, varying between 15 to 25 kg [5], regardless of plant species or cultivar or prevailing environmental conditions. However, the excess of this micronutrient is toxic for plants. The critical toxicity for Mn concentration varies widely among plant species and environmental conditions [1]. Even within a same species, the critical toxicity concentration can vary among its cultivars [6]. Besides disparity among Mn levels that induce toxicity, the symptoms of this toxicity in plant species may also be diverse [7]. Chlorosis and brown necrotic spots on leaves are frequently observed indicators of the Mn toxicity in plants [8]. Plant uptake of Mn is merely a function of the Mn oxidation state in the soil. The most soluble species in soil, Mn^{2+}, is also the most efficiently accumulated in plants [1]. It is therefore considered that Mn content of plants is a direct function of the soluble Mn pool in soils [5]. A mobilization of Mn^{2+} is produced by the rhizosphere acidification due to the release of H^+ or low molecular weight organic acids from plant roots [9]. Availability of manganese increases in acidic soils or anaerobic conditions [23]. Therefore, manganese is considered to be among the most important toxic metals in acid soils [10].

MATERIALS AND METHODS

The study area is placed on the margins of the town of Bor (44°04'25" N, 22°05'26"E, SE Serbia, Europe). Copper ore exploitation process in this area has resulted in formation of overburden piles covering an area of approximately 150 ha. They consist of non-selectively deposited volcanic rocks, mainly andesite and its volcaniclastic equivalents. This area is selectively covered with wild herbaceous species.

A total of 52 composite soil samples were taken from the upper 20 cm layer of the sampling plots. The soil samples were air-dried and then sieved through a 2 mm sieve. A soil–water solution (1:2.5) was used for determining the active soil acidity, while the 1M KCl solution was used for measuring the potential acidity of mine overburden soil. Soil electrical conductivity (EC) was measured with conductivity cell in 1:2.5 soil-water solution, while oxido-reduction potential (Eh) was measured meter with a platinum electrode, previously polished and tested by ZoBell's solution [11]. The saturated calomel electrode (0.244 V at 25 °C) was used as a reference electrode. Organic carbon was measured by the method of Tjurin [12] and total nitrogen contents were determined by the method of Kjeldahl [13]. The contents of plant-available forms of phosphorus and potassium were analyzed with the Al-method [14]. Soil textural classes (sand, silt and clay) were examined by dispersion with sodium-pyrophosphate following sedimentation with international pipette-B method. Pseudo-total Mn was extracted by aqua regia digestion (International standard ISO 11466: 1995). Pseudo-total contents give an assessment of the maximum potentially soluble or mobile contents of Mn, not bounded in silicates. Available fraction of Mn was extracted in 0.05 M EDTA. Manganese concentrations were determined by ICP-OES (SpectroGenesis EOP II, Spectro Analytical Instruments GmbH, Kleve, Germany).

Five frequent wild plant species were collected as composite samples from the overburden area. They were rinsed with tap water and carefully washed with distilled water, after which thez were separated to root and shoot parts. Three parts were microwave digested with HNO_3 i H_2O_2 and their manganese concentrations were determined by ICP-OES. In order to determine phytoremediation potential of selected plants, biological concentration factor (BCF) was calculated as ratio of metal concentration in plant roots to that in soil, biological accumulation factor (BAC) was calculated as ratio of heavy metal in shoots to that in soil, and translocation factor (TF) was described as ratio of heavy metals in plant shoot to the content in plant root [15].

Box-Cox transformation was conducted prior to statistical analysis in order to normalize data. Analysis of variance (ANOVA) and calculation of Pearson correlation coefficient was conducted in statistical package StatSoft 8.0.

RESULTS AND DISCUSSION

Average content of manganese in soils of Bor mine overburden (X_{invBC}=383 ppm) is lower than the European soil's natural background value [16], having enrichment factor of 0.76. Average content of available manganese Bor mine overburden soils exhibits 17.4 % of their total manganese content (ranging from 15.4 % at rhizosphere soil of *A. stolonifera*, up to 19.4 % for rhizosphere soil of *L. genistifolia*). Average levels of manganese in root and shoot of sampled plant species are generally low, having values of 24.7 and 26.2 ppm, which places them close to deficiency levels [5].

Table 1. Average pseudototal and EDTA-available manganese content in rhizosphere soils and roots and shoots of wild plants at Bor overburden site

Species	$Mn_{pseudototal\ XBc(inv)}$	$Mn_{EDTA-available\ XBc(inv)}$	$Mn_{rootXBc(inv)}$	$Mn_{shoot\ XBc(inv)}$
Linaria genistifolia	607	112	2.67	14.1
Epilobium dodonaei	556	108	6.27	5.01
Calamagrostis epigejos	277	42.8	87.2	119
Sanguisorba minor	452	87.4	1.37	N.D.
Agrostis stolonifera	214	33	256	158

Manganese content in plants varies greatly depending on the species. According to the results of analysis of variance (ANOVA), wild plant species show significant differences between their rizosphere soil Mn levels (F_{edta}=3 , p_{edta}=0.03 ; F_{pt}=8.02 , p_{pt}=0.00), as well as their root (F_r= 22.84, p_r=0.00)and shoot (F_s= 28.77, p_s= 0.00) Mn content. As presented in table 1, average content of Mn in plants tends to be higher in shoots then in roots of species *L. genistifolia* and *C. epigejos*, while the other wild species exhibit the opposite trend. The content of Mn in species *L. genistifolia*, *E. dodonaei and S. minor* is beyond deficiency limit. Species *C. epigejos* and *A. stolonifera* show highest concentration of Mn in their roots and shoots, while contents of Mn in their rhizosphere soil are lower compared to the rhizosphere soil of other investigated species.

Results presented in table 2 show high ranges of soil pH values, electrical conductivity, organic material content, available potassium and phosphorous , S_{EDTA} i S_{PT} content. Further, table xz shows main correlations of manganese content in soil and plants with physico-chemical mine soil properties and the content of soil sulfur.

Table 2. Range of main physico-chemical characteristics and correlation coefficients of manganese content in soil and plants with Bor mine overburden soil physico-chemical properties and content of sulfur (Eh – oxido'reduction potential, EC-electrical conductivity, OM – organic material, N_tot – total nitrogen content, K_2O – available potassium content, P_2O_5 – available phosphorous content, S_{EDTA} – EDTA available sulphur, S_{PT} -pseudototal content of sulphur, significant correlations are given with *)

Variable	Interval	Mn_{Root}	Mn_{Shoot}	$Mn_{EDTA\ available}$	$Mn_{pseudo-total}$
Silt (%)	0.2-2.49	-0.26	-0.29	-0.01	0.05
Clay (%)	0.33-3.12	-0.15	-0.13	0.10	0.12
pH (H_2O)	3.45-8.4	*-0.77	*-0.83	*0.52	*0.64
pH (KCl)	2.65-6.94	*-0.75	*-0.80	*0.57	*0.67
Eh (mV)	202-363	*0.72	*0.80	*-0.45	*-0.56
EC (μS)	76.9-2310	*0.54	*0.58	-0.11	-0.27
OM (%)	0.01-9.3	-0.24	-0.30	0.22	0.31
K_2O (%)	2.65-37	-0.44	-0.57	*0.49	*0.50
N_Tot (%)	0.01-0.08	-0.60	-0.63	0.35	0.38
P_2O_5 (%)	0.05-24	*-0.72	*-0.74	0.15	0.22
S_{EDTA}	121-13264	*0.58	*0.60	-0.13	-0.27
S_{PT}	1171-22719	*0.61	*0.59	0.15	0.01

Content of pseudototal and available Mn in rizosphere soil, as well as level of Mn in root and shoot of plant species strongly correlates with pH and Eh of mine overburden soil, confirming the known dependence of manganese mobility and soil Eh–pH conditions [5]. Observed correlation of Mn plant levels and available soil P in Bor overburden mine soils is in the accordance with the researches that have spotted negative correlation with available P content in soil and level of Mn accumulation in plants [17]. Although the exact mechanisms of the Mn–P interaction so far remained unknown, it has been suggested that P interferes directly with Mn at the uptake and translocation level [17], [18] ,[19].

Relation of electrical conductivity and plant manganese levels has been observed in some investigations, where both antagonistic and synergistic effects were recorded depending on the plant species and soil conditions, as well as the type of salt [20]. However, the impact of decreased or increased uptake of Mn under salinity stress is a phenomenon that requires further study (Han et al, 2014 [21]).Increased salinity in Bor mine overburden soils is a result of soluble sulphate salts in surface overburden layers, which is reflected through high correlation coefficient of sulfur levels and measured EC (r_{EDTA}=0.87, r_{PT}=0.80). Therefore, observed correlation of Mn plant content and measured EC as well as the correlation with levels of S could be in accordance with processes of soil acidification during dissolution of sulphur salts.

Table 3. Manganese concentration and accumulation factors of wild plants

Species	BCF_{PT}	BCF_{EDTA}	BAF_{PT}	BAF_{EDTA}	TF
Linaria genistifolia	0.04	0.02	0.02	0.12	5.28
Epilobium dodonaei	0.01	0.06	0.009	0.046	0.8
Calamagrostis epigejos	0.31	2.04	0.43	2.78	1.36
Sanguisorba minor	0.003	0.01	-	-	-
Agrostis stolonifera	1.19	7.75	0.74	4.79	0.62

Results presented in table 3 show high variability of concentration, accumulation and transfer factors for Mn between the selected wild species. Species *S. minor* showed lowest efficiency in accumulating and transporting Mn from overburden soil, while *A. stolonifera* had highest efficiency for concentration and accumulation of this element. However, higher transfer efficiency of this element belongs to *L. genistifolia* and *C.epigejos*.

Concerning the phytoremediation potential, species *A. stolonifera* showed potential for phytostabilization of manganese in Bor overburden mine soils, while species *C. epigejos* showed phytoaccumulation abilities for bioavailable content of Mn. Genus *Agrostis* has been recognized for their ability to accumulate Mn, e.g. grass *Agrostis gigantea* was used and has further been proposed for restoration of Mn-contaminated sites, due to its high threshold values for Mn toxicity [22], [23]. Some species of genus *Calamagrostis* (such as *Calamagrostis arundinacea*) have also been recognized for accumulating higher concentrations of Mn in roots and shoots [24].

CONCLUSION

Average content of manganese in soils of Bor mine overburden is generally lower than the European soil's natural background value. Content of manganese in root and shoot of wild plants growing on the Bor mine overburden mainly depends on pH-Eh soil system, content of available phosphorous and electrical conductivity. Manganese level in soils also corresponds to pH-Eh soil regime, as well as the content of available potassium.

Average Mn content of wild plants in Bor overburden significantly varies among the plant species. While the content of Mn in species *L. genistifolia*, *E. dodonaei and S. minor* is beyond deficiency limits, species *C. epigejos* and especially *A. stolonifera* show higher concentration in their roots and shoots, as well as the phytoremediation potential for this element.

For gaining stronger insight into geochemical and biogeochemical behavior of manganese in mine soils of Bor overburden, further investigations should take into account speciation of manganese in overburden soil, as well as synergistic and antagonistic relation of Mn behavior and uptake with other important chemical elements from Bor overburden, such as cooper, arsenic, lead and zinc.

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MONITORING OF ENVIRONMENTAL PARAMETERS BASED ON LABVIEW PACKAGE

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ABSTRACT

Monitoring of environmental parameters is of great importance for society. Today, they are accompanied by various parameters of the environment and in most cases, these are modern computerized systems. The development of computer technology make it possible to simultaneously measure, record, process, compares and displays a large number of signals, and all that with a relatively small investment. This paper presents the design of the measuring system consisting of computers, AD converter, 6 instrumentation amplifiers with appropriate filters and sensors 6 for selected environmental parameters. The software package for measuring, processing and display of the signal allows data acquisition and processing, display, saving as well as comparison of multiple sets of signals.

Key words: Ecological parameters; Monitoring; Computer Measurement; LabVIEW.

INTRODUCTION

The world is due to uncontrolled and offensive technological development, uncontrolled population growth as well as due to the continuous depletion of natural resources, in parallel increases the amount of pollution produced and waste. Intensive pollution of the environment is approaching a critical point, so it is necessary monitoring environmental parameters, which is quite complex and expensive process [1]. For this reason, go on a compromise between the desire of environmentalists and available funds principally obtained from industrial giants. Actually, the problem is that the industrial giants biggest polluters of the environment, so it is difficult to expect the separation of large funds for systems that will explicitly indicate the need to undertake environmental measures, which means big investments, i.e. reducing profits. Lately things have a chance, however, are changing.

The development of society both in economic and technological terms associated with environmental pollution. The current level of progress and knowledge indicates that can be matched to a certain extent, industrial development and pollution. By combining the two is achieved by the real effect of social progress [2].

Country shows interest and take measures that will force polluters to invest in environmental equipment, and on the other hand, the cost of equipment for monitoring environmental parameters significantly decline. This is especially true for systems based on the PC where you can install your own knowledge (design and software). Therefore, you can get a solid monitoring at a reasonable price that will allow monitoring pollution and will the weather warnings.

DESCRIPTION OF THE SYSTEM

In the specific case of selected environmental parameters are as follows:

- The concentration of CO2 in the air
- Insolation - monitoring the intensity of solar radiation during the day, month and year
- Air temperature
- Atmospheric pressure
- Relative humidity
- Noise level

Sensors for selected environmental parameters have different signal levels, internal resistance and other properties [3-5], so that their signals are conditioned (amplified, limiting, filtering, impedance adapting etc.) [6,7]. Due to the very small signal at the output of the sensors are applied instrumentation amplifiers INA 114 (Fig. 1.)

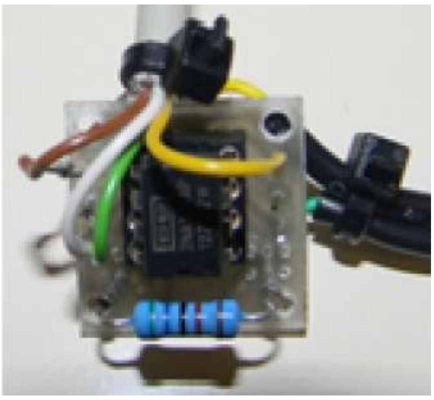

Figure 1. Instrumentation amplifier

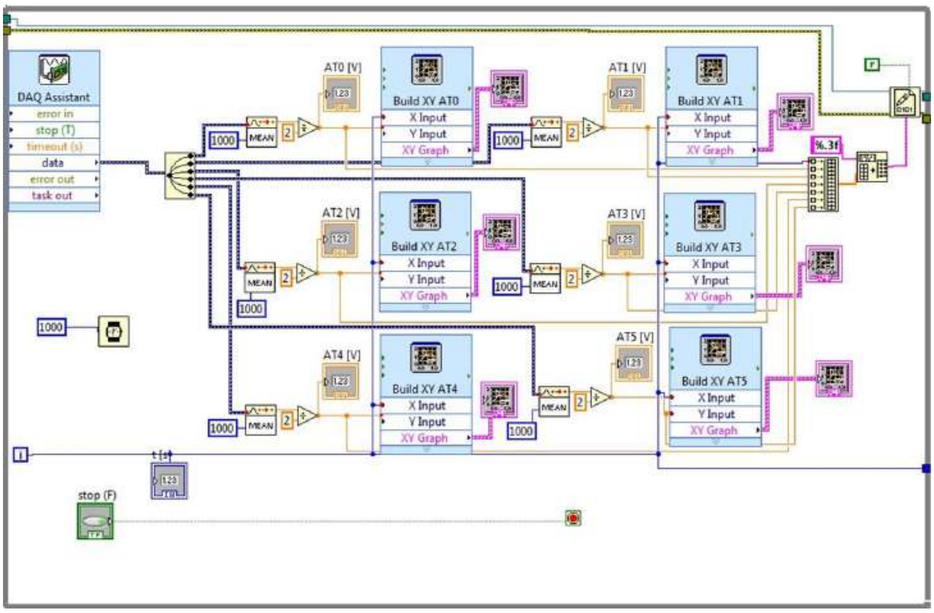

Figure 2. LabVIEW 2010 applications

To minimize the interference signal is further shielded conductors leading to AD converter (NI USB 6009). The digitized signals are introduced into the computer and processed in LabVIEW 2010 application (Fig. 2.) [8-12].

The appearance of the front panel (*Front panel*) is shown in fig. 3. Shown 4 of 6 available signals.

The system has been laboratory tested, calibrated, and then verified in real conditions.

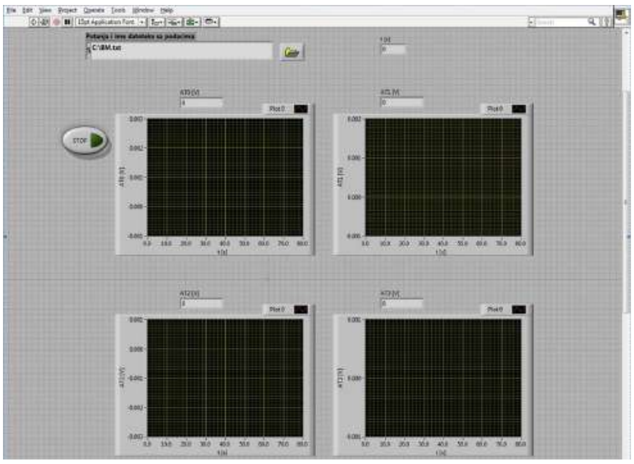

Figure 3. Front panel of the virtual instrument

Block diagram of the interface is shown in Figure 4. The inputs A0 to A6 come active signals that are observed, whereas R has represent the signals from the reference electrodes, and are connected to ground. The signals are processed and amplified in part IA0 to IA6 that represents the instrumentation amplifier INA 114 with associated circuitry.

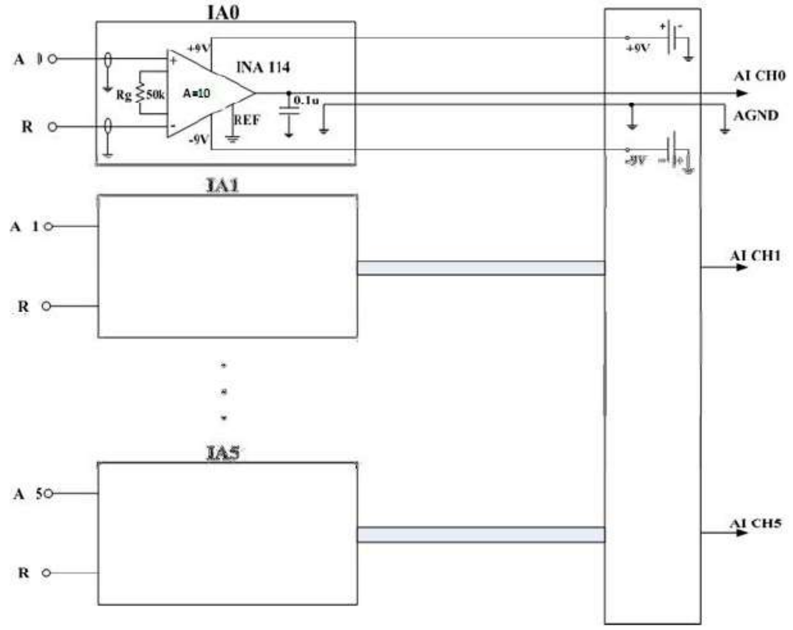

Figure 4. Scheme of the measuring interface

Such signals are further forwarded to the AD converter NI 6009 and continue through the USB connection to the computer, where it is a secondary processing and presentation of data. Photo of the complete system is shown in Figure 5

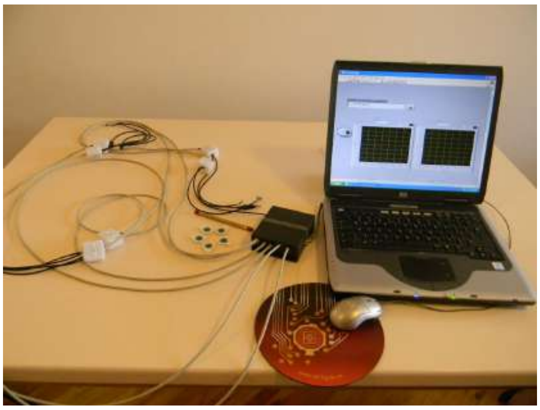

Figure 5. Photo of the System

CONCLUSION

For the monitoring of environmental parameters is made with 6 hardware instrumentation and application was made for data acquisition with 6 analog channels. Set up a system for environmental monitoring, which in addition to the aforementioned equipment includes a commercial data logger, PC and basic software. The system has been laboratory tested, calibrated, and then verified in real conditions. The results show that the system fully meets the specified requirements and can be compared to expensive commercial devices.

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REDUCING ENVIRONMENTAL IMPACT OF BIG DATA USING SERVER VIRTUALIZATION TECHNOLOGY IN DATA CENTERS

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ABSTRACT

We are faced with extremely large volume of data which nowadays called Big data. That amount of data could be processed only by capacities provided by modern data centers. Those data processing will have enormous impact on the environmental issues. Big power usage, low energy efficiency, big overall carbon footprint are some of negative impacts that data centers already produce and will produce in future years worldwide. One of the solutions for reducing these impacts is to implement virtualization technology in data centers. This paper is focused on the server virtualization in data centers and its positive feedback on the environment as green technology.

Key words: Big data, Data center, Energy efficiency, Server, Virtualization.

INTRODUCTION

If modern computers ancestors are analyzed, we found that, few decades ago, computers were a big machines situated in very large rooms with large consumption of energy for that time. That computers provides some basic calculations mostly for army purposes. Looking from the modern perspective, we can say that common characteristic to all computers for that time were related to one simple fact that there was a one big machine which provided some computations based on very small set of data. Through the years, complexity of computers and complexity of calculations which computers performed grown. Computers become the basic tool in every sphere of our modern lives, from everyday routines to special purposes. Mostly when we say computers our first association nowadays is a computer as a desktop computer or laptop, so maybe the term computing device is more precisely for dealing with a wide range of modern devices which collected and processing data and information (sensors, programmable logic controllers, mobile devices, computers etc.).

The amount of data which these computing devices generated over the years are constantly increasing. Modern technology provided adequate solutions for storage and processing which are constantly improved, so we have powerful memory chips or processors, but individual solutions nowadays, even so powerful and futuristic, are not enough for the "data-boom" which we have in the last decades. Last fact forced information technology to create special facilities which today are called data centers or datacenters. Data center presents an obtained collection of hardware and software resources with all their mutually relations and connections as the answer for storage and processing very large amount of data which is generated nowadays.

Today data centers provide the necessary base for dealing with Big data.

HOW BIG ARE BIG DATA

Big data is a term which was introduced in information technology few years ago to represent drastically changes about amount of data that are processing worldwide in every moment. Through the years Big data become not only a simple term in IT industry, it become more, the whole set of new procedures, techniques, improvements, methods and methodologies for analyze and represent extremely large amounts of data for variety purposes. Three dominant factors is crucial for understanding concept of Big data.

We already mentioned few times amount of data. Big data assumes extremely large volume of data to be gathered and processed. A decade ago IT industry saw a future of data in petabytes and all discussions and predictions were even in smaller units like terabytes. Now we have situation that average user for his purposes already has a storage capacity of few terabytes at home. So what is the real size of the data nowadays? We can only statistically predict the size of data worldwide, because huge data generations are done in very small time intervals, so sometimes assumptions about digitally presented data in the world are reviewed on the daily bases.

New statistical findings say that the amount of produced data will be about 35 to 40 zettabytes by 2020 (one zettabytes is equivalent of 1 trillion gigabyte or 10^{21} bytes). For better understanding how extremely large big data volume is, if already mentioned sum of 40 zettabytes compare to data stored and generated by every individual on Earth, we can say that there will be about 5 terabytes of data for every person on planet by 2020 [1].

Second crucial fact when we discuss about Big data is velocity of the generated data. In this case we also faced with extremely large values which are rapidly increased in the last couple of years which most of data analysts connected to the Internet technologies domination, especially with Internet of Things (IoT) phenomenon. IoT means that most of the modern devices are connected to the Internet and via global network they gathering, processed and sharing data. Also we must mention social networks as one of the dominant generator of data. About 90 percent of all data in the world is created in the period smaller than couple of last years [2].

At the end of these discussions about some Big data facts we also must emphasized the importance of sources of data. Again, we have situation to deal with extremely large values. It means that the variety of sources are increased every moment, day by the day. We have a direct connection between these sources and data, more sources, more generated data by them. Of course, somebody can ask about the relevance of some sources, but that not change the fact that data still will be generated, relevant or irrelevant.

DATA CENTERS AND THEIR IMPACT ON ENVIRONMENT

In previous chapter we discuss about of current and future amount of data on the global level. Logical conclusion is that extremely large volumes of data must be adequate processed. That extremely large sets of data can not be processed by some small home or office solutions, so we will use some special hardware and software solutions and techniques which are provided by data centers mentioned in introduction part.

We have a situation here that Big data need big resources or in accordance to the above, Big data need big data centers (or maybe nowadays we can wrote it down also as Big data need Big data centers). To represent size of modern data centers we can consider few of popular data centers in the USA. For example, if we looking data center power consumption. Digital realty in one of their many data centers use for constant power supply over 50 generators and Quality Technology has power capacity of 80 MW [3]. Or if we looking number of servers located on one place (in one data center), for example, we can discuss about Microsoft Corporation and their famous data center located in Chicago which has about 225000 running servers in every moment [3].

Data centers are based on many standards and recommendations issued by the relevant institutions such as IEEE, NIST, TIA etc. This standards defined crucial parts of every data center in both ways, hardware and software. For further analysis we will be focus on standard TIA-942 provided by TIA (Telecommunications Industry Association) and which is approved by ANSI (American National Standards Institute) [4]. We point out on this standard because in this standard are defined, among the rest, data center space and layout, crucial infrastructure issues, power, cooling and environmental considerations. Also, in further consideration we will be based on Uptime Institute Tier IV certification. Tier IV certified data centers are the most reliable data centers and also data centers with the most power consumption and with the most impact on the environment [5].

Power consumption

Lets see typical power consumption annually by one server. Relevant information is provided using public Green Calculator application by VMWare company [6]. Calculations are based on following assumptions: analyzed server is standard two processor server with operating power of 375 W and cooling power for this server is about 1.3 times bigger than operating power. Energy usage of this server together with energy for its cooling for one year is 7556 kWh. This energy is almost equivalent to energy which for one year typical household consume in 60-70 m^2 apartment.

If mentioned above apply for example to Microsoft data center located in Chicago with nearly 225000 running servers we got annually energy consumption of nearly 1.695.303 MWh which represent very imposing number.

That is only calculations based on servers and cooling systems, but in data centers we also have very large number of other equipment with very big power consumption (active network equipment, monitoring equipment, unlimited power supplies) so figures are definitely bigger then these above.

We can easy see from the previous examples that big data centers have big energy consumption. Some of them have a power consumption like small towns, so they have a special power plants dedicated only to their purposes.

HVAC - Heating, Ventilating, Air Conditioning

Every component has its some sort of thermal characteristic. Hardware vendors make efforts to decrease heating of devices using new designs, materials and other technologies and techniques, but the heating problem is still present partially by the component and then by the device at all.

In data centers problems related to heating is one of the dominant problems. That is direct consequence of highly concentrated equipment on one space. Source of the heating is various and not all of that heating sources are strictly related only on devices. For example sometimes in data centers air flow models by CFD (computational fluid dynamics) are not done on proper way or racks and cabinets not arranged to create hot and cold aisles etc.

So we have heating or overheating and all that heat in most of the cases are passed on to external environment. To prevent overheating we must use air conditioning systems which are consume a lot of energy. Also that systems sometimes contain components which are not environmental friendly.

Besides air conditioning systems, data centers must be equipped with ventilation systems from smaller ventilation components to large scale components. Environmental impacts are nearly the same as at air conditioning systems. Air conditioning and ventilation systems also prevent moisture and keep humidity in proper values.

HVAC systems have very important roles in modern data centers, but also have very large influence on data centers environmental impact.

Energy efficiency issues

Although hardware is improved drastically over last years, energy efficiency of servers in data centers is still on very poor level. That is direct consequence of very low utilization per server which is present even in today modern data centers.

Energy efficiency of each server could be represented as [7]:

$$server\_energy\_efficiency[\%] = \frac{server\_utilization[\%] \cdot output\_power[W]}{output\_power[W] + cooling\_power[W]} \cdot 100$$

This means if we have a server with 300W input power and 300W cooling power and server utilization of 20%, we have server energy efficiency of poorly 10%. For this particular case this means that only 60W used for real work of 600W needed for server power and cooling.

Unfortunately, some researches said that is the common practice that nearly 90% of energy is wasted instead to be used for real work.

Carbon footprint

Latest researches show that data centers produced 15-20% of technology carbon footprint.

For example data centers power consumption before year 2010 in Western

Europe was about 56 TWh annually. European Union in 2010 conducted some researches about energy consumption and reported that data centers power consumption in 2020 is estimated to 104 TWh annually [8].

When analyses this numbers we must have one important fact on mind. Whole energy produced and used by data centers are primary based on oil, gas, coil and nuclear energy and less on the renewable sources like solar or wind. Renewable sources in energy production is used with very low percentage (somewhere below 10%). That means that we have significant CO_2 releasing by producing energy which is used for data centers purposes.

VIRTUALIZATION AND ITS POSITIVE FEEDBACK ON THE ENVIRONMENT

There are a numerous ways of defining virtualization depending on the point of view. Virtualization in common sense is a way to create something virtual instead do it in real. In IT world virtualization means to create virtual server, storage, network or any other IT device or resource. Most sources agreed in one thing nowadays, virtualization is one of the key IT technology and it brought a revolution to different levels of using modern information technologies.

Virtualization is technology which combines hardware and software and which enables starting of multiple different operating systems on one server sharing common resources. By virtualization, system is divided on multiple independent virtual instances which performed tasks as independent servers [9].

In economical way, virtualization improved several economic factors. If we analyze ROI (return of investment) period, virtualization practice shows to us that it is much shorter now. In most cases period is shorter than a year (practically few months) instead of few years when we speaking about improvements related to IT. Virtualization downsized necessary infrastructure, number of servers is drastically decreased which impact that data centers could become smaller, so objects and areas for building data centers is smaller too. Also all necessary systems (for example HVAC systems) became smaller by size, capacity and cost which improves profit of data centers. Energy costs are also few times downsized which improves data center economy.

Reducing of power consumption

One of the biggest improvements in data centers when the virtualization techniques are implemented are the reducing of number of servers. This practically means that directly by reducing number of servers, we reduce energy needed for powering and cooling. Although the numbers individually by server itself could stay near previous values, we need to see bigger picture. By the virtualization, physically is still one server, but virtually we have more than one server per machine. So we can use that energy for power and cooling consumed not only one server. Energy are consumed by all virtual servers on one machine as is presented on an example on figure 1.

VMWare company in its calculations concluded that one two processor server has energy consumption for powering and cooling about 7556 kWh per year and that the correspondent virtual server achieve consumption of 944 kWh per year which gives us ratio of about 8:1 in favor of virtualization.

Virtualization ration could have different values, because every data center has its own specifications, so the virtualization will not have the same pattern in all data centers and will be implemented in the most optimal way for each data center particularly. According to that. resulting power savings will be also different for every data center, but common approach is searching for optimal powering solutions.

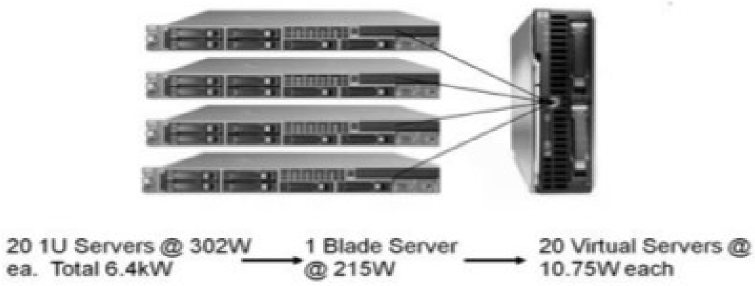

Figure 1. Data center blade server virtualization ratio [10]

HVAC reducing

We already said at the previous conclusions that the number of servers will be reduced by implementation of virtualization. That implies that we have also reducing of space where servers are located, so number of server rooms or containers in data centers will be decreased. We will have a much less number of hardware elements to be implemented in racks and cabinets, so their number will be smaller. Also in some cases racks and cabinets will be downsized. As the consequence of that tendency, we will have smaller number of hot and cold aisles so we will much less heating and overheating problems.

According for that number of HVAC systems will be reduced too. But reducing of the HVAC systems will not be only based on their number, these systems will be reduced also by their size, power usage and complexity. Also area needed for special HVAC segments is much smaller.

Significant fact is that in most cases when virtualization is implemented, we have a reducing of possible errors in computational fluid dynamics (CFD) when projecting air flows. This is direct consequence of already mentioned downsizing, so by downsizing we will have a less complex systems and facilities.

Influence of cabling issues is decreased too because as we have a less number of physical servers, we will have a less number of cables to provide for that infrastructure. That means that we have a much less situations of heat spreading through the cable holes and cable paths.

Energy efficiency improving

There are a numerous ways to improve energy efficiency per each server. For start we could improve energy efficiency by choosing servers with some energy certificate which guarantee that server has a components that give to it the best energy performance. For example servers with energy star or 80 plus certified power supply unit (PSU) in most cases will be much energy efficient than ones with PSU without any kind of certification.

One of the currently most efficient way to improve server energy efficiency brings virtualization. As we previously discussed one of the primary problem with servers is their low server utilization. Virtualization could increase these values because with virtualization technology we had a situation that one physical server operate with more virtual servers. On that way utilization of that physical server is increased with utilization of virtual servers. Even the low utilization of virtual servers increase real utilization of their physical host.

On figure 2 we can see that improving server utilization have a bigger effects on server energy efficiency than for example improving power supply efficiency. Improvements of virtualization are bigger than improvements of PSE even with the small values of server utilization.

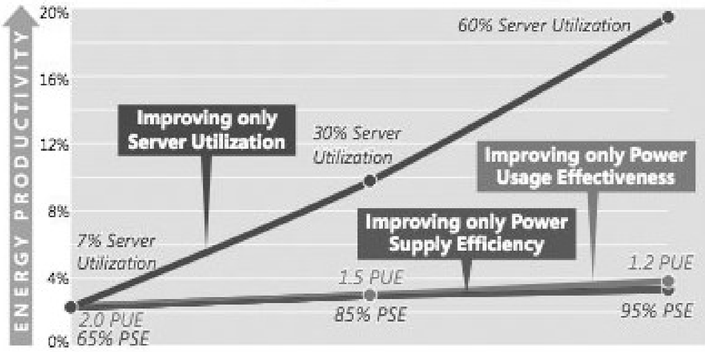

Figure 2. Effects of various improving to energy efficiency of server [11]

4.4 Carbon footprint reducing

In previous chapters we discussed about various positive impacts when we have virtualization technology implemented on our server. As could be seen we achieved significant energy improvements. When less energy is consumed and when energy is better used that implied less energy will be produced for data centers purposes. So if we produced less energy typically for data centers than we reduce data centers carbon footprint because we have decreased CO_2 emissions to atmosphere.

For better representation assume the we have a standard two processor server with operating power of 375 W, cooling power for this server is about 1.3 times bigger than operating power and that the CO_2 emission per kWh is about 0,718kg. By virtualization of mentioned server we reduce annually CO_2 emission for the amount of about 4747 kg [6]. This number is equivalent or in some cases and more than the annual CO_2 emission of typical passenger car.

As we see by virtualization we save the atmosphere for tons and tons of CO_2.

Other positive environmental effects

In previous discussion about virtualization environmental improvements we were focused on energy. But we must mentioned shortly some other environmental improvements which are realized by virtualization technology, too.

We said that using virtualization we drastically decrease the number of servers. That means that we also decrease the number of components which are implemented in that servers. So we can said that at the some level producing of the electrical components for data centers purposes will be decreased too. If we assume previous, we have a decreasing of electronic waste produced by data centers. And not only electronic waste. We can said that the other waste which are produced by data centers will be decreased too (for example because of less server and components shipping, package materials like boxes will be decreased too and similar).

If we for cooling purposes use water as a cooling fluid, by virtualization we have less demand cooling systems, so we can concluded that we have a less water used in process and also less waste water.

By reducing energy usage by virtualization technology we give significant chance to use a bigger amount of renewable energy sources for data centers purposes. We can assume that there will be a moment for data centers with virtualization techniques support when these data centers will be used solar or wind power as primary energy sources in some cases

CONCLUSION

Although virtualization technology is old few decades, with its latest improvements, now it is very impressive and functional technology. But even impressive there are still some resistance to virtualization and its benefits and still some data centers implemented their activities in traditional way.

Virtualization must be well planned and sometimes it is very hard and a long process, but it is one of the most payable technologies on IT market today. Benefits in economical way are huge, from chances for profit enlargement to good ROI achieved in very short terms.

But besides economical aspect of virtualization, this technology has the incredible green potential which is sometimes unfortunately forgotten. It leads us to efficient but also to one kind of environmental friendly computing. Virtualization environmental impacts are significant.

About this significance best says the example which is related to one of the most referent institutions in charge of environmental protection, U.S. Environmental Protection Agency (EPA). EPA started virtualization of its servers in 2009 in the National Computer Center (NCC) located in Durham, North Carolina, USA. By 2012, their data center was 32% virtualized. Today, about 85% of servers in NCC are virtual servers [12].

In figure 3 we represented importance of virtualization in both ways mentioned above (economical and environmental) on the example where we virtualized 100 servers.

*Calculations are based on the power consumption of a standard 2 CPU server

	Physical	Virtualized	Savings
Energy Savings:			
Annual Server & Cooling Energy Usage (kWh)	755,550	94,444	661,106
Cost Reduction:			
Physical Hardware[1]	$ 400,000.00	$ 60,000.00	$ 340,000.00
Annual Energy Cost[2]	$ 75,555.00	$ 9,444.00	$ 66,111.00
Environmental Impact:	Planting Trees	Cars off the highway [3]	Annual CO2 Emission(lbs/kg)[4]
These savings are equivalent to	1,569	89	1,046,531 lbs
			474,698 kg

[1] Assumes transition from 2CPU dual core to 2CPU quad core at $4000 per server and $6000 per server, respectively.
[2] Assumes $0.10/kWh, and operating power of 375 Watts per Physical Server and 469 Watts per Virtualized Host Server. Cooling power mulitple of 1.3x operating power.
[3] Assumes 12,000 miles per year and 20 mpg.
[4] Assumes 1.583 lbs CO2 emission per kWh.

Figure 3. Estimated savings and environmental impact by virtualization of 100 servers [6]

We live in age of information, so virtualization will impact all of us individually directly or indirectly. So as the environment. And that will be expressed in the future years when the Big data is dominant and when we can expect something that maybe will called Extremely big data because data are grown so fast and unpredictable. Investment in the implementation of the virtualization technology will be on of the crucial IT investment and one of the primary steps to sustainable development from the data point of view.

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DESIGN OF MICROSTRUCTURE OF CERAMICS BASED ON WASTE FLY ASH AND CLAY

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ABSTRACT

Ceramics microstructure was designed using waste flay ash (REK Bitola, Macedonia) and clay. The raw materials were characterized from chemical, mineralogical and thermal aspect. The ceramics was designed using the granulation less than 0.063 mm. The clay content varied from 10 to 90 wt.%. The consolidation of the compacts was realized at pressure of 45 MPa and sintering at different temperatures (900, 1000, 1500 and 1100 ^{o}C/1h, heating rate of 10^{o}C/min).

The designed microstructure of the composite with composition 60wt% clay and 40wt% fly ash sintered at 1100^{o}C/1h was found as optimal regarding to its properties: density- 2.089g/cm^2; water absorption- 7.02%, bending strength – 50.47 MPa and E-modulus - 25,35GPa. Technical coefficient of thermal expansion was $\alpha_{20\text{-}600}$=7.03x10^{-6}/^{o}C.

Key words: fly ash, clay, microstructure, sintering.

INTRODUCTION

Fly ash presents the by-product obtained during the production of electricity from the coal in thermal power plants. The raw materials in traditional ceramics are taken from nature i.e. from the deposits of the earth. Concerning the chemical and mineralogical composition there are similarity between the natural raw materials (clay) and fly ash. So, this waste can be successfully used as a raw material for production of traditional ceramics [1-3]. In recent years there is growth interest for utilization of waste fly ash in ceramics. For instance, Cicek and Tanriverdi [4] investigated the possibilities for using fly ash for production of light weight bricks based on 20% sand, 68% fly ash and 12% hydrated lime. Lingling et all. [5] used fly ash as replacement of clay in bricks production, so they proved that fired bricks with high volume ratio of fly ash has high compressive strength and low water absorption. Sokolar and Vodova [6] worked on the investigation of the influence of the addition of fly ash in the raw material mixture and the granulometry of fly ash on the properties of fired fly ash – clay body.

In the present paper, the aim was to design the microstructure of ceramics based on waste fly ash and clay and to optimize the content of clay relating to the properties of the fabricated ceramics.

MATERIALS AND METODS

Characterization of the fly ash and clay

Fly ash from thermal power plant REK Biota, Republic of Macedonia and clay near to the this region were used in this investigation. The particle size distribution for both raw materials was lower than 0.063 mm. The content of clay varied from 10-19wt.% Chemical composition of the fly ash was carried out by X-ray fluorescence (ARL 990XP) and classical silicate analysis was applied for clay. The phase composition of the fly ash and the clay was performed by using X-ray diffraction (Philips, model PV 105-1). The thermal properties of the fly ash and the clay were determined using a heating microscope (Leitz Wetzlar) in the temperature interval from room temperature (RT) to 1400^{0}C, in air atmosphere with a heating rate of 10 ^{0}C/min.

Consolidation of the fly ash and the clay

Ceramics was consolidated in laboratory conditions by pressing (Weber Pressen KIP 100) at P=45MPa using PVA as a binder. Sintering was performed in chamber furnace in air atmosphere at temperatures of 900, 1000, 1050 and 1100^{o}C, with holding time of 1h at maximum temperature and heating rate of 10^{o}C/min.

Characterization of the sintered samples

Bulk density of compacts was determined from the ratio between weight and volume of the compacts. Water absorption of the compacts was determined from difference in dry mass and surface dry mass after immersion in cold water. Water absorption values were determined from weight differences between the as-sintered and water-saturated sintered compacts after immersion in boiling water for 2 h.

Mechanical properties i.e. bending strength and E-modulus of fabricated compacts (6 pices, 50X5X5mm^3) were carried out using three point bending tester (Netzsch 401/3) with 30 mm span and 0.5mm/min crosshead speed.

Linear thermal expansion of the obtained ceramic compacts was determined using the dilatometer (Netzsch 402 E) in the air atmosphere and temperature interval RT-600^{o}C-RT, with heating rate of 2^{o}C/min.

The microstructure of the fractured surface of the compacts was analysed by scanning electron microscopy (Leica S440I).

RESULTS AND DISCUSSION

The chemical composition of the fly ash and clay is shown in the Table 1. It is evident from the Table 1 that in both systems there is a dominant presence of SiO_2, Al_2O_3 and Fe_2O_3, whereas in the fly ash there is a minor content of ecologically risky components like MnO and P_2O_5.

Table 1. Chemical composition of the fly ash and clay

Oxide	SiO_2	TiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	Na_2O	K_2O	MnO	P_2O_5	ZnO	PbO	SO_3	LOI	Σ
Fly ash	52.38	0.09	23.61	7.31	7.42	2.11	0.9	1.67	0.03	0.08	0.01	0.03	1.2	3.12	99.94
Clay	58.48	/	19.8	7.44	6.18	1.43	2.1	2.51	/	/	/	/	/	2.05	99.99

The XRD pattern of the fly ash showed the presence of amorphous phase and minerals such as: quartz, anorthite, hematite, albite and anhydritet. The clay was from illite type with the mineralogical composition: quartz, feldspar, aragonite, illite, chlorite and calcite.

The thermal characteristics of the both raw materials are given on the Table 2.

Table 2. Thermal characteristics of the fly ash and clay

Material	Significant shrinkage [^{0}C]	Softening temperature [^{0}C]	Melting temperature [^{0}C]
Fly ash	1050	1380	1440
Clay	1100	1280	1320

From the Table 2 it can be seen that the region of sintering for fly ash was in the temperature interval from1050 to 1380^{0}C, while for the clay it was in the temperature interval from 1100 to 1280^{0}C.

The dependence of density and water absorption with sintering temperature of the fly ash-clay compacts with different clay content from 10 to 90wt.% are presented in Figures 1 and 2.

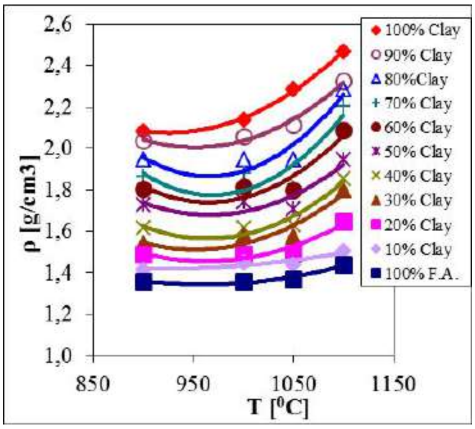

Figure 1. Density of the compacts sintered at different temperature

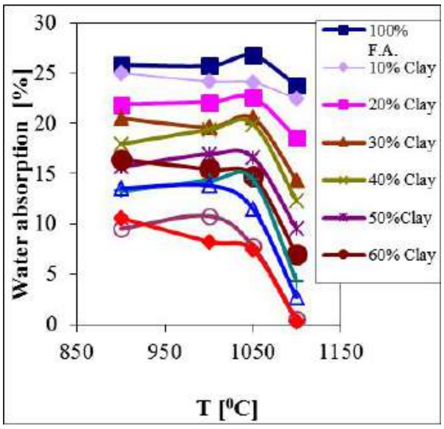

Figure 2. Water absorption of the compacts sintered at different temperatures

It is evident from the Figures 1 and 2 the slight increase of density/decrease of porosity up to 1050^{0}C. At the temperature of 1100^{0}C the density increase rapidly reaching the value of 2.5 g/cm^3 for the clay compacts and 1.4 g/cm^3 for the fly ash compacts. Generally, for the composites composed with different content of clay (from 10 to 90wt.%) it can be concluded that the clay influenced on the increase of density and decrease the water absorption.

The variation of the mechanical properties i.e. bending strength and E-modulus of the compacts with different clay content (from 10 to 90wt.%) with temperature are presented in Figures 3 and 4. It is evident that the clay influenced on the increase of the mechanical properties. The slight increase of the mechanical properties for the all compacts with different clay content (from 10 to 90wt.%) is evident up to the temperature of 1050^{0}C, but at temperature of 1100^{0}C the rapid increase, almost dabbled, of the mechanical properties is obvious. The bending strength and E-modulus of the clay compacts is 90 MPa and 34 GPa, respectively, and for the fly ash compacts the bending strength and E-modulus are 10 MPa and 4 GPa, respectively.

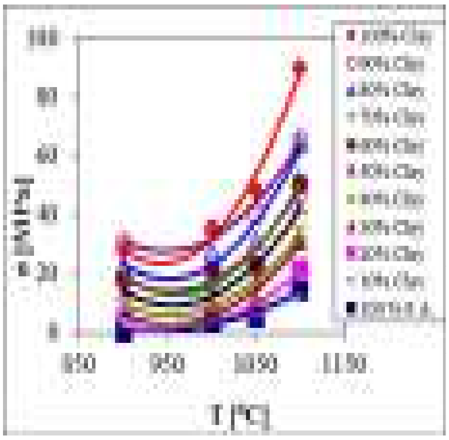

Figure 3. Bending strength of compacts sintered at different temperature

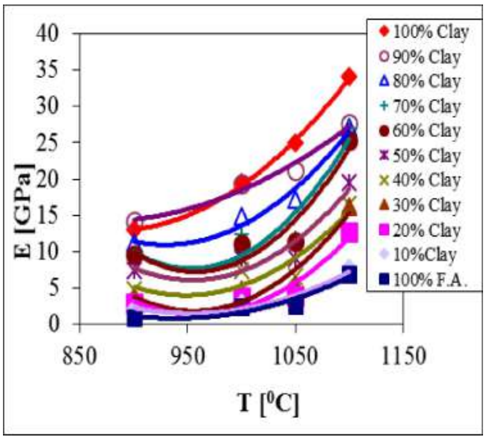

Figure 4. E-modulus of the compacts sintered at different temperature

The composite consisted of 60% clay and 40 % fly ash sintered at temperature of 1100^{0}C with heating rate of 10^0/min was chosen as optimal and it was the subject of further investigations.

The microstructure of the composite consisted of 60% clay and 40 % fly ash sintered at the temperature of 1100^{0}C is presented in Figures 5

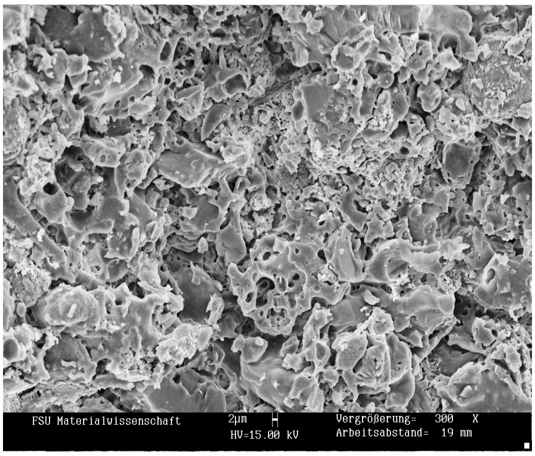

Figure 5. Microstructure of the composite consisted of 60% clay and 40 % fly ash sintered at temperature of 1100^0C with heating rate of 10^0/min

The thermal expansion characteristics of the composite consisted of 60% clay and 40 % fly ash sintered at the temperature of 1100^0C showed absence of hysteresis effect, proving that this material is in thermal equilibrium. The coefficient of thermal expansion for this composite was 7.03 x $10^{-6}/^oC$.

CONCLUSIONS

The designed microstructure of the compacts composed of 60wt.% clay and 40wt.% fly ash sintered at 1100^0C have the following properties: density: 2.089 g/cm3; water absorption: 7.02%, bending strength: 50.47 MPa, E-modulus: 25.35 GPa and coefficient of thermal expansion of 7.03 x $10^{-6}/^oC$ and it can be potentially used as building material where the waste fly ash (as NORM representative) is used.

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ANALYSIS OF THE IMPACT OF BLASTING ON CONSTRUCTION FACILITIES AND ENVIRONMENT IN THE PREPARATION OF THE TUNNEL PORTAL SARLAH NEAR PIROT (SOUTH SERBIA)

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ABSTRACT

This paper is related to the problems of the seismic effects on the environment and construction facilities near the working area. This effect is caused by the shockwaves generated by the blasting in territory of south Serbia, during the construction of the tunnel in one part of the highway Nis-Dimitrovgrad. Blasting is done in limestone. This paper will present an example of controlling and preventing damage in living area. Velocities determined with VIBRALOC measurer are analysed and compared with two scales for the assessment of shock wave intensity and soil oscillation velocity induced by blasting.

Key words: blasting, shock wave, measurement, environment, acceptable limit, standard.

INTRODUCTION

Adverse effects occurring while blasting, i.e. blasting seismic effects, shock waves, sound effects, dissipation of blasted rock mass, harmful gases etc. need to be studied and reduced to acceptable limits, especially as there are no regulations (for most of these effects) for this area of study in our country, thus different foreign standards are applied to each case. The reduction of seismic effects, namely their decrease to harmless limits can be successfully done through the reduction of the amaunt of explosives or the increase of the distance between a blast site and facilities.

Construction of the tunnel „Sarlah"-Pirot (east) is planned on the route of the highway Nis-Dimitrovgrad. During the preparation of the exit of the tunnel„ Sarlah " with drilling and blasting operations, it was necessary to develop a method of monitoring the seismic impact on surrounding buildings caused by mining. According to the design solution, tunnel „Sarlah " consists of two tubes, which are connected by a transversal line in the middle of the tunnel chainage.

Figure 1. The tunnel route,, Sarlah " with entrance and exit portal

The method „ cut and cover" was chosen for the construction of the exit section of the tunnel in regard with geotechnical and morphological conditions.

The work on the construction of the tunnel portal was carried out in several stages. In the first phase of work a wide excavation of the material of the third and fourth category was done for both tunnel tubes to the temporary entrance portal. The fissure zone that separates the two quasi homogeneous zones was taken as a limit of the underground excavation and the construction of the facility.

Excavations in the limestone complex(one of the quasi homogenous zones) will be performed by blasting and machine processing. The slopes of the complex will be excavated with the „ cut and cover" method.

Backfilling with the excavation material according to the elevations and slopes defined by project documentation will be done after the construction of both tunnel tubes.

CRITERIA FOR EVALUATION OF SHOCK WAVES CAUSED BY BLASTING

The intensity of seismic effects can be established by the measurement of one of basic dynamic parameters of the environment: oscillation velocity, (v), acceleration (a) or soil movement (x). The connection among these parameters can be established if one of them is determined instrumentally, which enables other parameters to be determined by calculation. One of the most frequent parameters used to evaluate seismic intensity is the oscillation velocity of induced soil (v). The maximum resultant oscillation velocity of soil (v_{max}) is obtained as the intensity of the vector of components in directions of X, Y and Z axes according to the formula:

$$v_{max} = \sqrt{v_v^2 + v_t^2 + v_l^2}\ , \qquad (1)$$

Where: v_v – tranverse component of soil oscillation(mm/s),
v_t - (mm/s), vertical component of soil oscillation(mm/s)
v_l - longitudinal component of soil oscillation (mm/s)

The criterion according to the IPERAS scale. One of the most common criteria that we use for the assessment of shock wave intensity induced by blasting has been established by the Institute of Physics of the Earth, Russian Academy of Sciences. The Russian scale is of a descriptive type related to the ocsillation velocity of soil particles and the degree of seismic intensity and is given in the form of 12 seismic degrees.

Criterion according to standard DIN-4150 – In the Federal Republic of Germany, maximal tolerable limits for the values of soil oscillation velocity are regulated in dependence on the significance and the state of facilities for the frequency span from 5 to 100 Hz. Tolerable limits for the values of the soil oscillation velocity according to DIN- 4150 are presented in Table 2.

RESULTS OF THE BLASTING AND MEASUREMENTS

Nine blastings were done at the site of the construction of the tunnel "Sarlah" . All blastings were done by the same method and the blasting number 1 will be shown here as a representative sample.

Results of the blasting and measurement No 1

Twenty eight vertical boreholes were made for this blasting with their depths between 1,6 and 3,0 m. Boreholes are arranged in two rows. The distance between boreholes was 1,4–1,6 m, while the distance between rows was 1.5 m. Borehole diameter was 45.0 mm. The explosive used for destruction of the rock mass was Balkanit, mark 28/140.

The following resources were used for this blasting :

- Total number of boreholes – inclined	N_k	= 28
- The depth of boreholes	L_{uk}	= 71,4 m
- The total amount of explosives	Q_{uk}	= 24,3 kg
- The maximum quantity of explosives per interval	Q_i	= 1,2 kg
- Nonel detonators, 25/500 ms	N_d	= 28 pieces.
- connectors of 25 ms	N_k	= 1 piece
- cap size	$L_č$	= 1,0 – 1,5 m
- electric detonator	N_{ed}	= 1 piece

Results of the measurement - Registration of seismic waves were carried out with 4 instrument. Measuring points were located in the following places:

- Measur. point MP-1	- House:	X = 7 628 555	Y = 4 780 703
- Measur. point MP-2	- House:	X = 7 628 529	Y = 4 780 723
- Measur. point MP-3	- House:	X = 7 628 420	Y = 4 780 742
- Measur. point MP-4	- House:	X = 7 628 405	Y = 4 780 756

Table 1 legend:

- Maximum quantity of explosive per one interval Q_i ,
- Overall quantity of explosive Q_{uk} ,

- Maximum oscilation velocity per component V_V; V_T; V_L ,
- The resulting maximum oscilation velocity$V_{max.}$,
- The real resulting maximum oscilation velocity$V_{st.}$ and
- Frequency per components, Hz

Table 1. Summary of the results

Measur. point, MP	Max.quan. expl. per one interval, *kg*	Overal quant. of exp. in kg.	Maximum oscilation velocity per comp. mm/s			Res. max. oscilation velo. mm/s	Real res. max. oscilation velo. mm/s	Frequency per components, Hz		
			V_V	V_T	V_L			*V*	*T*	*L*
MP-1	1,20	24,3	0,633	1,590	1,166	***2,071***	***1,690***	23,2	20,5	15,9
MP-2	1,20	24,3	0,545	1,508	1,012	***1,896***	***1,540***	16,0	21,5	33,7
MP-3	1,20	24,3	0,463	0,816	1,437	***1.716***	***1,590***	17,8	16,1	12,4
MP-4	1,20	24,3	0,529	0,880	1,311	***1,665***	***1,400***	18,6	14,2	11,0

Impact on the environment is determined according to the measured results. Vibration evaluation procedure is based on the unprocessed signal expressed by the intensity of vibration $KB_{F.}$ Maximum processed vibration intensity was determined during the assessment. Intensity of vibration during the evaluation KB_{FT} is also determined if necessary and can later be compared with the referential values.

Assessment of the results obtained in accordance with DIN 4150 is performed on the basis of two values KB:

- KB_{Fmax}-maximum weighted vibration intensity (maximum value of KB)
- KB_{FTr} - maximum effective value in the measurement period.

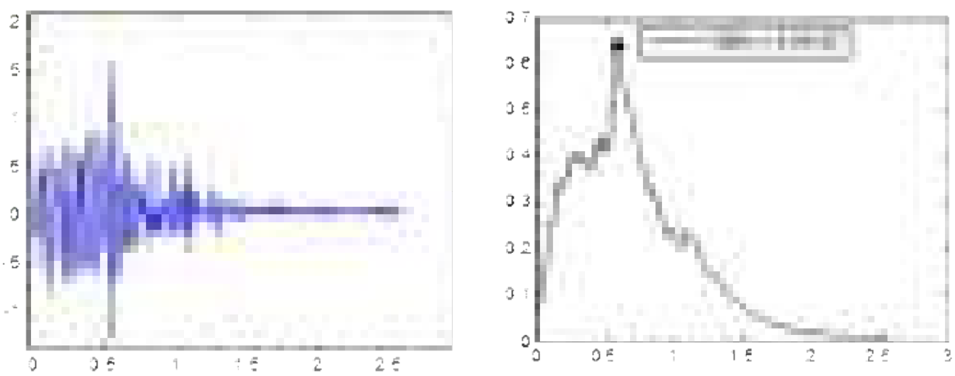

Figure 1.. The value of the transverse component of wave (V_T) and KB_{fm}. Blasting No I, measurement point MM-1.

Table 2. Mining parameters and measurement results conducted on the preparation of the tunnel „Sarlah"

Blasting No.	Measuring point M.P.	Max. quant. of exp. in kg.	Overallmax quantity per one inter. kg.	Maximum oscilation velocity per comp. mm/s			Res. max. oscilation velo. mm/s	KB fm	Frequency per components, Hz			Evaluation of measurement results		
				V_V	V_T	V_L			V	T	L	IPERAS (Russia)	DIN (German)	DIN (KB_{fm})
1	**2**	**3**	**4**	**5**	**6**	**7**	**8**	**9**	**10**	**11**	**12**	**13**	**14**	**15**
I	MM-1	1,20	24,3	0,633	1,590	1,166	**2,071**	**0,641**	23,2	20,5	15,9	**A**	**C**	**E**
	MM-2	1,20	24,3	0,545	1,508	1,012	**1,896**	**0,637**	16,0	21,5	33,7	**A**	**C**	**E**
	MM-3	1,20	24,3	0,463	0,816	1,437	**1.716**	**0,608**	17,8	16,1	12,4	**A**	**C**	**E**
	MM-4	1,20	24,3	0,529	0,880	1,311	**1,665**	**0,624**	18,6	14,2	11,0	**A**	**C**	**E**
II	MM-1	26,0	26,0	4,364	9,999	6,952	**12,936**	**3,482**	9,99	14,5	12,2	**A**	**D**	**F**
	MM-2	26,0	26,0	4,249	8,271	6,141	**11,143**	**3,287**	14,4	11,6	11,9	**A**	**D**	**F**
	MM-3	26,0	26,0	5,815	4,316	5,706	**8,145**	**2,253**	13,6	16,0	8,59	**A**	**C**	**E**
	MM-4	26,0	26,0	2,226	3,022	4,063	**5,531**	**1,635**	12,3	10,8	9,75	**A**	**C**	**E**
III	MM-1	42,0	21,0	3,595	8,740	6,683	**11,575**	**3,181**	13,7	15,6	17,9	**A**	**D**	**F**
	MM-2	42,0	21,0	4,726	9,823	4,882	**11,944**	**3,668**	7,76	26,0	10,2	**A**	**D**	**F**
	MM-3	42,0	21,0	4,912	4,449	5,951	**8,907**	**2,567**	9,41	11,2	8,75	**A**	**C**	**E**
	MM-4	42,0	21,0	3,438	2,932	4,522	**6,392**	**2,050**	10,3	13,0	7,55	**A**	**C**	**E**
IV	MM-1	79,92	8,80	3,573	3,399	5,023	**7,039**	**2,344**	21,3	19,0	19,4	**A**	**C**	**E**
	MM-2	79,92	8,80	1,941	3,133	2,299	**4,348**	**1,308**	17,6	15,3	20,0	**A**	**C**	**E**
	MM-3	79,92	8,80	1,840	1,685	2,947	**3,861**	**1,297**	10,3	16,3	13,5	**A**	**C**	**E**
	MM-4	79,92	8,80	1,806	1,916	1,939	**3,270**	**0,922**	13,1	14,1	9,27	**A**	**C**	**E**
V	MM-1	14,54	5,04	0,317	0,861	1,032	**1,381**	**0,402**	9,9	18,0	19,8	**A**	**C**	**E**
	MM-2	14,54	5,04	0,551	1,037	1,503	**1,907**	**0,468**	15,8	21,1	25,6	**A**	**C**	**E**
	MM-3	14,54	5,04	1,654	1,542	2,340	**3,209**	**0,950**	13,4	13,0	16,1	**A**	**C**	**E**
	MM-4	14,54	5,04	1,658	1,175	1,192	**2,293**	**0,636**	17,4	19,1	9,97	**A**	**C**	**E**
VI	MM-1	242,32	47,32	1,806	3,039	3,834	**5,215**	**1,778**	18,2	16,9	15,3	**A**	**C**	**E**
	MM-2	242,32	47,32	2,458	7,399	4,181	**8,847**	**2,775**	31,2	25,6	28,4	**A**	**C**	**E**
	MM-3	242,32	47,32	3,374	3,794	6,167	**7,988**	**2,114**	14,6	11,6	12,3	**A**	**C**	**E**
	MM-4	242,32	47,32	2,579	2,909	6,684	**7,732**	**2,634**	7,08	9,94	9,69	**A**	**C**	**E**
VII	MM-1	232,5	17,5	1,476	1,498	1,694	**2,700**	**0,704**	23,7	13,8	15,9	**A**	**C**	**E**
	MM-2	232,5	17,5	2,104	4,342	2,721	**5,539**	**1,637**	85,2	25,3	32,6	**A**	**C**	**E**
	MM-3	232,5	17,5	1,588	2,713	4,421	**5,425**	**1,724**	13,6	11,2	19,5	**A**	**C**	**E**
	MM-4	232,5	17,5	-	-	-	**-**	**-**	-	-	-	**A**	**C**	**E**
VIII	MM-1	190,5	18,0	0,925	1,299	1,649	**2,294**	**0,694**	11,1	13,0	16,6	**A**	**C**	**E**
	MM-2	190,5	18,0	1,284	2,592	2,234	**3,655**	**0,947**	11,2	17,4	8,56	**A**	**C**	**E**
	MM-3	190,5	18,0	2,558	3,530	6,533	**7,854**	**2,609**	16,7	7,57	12,0	**A**	**C**	**E**
	MM-4	190,5	18,0	2,094	2,954	5,199	**6,335**	**2,351**	17,0	11,2	8,17	**A**	**C**	**E**
IX	MM-2	21,0	21,0	0,576	1,440	0,885	**1,785**	**0,534**	19,9	17,6	16,1	**A**	**C**	**E**
	MM-3	21,0	21,0	1,544	3,552	3,050	**4,930**	**1,522**	13,8	16,0	14,5	**A**	**C**	**E**
	MM-4	21,0	21,0	2,601	2,819	2,927	**4,825**	**0,982**	12,8	16,6	20,9	**A**	**C**	**E**

CONCLUSION

Blasting and measuring of the intensity of the oscillation velocity on the development of slopes of the tunnel portal "Sarlah"were performed under the following conditions:

- nine blasting were monitored for the purposes of this paper,
- the amount of explosives used in individual blastings varied between 5,04 and 47,32kg,
- all blastings were performed with one type of explosives : Balkanit, label 28/175;28/140;60/1000 and ANFO in packages of 25 kg.
- activation of boreholes was conducted with Nonel detonators

Based on the obtained results, which were processed in the course of this research, it is possible to state the following:

1. Nine blastings were performed, 35 results of osillation velocities were instrumentally recorded on four measurement points.
2. Registered oscillation velocity values at the construction facility (measurement points MP-1; MP-2; MP-3; MP-4) are in the domain of allowed values according to the Russian IPERAS scale, and have no impact in terms of damage to construction facilities
3. Registered oscillation velocity values of blastings number 2 and 3 at the measurement point MP-1 i MP-2 are slightly above the allowed values, according to the German DIN scale.
4. Registered oscillation velocity values of blasting number 7 (MP-4) are not registered, oscillation velocity values are below the sensitivity of the instruments.

In order to preserve the environment and buildings in the immediate vicinity of the working area, or where blasting is done, it is necessary to make studies which will serve as the control of parameters of mining. Method of determining the degree of harmfulness of the shock waves caused by blasting on the environment and buildings may be used for other purposes. A possible application could be determining the impact of traffic in urban areas and preventing further disruption of the environment.

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POTENTIAL TOXIC EFFECTS OF ZINC IN METAL INDUSTRY

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ABSTRACT

Technological procedures in metal industry which are major sources of zinc exposure are: casting, welding, smelting, rolling and electrolysis of zinc, its alloys and compounds, which enables simultaneous exposure and other metals (cadmium, arsenic, manganese, lead, etc.), which all brought on the need to study its potential toxic effects. Given that chronic exposure of zinc compounds leads to irritant effects on mucous membranes of the eyes and upper respiratory tract, and skin, with possible sensitization in the form of chronic eczema, we performed the statistical analysis of the association of age and length of service and zinc concentrations.

We used the data from the annual reports of social services and medical statistics, medical records of the professional primary and specific health care and expert findings of the Public Health Institute in Nis. The concentration of zinc in biological samples was determined by spectrophotometric methods. The statistical analysis of results was performed using software packages Excel, Matlab and SPSS19.0. Research has shown that chronic exposure to zinc results in an increase of its concentration in biological material, but there is no negative impact on the health of the exposed population, as determined on the basis of the identified symptoms.

Key words: zinc, chronic exposure, potential toxicity, metal industry.

INTRODUCTION

The essential metals are three levels of biological activity: low concentrations (traces), which are necessary for the growth and development, homeostatic level, which is located in depots and toxic levels. Zinc is an essential oligoelement, which can be found in significant amounts in the human body, approximately 0,02-0,03 g/kg of body weight of it. Of the overall amount of zinc in the human body, 20 % of it can be found in the skin, and it can be found in significant amounts in the pancreas, teeth, bones, blood, liver, kidneys, and nervous system [1], [2].

The increased zinc content can be connected to the occurrence and development of neurological disease. The significant increase of zinc in the human body can lead to a disturbance in neurological functions and the occurrence of multiple sclerosis among workers involved in production processes where zinc is the basic ingredient. Zinc contents ranging from 6,54 to 16,35 mg/dm^3 lead to minor damage, while amounts exceeding 16,35 mg/dm^3 are neurotoxic [3].

In the workplace, it occurs in the form of Zn^{2+} ions, where it usually enters the body through inhalation [4].

Most of the available information on the toxicity of inhaled zinc focuses on metal fume fever, a collection of symptoms observed in individuals exposed to freshly formed zinc oxide fumes or zinc chloride from smoke bombs. The earliest symptom of metal fume fever is a metallic taste in the mouth accompanied by dryness and irritation of the throat. Flulike symptoms, chills, fever, profuse sweating, headache, and weakness follow [5], [6]. The symptoms usually occur within several hours after exposure to zinc oxide fumes and persist for 24 to 48 hours. An increase in tolerance develops with repeated exposure; however, this tolerance is lost after a brief nonexposure period. Studies of the health effects of subchronic or chronic exposure to inhaled zinc compounds were not located in the available literature.

Epidemiologic studies of workers in metal industy have not found an increased incidence of cancer associated with occupational zinc inhalation [7].

On the other hand, various studies have indicated that zinc administration will generally block cadmium carcinogenesis [8]. Also, Toxic levels of cadmium may inhibit zinc absorption [9].

Zinc is essential metal that can be toxic at high doses of exposure [10].

Zinc toxicity is uncommon and occurs only at very high exposure levels. The association between zinc and cancer incidence rates is unclear [11].

Determination of the concentration of zinc in biological samples (whole blood, plasma, serum, urine) serves as a biological monitoring in assessing risk being exposed zinc. The concentrations of zinc in the urine unexposed individuals is in the range of 4,62 to 9,23 μmol/24h (300 to 600 μg/24h). The concentrations in the serum or plasma are approximately 15,38 μmol/dm^3 (0,1 mg/100 ml) [12]. In exposed workers concentrations were significantly higher, but there isn't correlation between the concentration that indicate increased exposure and those that occur during intoxication.

The given researches indicate the importance of the potential toxic effects of zinc on the exposed population and suggest establishing statistical correlations of zinc concentrations, age and length of service.

MATERIALS AND METHODS

Biomonitoring is based on the determination of the concentration of zinc in biological samples (serum and urine) in exposed and control groups of patients. The applied analytical method is of the retrospective epidemiological cohort study type, covering the period from 2001 until 2010. The exposed cohort consisted of the respondents employed in "NISSAL" and respondents were male, average age 45.4 years, who worked at least one year in the metalworking processes during the observed period. The control cohort consisted of the respondents of reference technology systems, male, average age 44.1 years, which were employed in the administration during the observed period.

We used data from the annual reports of social services and medical statistics, medical records of the professional primary and specific health care and expert findings of the Public Health Institute in Nis. Analyses of biological material in exposed and control groups were analyzed in the Public Health Institute in Nis and the Military Medical Academy in Belgrade. The analysis of the concentration of cadmium in the biological material of the exposed and control groups of patients was performed using the method of flame atomic absorption spectrophotometry.

The results of zinc concentrations in biological samples were analyzed using standard statistical methods: descriptive statistics technique (mean and standard deviation, frequency, percentage) to determine the severity of basic research variables, correlation techniques to determine the direction and degree of association between the variables, the Student's t statistic for major independent samples and the chi-square test for differences in frequency.

Statistical analysis and the presentation of the results was performed by software packages Excel, Matlab, SPSS19.0 (Statistical Package for the Social Sciences).

RESULTS

In the statistical analysis of biological material, we started from the analysis of the expression of zinc in exposed and control groups, as shown in Table 1.

Table 1 *The level of zinc in biological material in exposed and control groups*

The measured parameter	Group	Min	Max	AS	SD	Mod	DNV
Zinc (serum), μmol/dm^3	Exposed	2,11	38,60	18,43	6,28	19,32	4,59-30,60
	Control	9,56	18,01	14,31	1,84	12,46	
Zinc (urine), μmol/dm^3	Exposed	1,30	18,90	9,02	2,51	9,32	14,68
	Control	1,06	14,59	4,74	2,74	3,42	

Min - minimum value; **Max** - maximum value; **AS** - mean; **SD** - standard deviation; **Mode** - the most frequent value; **DNV** - allowed normal value

The average concentration of zinc in serum is 18,43 μmol/dm^3, which is a medium concentration, and is slightly lower than the most frequent value of 19,32 μmol/dm^3, while the maximum value of 38,60 μmol/dm^3 was present in 11 patients, above the concentration limit (4,59 to 30,60 μmol/dm^3). The mean concentration of zinc in urine is 9,02 μmol/dm^3, which is slightly lower than the most frequent value of 9,32 μmol/dm^3, while the value of the maximum concentration of 18,90 μmol/dm^3, present in 7 patients, was above the maximum allowed concentration (14,68 μmol/dm^3). Pearson's correlation coefficient estimated the correlation between the age structure and length of service of exposed and control groups, and zinc concentrations in biological samples. Based on the results, it was determined that there is a statistically significant correlation between the concentration of zinc in biological material and the age and length of service. These correlations are positive and indicate that the concentration of zinc in biological material increases with the increasing age and length of service, as a result of many years of exposure. The value of the correlation coefficient is above 0.60, which indicates the high correlation between age and zinc concentrations in biological samples, with statistical significance at the 0.01 level.

The correlation between the age structure and the length of service in the exposed group and zinc concentrations in biological samples is shown in Table 2.

Table 2. The correlation between the age and length of service of the exposed group and zinc concentrations

Zinc (serum), µmol/dm^3	Age	r	0,752**
		p	**0,000**
		N	434
	Length of service	r	0,843**
		p	**0,000**
		N	434
Zinc (urine), µmol/dm^3	Age	r	0,537**
		p	**0,000**
		N	410
	Length of service	r	0,593**
		p	**0,000**
		N	410

r - correlation coefficient, **p** - statistical significance, **N** - sample size.
*** Statistical significance at the 0.01 level*

The dependence of the concentration of zinc in biological materials on the age in the factory Nisal was performed in MATLAB and is shown in Figure 1.

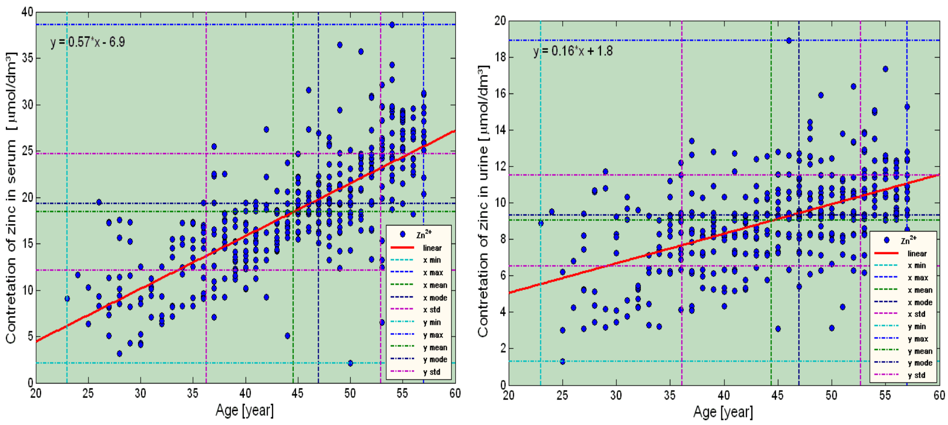

Figure 1. Dependence of the concentration of zinc in serum and urine of age

Linear dependence of the concentration of zinc in serum and urine on the age in the exposed group shown in Figure 1 are of the form: Y=0,57·X-6,9 and Y=0,16·X+1,8, which means that with the increase in the age limit for one year, concentrations increase, in average by 0,57 and 0,16 mol/dm^3, respectively.

The dependence of the concentration of zinc in biological material on the years of exposed work in the factory Nisal was performed in MATLAB and is shown in Figure 2.

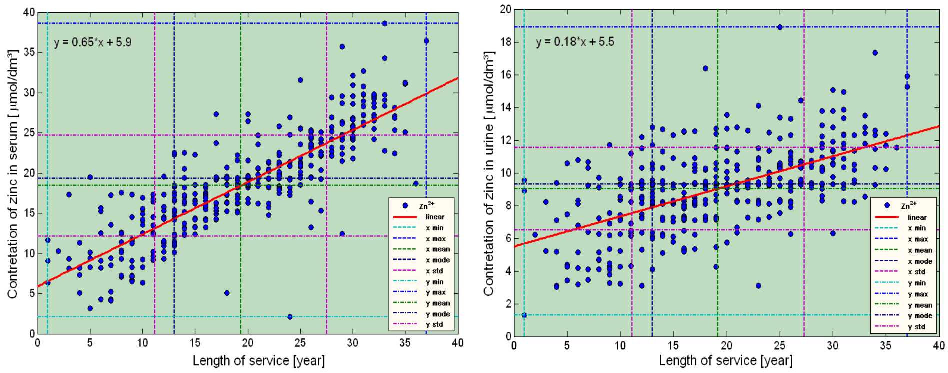

Figure 2. Dependence of the concentration of zinc in serum and urine of length of service

Approximate linear dependence of the concentration of zinc in serum and urine on the exposed length of service in exposed groups of patients is shown in Figure 2 in the linear form: Y=0,56·X+5,9 and Y=0,18·X+5,5 it was found that with the increase in the exposed length of service for one year, concentrations increase in an average of 0,56 and 0,18 µmol/dm^3, respectively.

DISCUSSION

The average concentration of zinc in serum is 18,43 µmol/dm^3, which is a medium pronounced concentration, and is slightly lower than the most frequent value of 19,32 µmol/dm^3, while the maximum value of 38,60 µmol/dm^3 is above the concentration limit (4,59 to 30,60 µmol/dm^3).

The mean concentration of zinc in urine is 9,02 µmol/dm^3, which is slightly lower than the most frequent value of 9,32 µmol/dm^3, while the value of the maximum concentration of 18,90 µmol/dm^3 is above the maximum allowed concentration (14,68 µmol/dm^3).

With regard to industrial exposure, metal fume fever resulting from inhalation of freshly formed fumes of zinc presents the most significant effect, but data on the effects of inhaled zinc are primarily limited to short-term studies examining metal fume fever in occupationally-exposed humans.

Based on the identified symptoms in this research, zinc intoxication was not determined, which is in accordance with the available data of other authors. Also, based on the given and the existing data of many authors, the determined concentrations of zinc in serum and urine, although increased, do not cause harmful effects on the health of occupationally-exposed people. Toxic effects of zinc exposure appear rarely and are difficult to identify because they do not only depend on the quantity but also on the interaction with other microelements such as copper, iron and calcium, and toxic metals present in metal processes.

For examples, numerous studies have demonstrated that zinc can decrease the carcinogenicity and toxicity of cadmium [13].

The level of zinc in serum and urine of exposed groups during the study period was positively correlated with the age ($r=0,752$, $p<0,01$ and $r=0,843$, $p<0,01$ respectively). The correlation is high and positive, which indicates the significance of the connection.

The high correlation between the concentration of zinc in serum and urine and the exposed length of service in exposed subjects during the time of study was also determined, ($r=0,537$, $p<0,01$ and $r=0,593$, $p<0,01$, respectively).

CONCLUSION

A retrospective cohort epidemiological study showed that the systematic effects of zinc exposure result in an increase of its concentration in biological material, but zinc intoxication has not been established within this research. The level of zinc in serum and urine of the exposed group during the study period was positively correlated with the age, and the exposed length of service. These data confirm the association between the occupational exposure to zinc as well as the age and length of exposed service.

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METAL POWDER PARTICLES AS HEALTH, ENVIRONMENTAL, AND SAFETY HAZARD

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ABSTRACT

Despite of powder metallurgy advantage, during the all stages in making powder metallurgy products such as powders' production, handling with powders, green compacts, and part-finished products, metal powder dust is generated. This paper describes the metal powder particles as potential health, environmental, and safety hazards and some prevention and protection measures in powder metallurgy industry from these hazards.

Key words: powder metallurgy, metal powder, health, environment, safety, explosion.

Powder metallurgy and its advantages

Powder metallurgy (PM) is very old processing technology, older than ingot metallurgy which includes melting and casting. Ancient people knew for solid state reduction of ores and forming them in to require shapes and sizes because, the energy was not available for melting in that time. PM technology is in vogue even today in spite of human's ability to generate very high temperatures [1,2].

There are five main stages in making PM products:

- production of metal and alloy powders,
- mixing of powders with additives and lubricants,
- compacting the mixtures in a suitable die into preforms - green compacts,
- heating/sintering of green compacts in a controlled atmosphere to the required densities and,
- post-sintering operations to final products.

PM is one of the most promising methods for production the materials which are otherwise not possible to be fabricated by any other conventional processing methods [3]. PM processing offers lot of advantages over conventional processing methods [4]. Some of advantages may be classified as follows:

- Products can be produced from refractory metals (niobium, molybdenum, tantalum, tungsten, and rhenium) with high melting point without difficulty and with less cost.
- PM can produce alloys and composites from a great variety of compositions with desired mechanical and physical properties.
- PM produces near net shape components. Dimensional tolerances of products are improved so further machining is not needed. Scrap is almost eliminated or reduced.
- Use of automated equipment in PM processing technology enables the high production rates even for complex products with low unit cost.
- Infiltration and impregnation of other materials is possible on PM products for obtaining some special characteristics for specific applications.
- Products with controlled porosity can be produced.
- PM offers chances for production materials which cannot be obtained by classical processing methods [5,6].

Despite of PM's advantage, during the all stages in making PM products such as metal powder production, handling with powders (fig. 1), green compacts, and part-finished products, metal powder dust is generated. Metal powder dust represents a serious health, environmental, and safety hazard [7]. The purpose of this paper is to inform about metal powder particles hazards and to get some effort in preventing health, environmental, and safety hazards from metal powders.

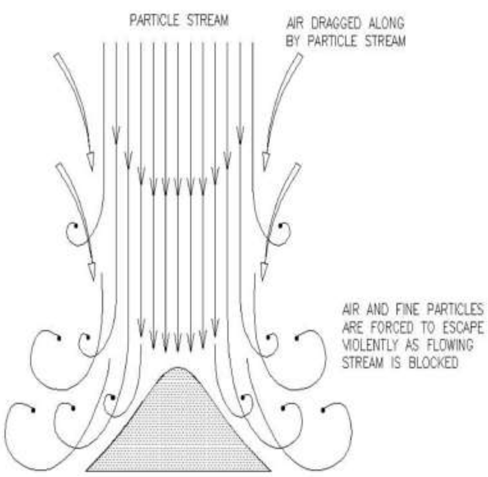

Figure 1. Metal powder dust generation during powder handling [7]

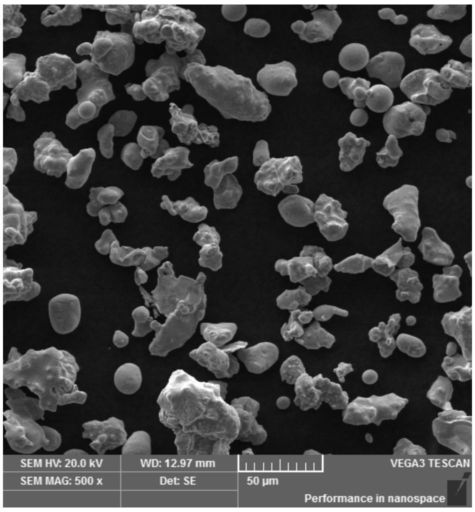

Figure 2. SEM microphotograph of atomized copper powder

METAL POWDERS AS HEALTH AND ENVIRONMENTAL HAZARD

The main sources of metal powder dust in PM industry are melting furnaces, atomization units, powder drying, classification, loading and unloading units, dosing and packing. Table 1 gives the example of a dust concentration and particle size distribution in aspiration exhausts during the production of copper atomized powder [8]. SEM microphotograph of copper atomized powder is given in fig. 2.

A danger level of metal powder dusts for human health depends on chemical composition and their oxidation level, particle size, concentration, action duration, penetration routes into organs, presence of impurities. The metal powder dust concentration at workplace atmospheres has to be maintained below threshold limit value - TLV (maximum average airborne concentration of a hazardous material to which healthy adult workers can be exposed during an 8-hour workday and 40-hour workweek-over a working lifetime-without experiencing significant adverse health effects). Table 2 gives the TLV values of some metal powders [8].

Table 1. Dust concentration and particle size distribution in aspiration exhausts during the production of copper atomized powder [8]

Technological operation	Dust concentration in aspiration exhausts (g/m3)	Weight powder distribution by particle size (µm) fraction (%)						
		<4	4-6.3	6.3-10	10-16	16-25	25-40	>40
Copper melt preparation in induction furnace	0.007	All particles are finer than 2.5 µm						
Water atomization of copper melt	0.02	All particles are finer than 10 µm						
Drying copper particles in vibrodryer	0.1	38	22	26	10	4	-	-
Sieving of powders	0.05-1.2	36.5	8	12.5	15	18.3	4.8	4.9
Blending in mixers								
- Double-cone mixers	0.36	24.1	22.6	20.9	1.6	0.8	24	16
- Impeller mixers	3.2	16	24	0.8	1.6	2.9	22.6	14.1
Unloading from conveyor into bin or technological apparatus	1	14.8	6.8	-	9	31.8	16.8	20
Loading-unloading of powder from conveyor to conveyor	2.7	13.9	5.3	3.2	8.9	31.9	16.1	20.7
Elevators (changing place)	2.96	6.5	39.3	32.1	11.6	6.6	4	-

Table 2. TLV values of some metal powders [8]

Substance	TLV (mg/m^3)
Aluminum alloys	2
Antimony	0.5
Barium	6
Beryllium and its compounds	0.001
Bismuth	0.5
Cadmium	0.05
Cobalt	0.5
Copper	1
Lead and its inorganic compounds	0.01
Molybdenum	3
Nickel	0.05
Titanium and its oxides	10
Tungsten, tungsten carbide	6

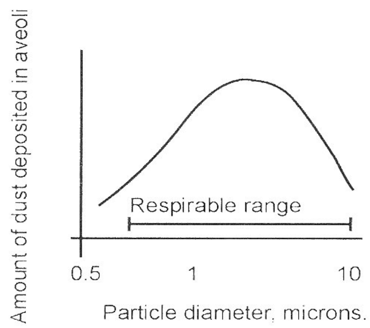

Figure 3. The respirable range [9]

Higher concentration of metal powder dust than TLV value can be absorbed into the body and give rise to chemical/biochemical reaction which can be very dangerous. The most significant metal powder hazards are due to contact with skin (dermatological diseases which are possible to prevent with the creams using and protective clothing), eyes (cause soreness but not usually permanent damage unless powder dissolves and chemically attack the eye), and lungs and respiratory system. Metal powder particles can enter in the respiratory system as this can cause both acute and chronic health effect. Not all metallic particles will make it into the mass transfer region of the lungs/alveoli, only the particles in the respirable range which is given in fig 3. Particles above this range can be removed by detent on nasal hairs, back of the throat and spliting in the respiratory tract. Particles below this range may be exhaled after entering and they leave the lungs [9]. Particles in this range penetrate into the human body through the respiratory system, causing a local effect on the lungs and other parts of the system and then passing into the blood stream and causing systemic effects. Very soluble substances are easily absorbed from all parts of the respiratory tract. Insoluble particles are deposed in the respiratory system.

Metal particles cause various biological effects [10]:

1. Pneumoconioses: The pneumoconioses are lung diseases that result from the inhalation of certain types of particles (silica, asbestos, coal mine dust, beryllium, kaolin, barium, tin, iron oxide, talc, and graphite). This particles lead to loss of elasticity in the lung and impair gas diffusion.
2. Systemic poisoning: The inhaled particles can penetrate into the circulation and internal organs of the body after dissolution. Lead, cadmium, beryllium, nickel, chromium and manganese are well known toxic metals [11, 12].
3. Cancer: Nickel, arsenic, and radioactive particles can cause a lung cancer.
4. Irritation: Irritant metal powder particles (Cd, Be, V, and Zn) may lead to bronchitis, pneumonitis, and pulmonary edema.
5. Allergic reactions: Metal dusts (Ni, Cr) may produce inhalant allergy, asthma, hay fever, or urticaria.
6. Metal fume fever: This condition occurs after exposing to freshly generated fumes of zinc oxide or magnesium oxide.
7. Infection: Particles can contain some fungi, viral, or bacterial pathogens which can cause infectious diseases.

METAL POWDERS AS SAFETY HAZARD

The metal powders have very large surface to volume ratio which means that they are more reactive than in the solid form. If handling with these powders is inappropriately, this can lead to potentially fires and explosions [13]. Metals in powder condition which have the affinity for the oxygen have the further potential to ignite or explode. Powders in layer or dust deposits are not explosive, but some ignition source can ignite and burn them. The primary explosion usually breaks up the deposit leading to dust cloud formation (fig. 4). The flame now can expand throughout the cloud and can generate large-scale explosion [8].

The fires and explosions due to metal powders are unfortunately a regular occurrence in PM industry over the world, with many fatalities and injuries reported each year. Particles of some metal such as iron, aluminum (fig. 5), and titanium can form suspensions in the air that may lead to an explosion. The some examples of industrial explosions due to metal powders and dust are: in 2003, a series of explosions were occurred at the Hayes Lemmerz manufacturing plant in Huntington, Indiana by ignition of aluminum dust; in A.L. Solutions titanium plant in West Virginia which processing titanium powder, an explosion occurred in 2010; in 2011, explosions occurred at the Hoeganaes Corporation in Gallatin, which produce iron powder; in 2013, the explosion happened at ATI Rowley Operations due to titanium dust [7,14]. These few examples demonstrate the dangers of explosions due to metal dusts but in the world, there are every year a large number of explosions.

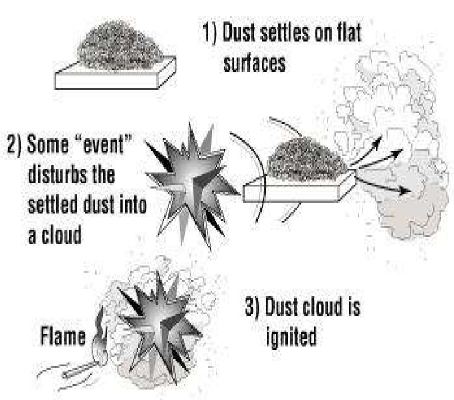

Figure 4. Illustration of primary dust explosion [14]

Figure 5. SEM microphotograph of atomized aluminum powder

PREVENTING HEALTH, ENVIRONMENTAL, AND SAFETY HAZARDS FROM METAL POWDERS

As can be seen from the above, exposure to metal powders can have a bed influence on the employees' health when exposure is over a long time. The workplace atmosphere parameters must be in accordance with the world standards. The recommendations to control exposure to hazards include: totally enclosed process; providing good ventilation; minimizing the powder transfers; reducing the number of exposed employees, nonessential access of employees and the period of exposure; excluding powder contacts with substances which lead to its oxidation, combustion or explosion; frequent cleaning metal powder dust from walls, surfaces, etc; providing the safe storage and disposal of hazardous substances [8].

The explosion hazard from metal powders can be minimized or eliminated by good cleaning, preventing the dissemination of metal powder dust, eliminating igniting sources, using inert atmospheres, and venting. Reduction of oxygen concentration is significant for dust explosion prevention. Because of that the oxygen is frequently replaced by nitrogen, carbon dioxide, and flue gas. Inerting also can be done by adding inert powders such as $CaCO_3$, $CaSO_4$ (so called diluents) which reduce the explosibility of the metal powder dust [10].

CONCLUSIONS

Powder metallurgy offers the some advantages and benefits compared with alternative technologies. But working with different metal powder particles carries with it some potential health and safety hazards for employees in PM industry, as well as some environmental hazards. Some examples of improper metal powder handling which led to the incidents with the loss of human's lives are presented in the paper. To reduce metal powder hazards, it is necessary to minimize the dust generation whenever is possible by enclosing and isolating of all operations and providing local exhaust ventilation. Using respirators or protective equipment is necessary to reduce potential health hazard of employees. The purpose of this paper is to provide primary information on understanding and preventing metal powder particles hazards.

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INFLUENCE OF POTASSIUM SORBATE ON ELECTROCHEMICAL BEHAVIOR OF COPPER IN SULFURIC ACID MEDIUM

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ABSTRACT

Inhibition of copper corrosion by 2,4-hexadienoic acid potassium salt (potassium sorbate) as environmentally friendly inhibitor in acidic sulfate medium was investigated. Electrochemical methods: open circuit potential and potentiodynamic measurements were used in the investigation. Obtained results show that 2,4-hexadienoic acid potassium salt has good inhibitory properties in an acidic solutin. The maximal inhibition efficiency, in the examined conditions, was 92.3%. Adsorption of inhibitor molecules obeys Langmuir adsorption isotherm.

Key words: potassium sorbate, copper, sulfuric acid, corrosion.

INTRODUCTION

The use of copper in different industries is being increasingly due to its excellent properties such as thermal and electrical condustivity. However, copper dissolution in aggressive medium is the major problem in its applications [1]. Hydrochloric and sulphuric acids are widely used to remove unwanted scale such as rust. In order to reduce the copper corrosion process, differente corrosion inhibitors are used [2]. This is one of the most practical methods to protect metals [3], due to the predominance in their chemical structures and properties, such as containing polar groups, conjugated double bonds or various hetero-atoms (S, N, O) [4-6]. Inhibitors act by adsorption of ions or molecules onto metal surface and allow the formation of chelate on the metal surface via transfer of electrons from the organic compound to the metal [7]. However, the most of investigated compounds are environmentally toxic. Beside of that, many authors examined inhibition effect of environmentally friendly inhibitors such as 2,4-hexadienoic acid potassium salt [8-11].

MATERIALS AND METHODS

A three electrode cell system containing copper working electrode whose surface was 0.49 cm^2, saturated calomel electrode (SCE) as a reference and platinum electrode as auxiliary were used. The experiments were conducted in 0.01M H_2SO_4 without and with addition of various concentrations of potassium sorbate (2.5g/l, 5g/l, 10g/l and 20 g/l). The electrochemical methods were applied in the investigation: open circuit potential measurements and potentiodynamic polarization measurements. Linear voltammograms were recorded from the open circuit potential to 0.1V (SCE) in the anode direction and -0.25V (SCE) in the cathode direction, at a scan rate of 1 mV/s. Cyclic voltammograms were recorded from -1.0 V up to 1.0 V (SCE), at a scan rate of 10 mV/s.

RESULTS AND DISCUSSION

Open circuit potential

Open circuit potential of pure copper in 0.01 M H_2SO_4 without and with potassium sorbate is mesured over 10 minutes. Figure 1 illustrates that OCP value of copper slightly shifted towards negative direction at the beginning of immersion. This fact may be due to the adsorption of SO_4^{2-} ions on copper surface and formation of soluble $CuSO_4$ species [12]. When potassium sorbate is present in an acidic solution, the potential shifts in more negative direction compared to the blank solution. This behavior may be attributed to the adsorption of the inhibitor molecules or to deposition of reaction products on the metal surface.

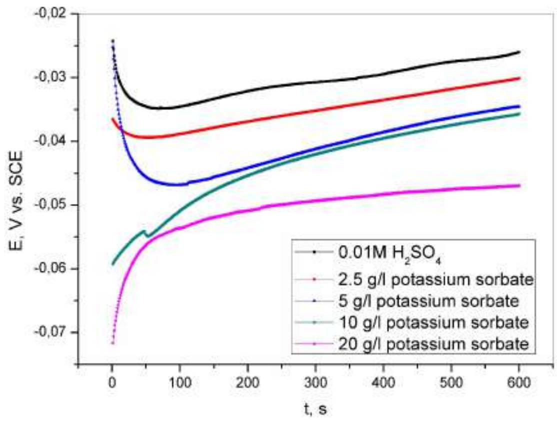

Figure 1. Open circuit potential for copper in 0.01M H_2SO_4 solution without and with the addition of various potassium sorbate concentrations

Potentiodinamic measurements

Dissolution of copper in naturally aerated acidic solutions follows the reactions [13]:

$$Cu = Cu^{+} + e^{-} \text{ (fast)} \qquad (1)$$
$$Cu^{+} = Cu^{2+} + e^{-} \text{ (slow)} \qquad (2)$$

The cathodic reaction for copper in acidic solutions is oxygen reduction according to the reaction [14]:

$$O_2 + 4H^{+} + 4e^{-} = 2H_2O \qquad (3)$$

The potentiodynamic polarization curves of copper in 0.01M H_2SO_4 without and with various concentrations of potassium sorbate are shown in Figure 2. It is clear from the potentiodynamic polarization curves that increasing inhibitor concentrations shift progressively the corrosion potential towards negative direction compared to the inhibitor-free solution. In the presence of potassium sorbate, Ecorr is maximum shifted 28mV (SCE) compared with blank solution. This point to that potassium sorbate acts as a mixed-type of inhibitor with pronounced influence on the cathodic reaction [15].
Kinetic parameters of copper corrosion such as corrosion potential (E_{corr}), corrosion current density (j_{corr}), anodic and cathodic Tafel slopes (b_a and b_c) as well as the degree of the inhibitor efficiency are presented in Table 1. The inhibition efficiency is calculated according to the following equation:

$$IE = \frac{j_{corr} - j_{corr\ (inh)}}{j_{corr}} \times 100\ [\%] \qquad (4)$$

Where j_{corr} and $j_{corr\ (inh)}$ present corrosion current density, without and with the addition of potassium sorbate, respectively. It is clear from the results in Table 1 that the current density decreased with potassium sorbate concentration increase, indicating its inhibitory effect. The values of cathodic (bc) Tafel slopes are found to change with inhibitor concentration, which clearly indicates that the inhibitor contolled cathodic reaction. The inhibition efficiency of potassium sorbate increased with increasing its concentration in 0.01M H_2SO_4 solution.

Table 1. Kinetic parameters of copper corrosion in sulfuric acid solution in the presence of various potassium sorbate concentrations

C_{inh}, g/l	E_{corr}, V	j_{corr}, A/cm^2	ba, V/dec	-bc, V/dec	IE%	-ΔG, kJ/mol
/	-0.03	$1.84\cdot10^{-6}$	0.045	0.136	/	10.85
2.5	-0.033	$6.58\cdot10^{-7}$	0.044	0.072	64.2	
5.0	-0.03	$4.09\cdot10^{-7}$	0.065	0.068	77.8	
10.0	-0.039	$2.90\cdot10^{-7}$	0.053	0.055	84.2	
20.0	-0.058	$1.41\cdot10^{-7}$	0.056	0.073	92.3	

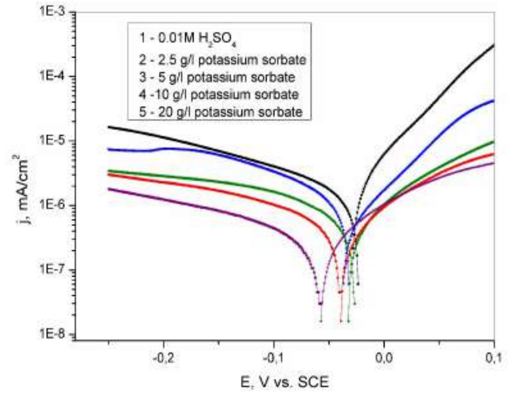

Figure 2. Potentiodynamic polarization curves for copper in 0.01M H_2SO_4 solution without and with the addition of various potassium sorbate concentrations

Cyclic voltammetric measurements

The cyclic voltammograms of Cu in 0.01 M H_2SO_4 with and without potassium sorbate in the potential range from -1.0 to +1.0 V versus SCE is present in Figure 3. Cyclic voltammetry curve for copper in naturally aerated sulfate solution indicates that Cu undergoes oxidation to Cu^+ ions [16]. In the reverse scan, the cathodic peak represents the reduction of copper ions.

Cyclic voltammetric curves confirm that potassium sorbate has ability to protect copper electrode from corrosion in the sulfate medium. The formation of thin layer of potassium sorbate onto copper electrode can provide protection against aggressive ions attack [10]. As can be seen from the Figure 4 lower concentrations of investigated compound can protect the copper surface until ~ 0.5V (vs. SCE). Then, the corrosion current density starts to increase, with increasing the potential value, due to formation of Cu^{2+} species [17]. The reduction peak in the reverse cathodic scan direction was not observed. This is attributed to the fact that the inhibitor is strongly adsorbed to the surface [18].

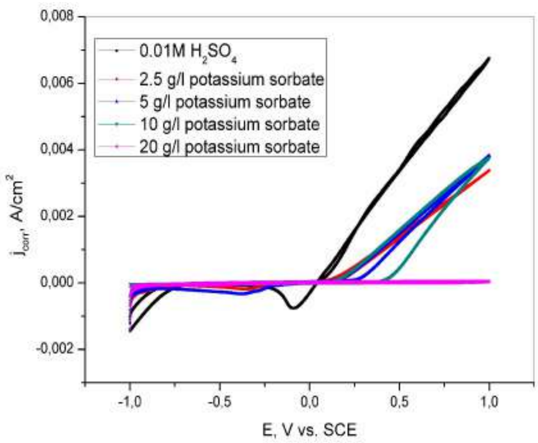

Figure 3. Cyclic voltammetric curves for copper in 0.01M H_2SO_4 solution without and with the addition of various potassium sorbate concentrations

At higher concentrations of potassium sorbate it was detected a copper passivity in the whole potential range. This indicates that copper surface was cover with a stable protective film at a potential ranging from -1.0 V up to 1.0 V (SCE) [9].

Adsorption isotherm

To obtain more information about the interaction between the investigated organic inhibitors and the electrode surface, Langmuir adsorption isotherm was tested. The Langmuir adsorption isotherm can be presented in the following way [19]:

$$\frac{c}{\theta} = \frac{1}{K} + C \tag{5}$$

Where K represents adsorption constant, C is concentration of investigated inhibitors, whereas θ represents the degree of surface coverage. The Gibbs energy of adsorption is calculated according to the equation:

$$K = \frac{1}{55.55} \exp(\frac{-\Delta G}{RT}) \qquad (6)$$

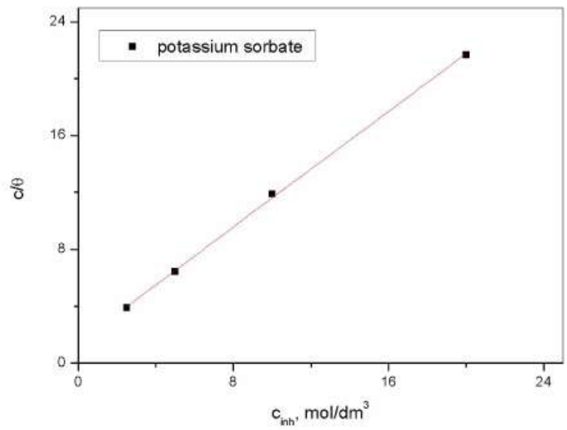

Figure 4. Langmuir adsorption isotherm of potassium sorbate in an acidic sulfate solution

A linear relation between Cinh/θ and Cinh indicates that the adsorption of potassium sorbate on copper surface obeys Langmuir adsorption isotherm. This isotherm points to that the adsorbed molecules occupy only one site on the electrode surface [19]. The calculated value of Gibbs free energy for copper (Table 1), in this investigation, confirmed that adsorption of inhibitors involves physical process on electrode surface.

CONCLUSION

The obtained results confirmed that the addition of potassium sorbate to the 0.01M H_2SO_4 solution caused inhibition of copper corrosion. The presence of potassium sorbate shifts the open circuit potential in negative direction compared with blank solution. From the potentiodynamic polarization curves it is clear that potassium sorbate acts as a mixed-type of inhibitor. The adsorption of potassium sorbate obeys Langmuir adsorption isotherm. The value of the Gibbs free energy indicates to physisorption of the inhibitor molecules onto copper surface.

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STRATEGIES FOR RESTORING THE EXISTING CITY DUMP STATION „SERIJAT“ IN STRPCE

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ABSTRACT

Rational solid waste disposal methods present one of the crucial factors in developing and maintaining strategies for satisfying needs of present generations without affecting quality of life for the future generations [1]. The final element in that process is disposal of the waste. That is the process in which all available solid waste reach its final destination and that is the city dump. Problem of removing solid waste is nowadays solved by its sanitary disposal. Modern sanitary city dump present a system of special units, where the waste is buried into the ground or disposed on the surface but on a way to eliminate all negative influence it could have on the environment.This work present proposed solution for the city dump located on so called place “Šerijat” in Strpce.

Key words: solid waste management, city dump, filtered water, lagoon.

INTRODUCTION

Even though we are living in the XXI century, waste disposal awareness is still low. To solve the problems of solid waste disposal (particularly recycling and disposing) , the state has formed corresponding departments and adapted many regulations which have been coordinated with EU regulations; and should contribute in reducing solid waste, by collecting, recycling and safe waste disposal.

Solid waste could be classified as: food waste, ashes, garbage, damaged vehicles, industrial waste and filtered water waste [2].

By the way city dumps are created they could be divided into randomly choosen dumps; dumps choosen by some institution (without ground analysis and dump control); and the city dumps arranged according to ecological regulations and standards.

Construction of the sanitary dump stations is only part of the complex process of solid waste management; it also includes waste selection, recycling, transportation, and disposal. However, construction of the sanitary dump stations is just part of this complex and long lasting process.

RESTORING THE EXISTING CITY DUMP

The city dump station called "Šerijat"located in Štrpce municipality was in use for short time, because this location was used as dump station for both Štrpce and Kačanik municipalities. To restore the existing dump station it is necessary to clean the scattered waste from the ground; to form dump station which is suitable to configuration of the ground; and to cover it. Because it could still be used as a dump station, ground has not been afforested, but the final cover is made of waterproof material (HDPE) on top of the existing waste. From the compulsory distance from the site, there are no water sources, residential areas or industrial estates; protected cultural heritage , monuments and the like; so if the existing dump station is restored it could be built on the ground of about 10.4 ha.

Table 1 shows the population and its increasment of 0,4% in regard to the census from 1991 when 12712 inhabitants were registered, and the table also shows waste increasment per consumption from 2% annually.

Table 1. Demographic structure within the ecological status of Štrpce Municipality

Year	Population	Waste capacity per resident	Light waste capacity	Dense waste capacity	Waste capacity after being one year on the city dump	Total waste capacity of the city dump
-	-	m^3	m^3	m^3	m^3	m^3
1999	12770	0.75	9577	5746	0	4625
2000	12821	0.765	9808	5884	2873	8758
2005	13076	0.84	10983	6590	3223	24976
2010	13331	0.915	12197	7318	3585	42804
2015	13587	0.99	13451	8070	3958	62600
2020	13842	1.065	14741	8845	4344	75493
2025	14097	1.14	16070	9642	4740	83075
2030	14353	1.215	17438	10463	5148	90887

Total waste capacity over a period is 90887 m^3. Layer of the ground used for sanitary cover is 20% of the waste capacity. Total waste and ground capacity is around 109070 m^3. Total area of the city dump is 104170 m^2. Over examined period, waste could be disposed in the layer of about 1, 5 m (waste + cover).The city dump areas include entrance and exit areas, protective vegetation; traffic lines; hydro technical objects (lagoons, water supplies; pumping stations etc)

It can be concluded that the city dump station could be suitable for solid waste disposal in Štrpce Municipality for the next 50-60years.

Drainage system

Which measures for protecting the ground and water are going to be taken depends from the amount of rainfall, its intensity, duration and frequency. Intensity and frequency influence of forming infiltration water and runoff. Water which drain from the city dump stations could be: rainfall, sewerage and infiltration water. Rainfall should be drained by using peripheral ground canals of trapezium shape, which are located around the city dump station. On the city dump stations certain sloping surfaces toward lagoons are made, so that the water could drain; which should prevent that rainfall drain toward disposed waste locations.Infiltration water from the city dump stations are drained through PVC pipes of suitable diameter and inclination towards lagoons, where biological treatment of wastewater is taking place. Refined water could be returned into the city dump by pouring or emptying it.

As a result of duration, frequency and intensity of the rainfall, the infiltration water are formed and drained off, which present the biggest threat for the environment [3]. In other words, the aim is that minimal amount of water is present on the city dump station, regardless of the source (rain, snow, runoff, infiltration water).

LAGOONS

For collection and biological treatment of wastewater two lagoons were constructed. The first is used for collecting natural/obligatory aeration and stabilization; and the second is used for collecting biologically treated wastewater, which is used as store water supply and if needed for pouring and extinguishing.

The garbage on the city dumps is biologically treated under the influence of the micro organism. First of all, we are talking about food waste and similar organic waste. Biological treatment of the garbage is performed in several stages, illustration 1.

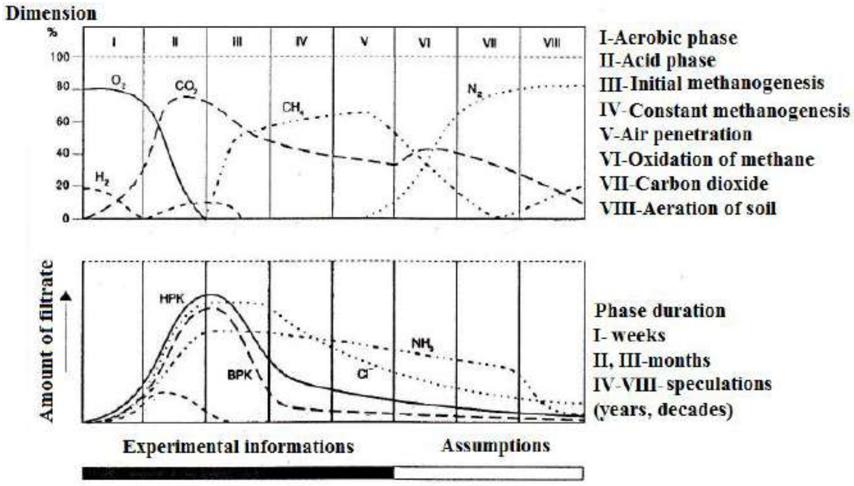

Figure 1. Chart of biological treatment on the city dump

Aerobic phase. Organic waste (carbon hydrates, fats, proteins, organic matters with nitrogen etc) degradation is releasing energy. This phase is in progress for few weeks. Because of the small aerobic degradation, emission of CO_2, NH_3 from the surface of the city dump is irrelevant, so any treatment for environment protection is not needed.

Anaerobic phase.Spreading new layer of garbage on top of the existing one is causing shortage of the oxygen and because of that process of biological treatment is changed into anaerobic stage (oxygen free). This phase is in progress for a long time.

Hydrolysis phase. Complex, insoluble substances are treated with special unicellular enzyme.

Acid phase. Organic matters are dissolving under the influence of anaerobic micro organism releasing CO_2 and H_2. Infiltration water received in this stage has low pH value, and this phase is in progress for several months. Gas emission is irrelevant, so any treatment for environmental protection is not needed.

Methane phase. This is the phase where acid products CO_2 and H_2 are dissolved under the influence of methane bacterium into CH4 and CO_2. On this phase gas methane is released, which presents threat for safety, because it could cause fire on the city dump.

Duration of the each phase of biological treatment depends from the type of the waste and conditions at the city dump, such as moisture and the temperature. Each phase could progress faster, by keeping required moisture on the city dump and by isolating layer of the waste area; first of all in the phase of methanogenisis by spreading new layer of the ground (reactor" dump). On this way recultivation of the city dump, which could last for more that ten years, is reduced by half, with what the process of returning occupied ground to its function is faster. This treatment reduce the threat the city dump has on the environment, but it also shorten the time the city dump cause threat to the environment [4].

Short general explanation for biological treatment of the city dump station

It was not easy to decide what type of the city dump should be built "classic" or "reactor"; but it has been chosen the one with faster biological dissolve process, as the most appropriate solution.

This is the short general explanation for the city dump with faster biological dissolve process:

- The garbage should be disposed in phases and covered with new layers of ground
- Infiltration waters should be collected by channels and drained into lagoons
- Infiltrated water should be optionally be treated in lagoons
- Maintaining humidity by pouring (returning infiltrated water from lagoons)
- Collecting and removing methane from the city dump

COLLECTING INFILTRATED WATER

Infiltrated water is drained to the first basin of the lagoon.

The first basin of the lagoon is divided on two "basins" which are separated. The function of the first basin is to refine water from the dump by removing organic waste using natural or compulsory aeration on the surface. Compulsory aeration is done by floating aerator. The second basin is used for both aerobic and anaerobic treatment of infiltrated water; where on the surface are performed aerobic and in the mud at the bottom of the basin is performed anaerobic treatment. Concentration of these substances is completely different to proportion of the rainfall, so it needs less time to dissolve. In rainless years, concentration of organic matters in infiltrated waters is, despite the pouring, big; so infiltrated water should be diluted to complete the treatment. Because of this, more water is required to maintain humidity and low concentration of organic matters in the first basin of the lagoon. In order to provide the proper amount of water needed for pouring; it is necessary to control the amount of water in lagoons and refill if needed to obtain desired result.

Aerobic treatment initiated in the first basin of the lagoon is occurring in the second basin of the lagoon, through natural process without outside influence. Oxygen needed for the aerobic treatment is provided through aeration with floating aerator.

The purpose of the lagoon is to collect water supplies needed to maintain humidity on the city dump station. From the lagoon the water is taken to the pumping station, which provides the water for hydrant and pouring of the city dump.

Infiltrated water estimation

According to the information about monthly rainfall received from the weather station on Brezovica, table 2, calculation has been done for infiltrated water in the lagoon on the city dump station [5].

Table 2. Monthly rainfall 2000 – 2005 i 2008-2013. year (mm)

Month	JAN	FEB	MAR	APR	MAJ	JUN	JUL	AVG	SEP	OKT	NOV	DEC
average	64.77	54	63.44	65.98	58.54	69.51	51.34	48.85	47.82	40.12	68.69	53.13
Max.	170.7	93.3	118.4	150.4	150.5	183.9	122.2	125	115.5	89.2	168.5	113.9
year.	2002	2002	2009	2008	2009	2000	2011	2000	2012	2008	2001	2004

According to the above presented informations it could be seen that month with the most rainfall was July 2012 with 183, 9 mm. The surface needed for the first basin of the lagoon F1 was calculated by taking into consideration the capacity of infiltrated water which is 1715 m^2. The first basin of the lagoon should be F_1=470 m^2, and the second F_2=1245 m^2. From the informations presented above it could be seen that both basins are sufficient for monthly rainfall, but only the first basin would be enough for average monthly and maximal daily rainfall.

Analysing heavy rain features in Štrpce in order to construct a system for infiltrated water on the city dump

Heavy rain features, in the vicinity of the city dump, were analysed with the probability of 1%, 2%, 5%, 10%, 20%, i 50%. Maximal annual rainfall records from 2000 till 2013 were used to determine its probability, Table 3.

Table 3. Maximal annual rainfall recorded on weather station on Brezovica (915 meters above sea level)

Maximal annual rainfall on Brezovica					
Year	Date	Max. rainfall	Year	Date	Max. rainfall
2000	13.06	27.0	2008	20.04	35.4
2001	06.01	29.6	2009	28.03	57.0
2002	05.01	59.1	2010	28.10	40.0
2003	29.09	41.3	2011	21.09	47.0
2004	18.12	33.6	2012	01.08	25.0
2005	01.03	31.7	2013	14.11	32.0

It is assumed that rain intensity values abide by Pearson III distribution [6], and according to the information of maximal daily rainfall received from the weather station in Štrpce, it is determined the probability of heavy rain manifestation lasting for 24 hours according to Pirson III and Log Pearson III for repeated sequences of maximal rainfall. Values are presented in the Table 4.

Table 4. Intensity value by Log Pearson III distribution for certain repeated sequences

REPEATED SEQUENCE	PROBABILITY	LOG PIRSON III
100	1.00	75.70
50	2.00	68.90
20	5.0	59.85
10	10.00	52.90
5	20.00	45.76
2	50.00	23.77

Using model $H(T,P)=\frac{a\cdot T}{1440}\left(\frac{1440A+1}{AT+1}\right)^{B}\cdot H_d(P)$ maximal rainfall values have been determined for different probability values.

Diagram of probably maximal rainfall values, with define duration T (5, 10, 30, 60, 120, 240, 720, 960, 1200, 1400) was shown on the illustration 2, and maximal rainfall on the illustration 3.

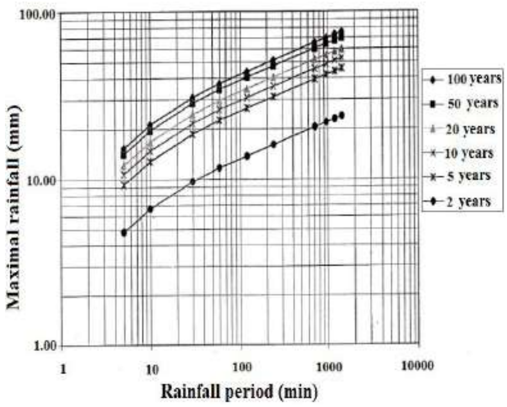

Figure 2. Probably maximal rainfall with defined duration of 2, 5, 10, 20, 50 and 100 years in Štrpce

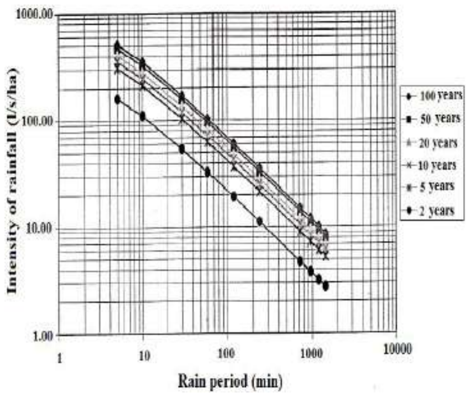

Figure 3. Probably maximal intensity of rainfall for repeated sequences of 2, 5, 10, 20, 50 and 100 years in Štrpce

CONCLUSION

Human society have recently started to search for solutions to reduce pollution (15-20 years) . International Regulations for environmental protections were adapted at first, and than solutions for actual problems were examined closely in order to solve the problems. The Republic of Serbia has adapted many regulations for environment protection and safe waste disposal. The most important are: Waste management control; Regulations for environmental protection; Regulations for municipal services; Waste material disposal regulations. Beside official documents The Republic of Serbia adapted many Strategies for Waste disposal 2010-2019[7]. Other official documents are: Regulations for environmental evaluation; Regulation for integrated prevention of environmental pollution; Spatial plan for the Republic of Serbia 2010-2020.

It could be expected further development of technologies which would influence and development of the existing city dump stations. In time, sanitary waste areas especially the bigger ones, could be used as power plants. Further development is expected and for recycling, waste reduction and waste disposal management.

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CEMENT MANUFACTURING TECHNOLOGY AND CO-PROCESSING OF MATERIALS DERIVED FROM WASTE

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ABSTRACT

Considering increasing waste production on the one hand and the resource demands of the cement process on the other, cement companies started to look at waste as a source of raw material and energy. Cement plants play a vital role in communities, conserving natural resources by utilizing waste for its production. Co-processing is a term used to refer to the use of suitable waste materials in manufacturing processes for the purpose of energy and resource recovery and the resultant reduction in the use of conventional fuels and raw materials through substitution.

Key words: co-processing, cement production, waste, alternative fuels, alternative raw materials.

WHAT IS CEMENT?

The first step in making cement is to heat limestone with small quantities of other materials (such as clay, sand and iron) to 1,450°C in a kiln, a process which requires large amounts of fuel. The resulting hard intermediate product is called clinker, which is ground with a small amount of gypsum into a powder to make ordinary Portland cement (OPC).

Blending additional constituents, such as coal fly ash, additional limestone, pozzolana (a naturally occurring volcanic ash), and blast furnace slag with the clinker creates blended cements with different properties depending on the materials added. OPC and blended cements are the most commonly used types of cement. [1]

Clinker contains the oxides of calcium (CaO), aluminum (Al_2O_3), silica (SiO_2) and iron (Fe_2O_3). Changing the final composition can impact the properties of the cement produced its reactivity, strength and setting time.

Cement must conform to the strict building standards set for it. Consequently, the manufacturing process itself must be closely monitored and controlled to obtain clinker and cement that meet these standards.

CEMENT KILN SUITABILITY FOR PROCESSING WASTE

A cement plant consumes 3,000 to 6,500 mega joules (MJ) of thermal energy per ton of clinker produced, depending on the raw materials and the process used.

Most cement kilns today use coal and petroleum coke as primary fuels, and to a lesser extent natural gas and fuel oil. As these fuels burn they provide energy, and some leave fuel ash containing silica and alumina compounds (and other trace elements). These combine with the raw materials in the kiln, contributing to the structure of the clinker and forming part of the final product. Energy use is the largest component of production cost, typically accounting for at least 30-40% of the total. The main characteristics which provide suitability of cement kilns for processing waste are presented in Figure 1.

- Kilns operate at high temperatures, where the process requires: 2,000°C or higher in the flame of the main burner, 1,450°C in the material to make clinker, and 1,000 to 1,200°C in the calcination zone;
- The typical residence time of combustion gases in the kiln is more than five seconds at a temperature higher than 1,000°C. By contrast, gas residence time in a typical incinerator is two seconds. Residence time for solid materials varies from 20 minutes to an hour depending on the cement process;
- The process takes place under oxidizing conditions with good mixing conditions, assuring good combustion and avoiding the generation of carbon monoxide (CO) and other deleterious compounds. The thermally consistent conditions in a kiln guarantee the complete destruction of organic components in the waste;
- Waste materials in the kiln are in contact with a large flow of alkaline (basic) materials that neutralize potential acid off-gases from combustion;
- Any inorganic mineral residues from combustion – including most heavy metals[1] – are trapped in the complex matrix of the clinker and cement;
- Complete combustion and the trapping of mineral residues mean that in most cases there is no ash residue from the process[2].
- Cement kilns are often fitted with waste heat recovery and power generation systems.
- Systems do not alter the emission profile of the cement kiln, including the formation of dioxin/ furan or VOC emissions.

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[1] Some volatile heavy metals (e.g. mercury (Hg), cadmium (Cd), thallium (Tl)) are not completely immobilized in this way; so their content in raw and/or waste materials must be assessed and controlled.

[2] Excess chlorine or alkali which may be in some virgin materials may produce cement kiln dust or bypass dust which must be removed, recycled or disposed of responsibly.

Characteristics	Temperature and time
Temperature at main burner	>1450°C: material >2000°C: flame temp.
Residence time at main burner	>12-15 sec and >1200°C > 5-6 sec and > 1800°C
Temperature at precalciner	>850°C: material >1000°C: flame temp.
Residence time at precalciner	> 2-6 sec and >800°C

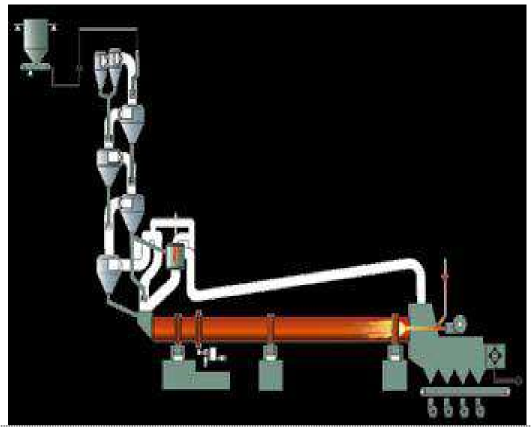

Figure 1. The advantages of co- processing [2]

TURNING WASTE INTO A SOURCE OF RAW MATERIAL AND FUEL

The cement industry has many opportunities to replace a portion of the virgin natural resources it uses with waste and by-products from other processes. These may be used as raw materials, fuels, or as constituents of cement, depending on their properties. Alternative fuels and raw materials must meet quality specifications in the same way as conventional fuels and raw materials.

Alternative raw material use - Selected waste and by-products containing useful minerals can be used as raw materials in the kiln, replacing raw materials such as clay, shale and limestone. The use of wastes as raw materials such as in the clinker burning process involves the substitution of sulfur and the oxides contained in the wastes used as raw materials. These include calcium oxide (CaO), silica (SiO_2), alumina (Al_2O_3) or iron oxide (Fe_2O_3) for the respective raw material constituents. Power station ash (fly ash), blast furnace slag, and other process residues can be used as partial replacements for the natural raw materials. Other waste materials are supplied as so-called 'inter-ground' additions to the grinding plants. Fly ash can be used both as raw material in the production of clinker (mainly for its content of alumina) and as an inter-ground addition for cement. Fly ash can replace up to 50% of the Portland cement clinker. Furthermore, suitable industrial gypsum lends itself for use as a sulfate component. An overview of wastes used as raw materials classified into different groups according to their chemical composition is shown in Table 1.

Table 1. Example list of wastes used as raw materials classified by their chemical composition and used in cement kilns in the EU-25 [3]

Raw material group	Examples of wastes used as raw materials
Ca group	Industrial lime (waste limestone) Lime slurries Carbide sludge Sludge from drinking water treatment
Si group	Spent foundry sand Sand
Fe group	Blast furnace and converter slag Pyrite ash Synthetic hematite Red mud
Al group	Industrial sludge
Si-AL-Ca group	Fly ash Slags Crusher fines Soil
S group	Industrial gypsum
F group	CaF_2 Filter sludge

Like ash from conventional fuels, the ash from waste fuels provides mineral components for the cement clinker. Clinker required a defined composition which is crucial to the characteristic hydraulic properties of the cement. This means that all raw materials and fuel ash must be carefully matched in terms of mineral composition and feed rate to obtain the desired clinker composition.

<u>Alternative fuel</u> - Conventional fuels, such as fossil fuels, can be replaced by waste fuels, i.e. waste fuels derived from pretreated and sorted waste fractions including solid and liquid recovered fuels, and/or biomass. A wide range of different types of wastes are used as fuels including the remaining ashes. Waste materials can be solid, liquid or pasty that are defined by their origin, e.g. industrial, agricultural and municipal sources.

The clinker-burning process offers good conditions for using different types of waste materials replacing parts of conventional fuels. As listed in Table -2, different types of wastes are used as fuels in European cement kilns, categorized as hazardous and nonhazardous wastes. As these calorific waste materials can replace primary fuel in cement kilns, a consistent waste quality is essential (e.g. adequate calorific value, metal, halogen (e.g. chlorine) and ash content, the waste has to be suitable for the burners). There is a constant increase in the use of waste fuels in clinker production; however, the increase in the use of non-hazardous waste is more significant than the use of hazardous waste [3] Table 2. presents a list of wastes used as fuels, clustered into 14 groups. These groups span several EWC listings.

Table 2. Different types of wastes used as fuels in EU-27 cement kilns in 2003 and 2004 [3]

Group Nr.([1])	Types of waste fuels (hazardous and non-hazardous)
1	Wood, paper, cardboard
2	Textiles
3	Plastics
4	Processed fractions (e.g. RDF)
5	Rubber/tyres
6	Industrial sludge
7	Municipal sewage sludge
8	Animal meal, fats
9	Coal/carbon waste
10	Agricultural waste
11	Solid waste (impregnated sawdust)
12	Solvents and related waste
13	Oil and oily waste
14	Others
(1) Each grouping spans several EWC listings	

PRE-PROCESSING OF WASTE MATERIALS FOR THE CEMENT MANUFACTURING PROCESS

The co-processing of waste in the cement industry as a substitute fuel or raw material source usually requires that waste feed stocks be pretreated or pre-processed (for example, through sorting, shredding, grinding, blending or mixing, among others) to produce a uniform waste stream. The quality assurance of these processes is driven by the need to meet the specifications (for example, limits on contaminants such as chlorine and heavy metals) which are set by the receiving facility to produce clinker and cement according to specific standards, while guaranteeing that environmental standards are being met. For optimum operation, cement kilns require uniform waste material flows in terms of quality and quantity. Although for certain wastes this can only be achieved by pre-processing, in some cases, for example used oil or tires, wastes may be used "as-delivered" without further processing.

Pre-processing in general can be defined as those operations that lead to homogenization of the chemical composition and/or physical characteristics of the wastes. This is carried out with the aim of adapting a waste to suit a selected treatment operation, and as such, pre-processing should only be carried out because it is a technical requirement from the cement plant operator to guarantee a homogeneous and stable feedstock, and not to circumvent waste acceptance criteria. Pre-processing should produce a waste that complies with chemical and physical specifications that are fixed by the end users [1].

COMMONLY RESTRICTED WASTE

Although both conventional fuels and raw materials may be substituted in part by waste of suitable composition, the quality of the clinker and cement products must be maintained and the products must not be misused as a sink for heavy metals. Waste, which owing to its chemical composition, material properties or potential hazards, may influence the safety or operation of a cement plant, or whose use in a cement plant would lead to significant additional environmental impact, should not be co-processed in cement plants. It is therefore necessary to specify quality requirements for the waste employed and in certain cases to restrict the use of certain wastes. As a consequence, the following is a list of waste materials that should not be considered for co-processing in cement plants:

- Radioactive waste from the nuclear industry
- Electrical and electronic waste (e-waste)
- Whole batteries
- Corrosive waste, including mineral acids
- Explosives and ammunition
- Waste containing asbestos
- Biological medical waste
- Chemical or biological weapons destined for destruction
- Waste of unknown or unpredictable composition, including unsorted municipal waste
- Waste raw materials with little or no mineral value for the clinker (i.e. heavy metal processing residues).

Individual facilities may also exclude other materials depending on the local raw material and fuel chemistry, the infrastructure and the cement production process, the availability of equipment for controlling, handling and feeding the waste materials, and site-specific health, safety and environmental issues.

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THE SUCROSE OXIDATION ON BORON-DOPED DIAMOND IN THE BRINE WATER - CYCLIC VOLTAMMETRY

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ABSTRACT

The possibility of direct electrochemical oxidation of sucrose in alkaline electrolytes on boron-doped diamond (BDD) was explored by cyclic voltammetry and showed that it starts at potentials >1.1 V against standard calomel electrode, negative regarding potentials of the oxygen or chlorine evolution. The analysis of CV's shoved that direct electrochemical oxidation of sucrose is complex diffusion controlled process. The mediated oxidation by the oxygen and the oxygen transfer mediators would start at anodic potentials >1.8 V against SCE. The activation of BDD surface by anodic polarization pretreatment enables adsorption of carbohydrate molecule on the electrode before electrocatalytic oxidation.

Key words: boron-doped diamond; sucrose; electrochemical oxidation; cyclic voltammetry.

INTRODUCTION

The electrochemical treatments of organic compounds founded wide range of applications recently, because of its relative technological versatility and ease of the process control with respect to the processes of chemical treatments by strong oxidants [1-8]

The electrolytic treatment of sucrose already attracted interest in the various technological fields such as are: the new material synthesis (for example, water-soluble amphiphilic biocompatible polymers for biological membranes, biodegradable polymers, carboxyl acids, esters or lipids), the processes of the chemical oxygen demand (COD) reduction of the wastewater from sugar refineries and in the electrical power generation in the microbial fuel cells [1–7].

BDD thin films, grown on a suitable substrate (p-Si, Ti, Nb, W and Mo) by chemical vapor deposition (CVD), are relatively new electrode material that possesses a number of unique electrochemical properties, distinguishing them from the other traditional dimensionally stable electrodes (DSE) [5,6]. The high potential difference between the hydrogen and oxygen evolution reactions (HER and OER respectively) of the BDD electrode, so-called 'wide potential window', is consequence of the high overpotential of these reactions and enables particular electrochemical processes at high electrode potentials without interference of the hydrogen and oxygen evolution. [3,4,8–11].

Small number of papers treats the electrochemical reactions of the hydrocarbons on the diamond electrodes. The physical and chemical characteristics of the specific diamond electrode have strong influence on the process of organics oxidation. Some diamond anodes favored partial and selective oxidation of organics (i.e., conversion), while the other favored complete combustion to CO_2 [4 – 6, 8 – 11].

The formation of the functional groups (=C–H_2, =C=O, B≡C–H, C=CH–O, B≡C–OH) on the synthetic boron doped diamond surface during the electrode conditioning has important influence on its electrochemical behavior. The exploration of the possibility of direct electrochemical sucrose oxidation at BDD electrode at potentials negative regarding OER has not been reported in available literature, as it has been thought improbable because of the chemical inertness of the diamond. However, chemical or electrochemical treatments of the doped diamond change the activity of its surface by generation of various functional groups. This could ease chemisorption of the organic compound and its electrochemical interaction with diamond and direct exchange of the electrons [3, 4, 8 – 12].

In this paper the BDD electrode anodic behavior in the brine sucrose solution is explored by the cyclic voltammetry (CV).

EXPERIMENTAL

Electrochemical experiments were carried out in the standard three-electrode system consisted of highly boron-doped synthetic diamond, as a working electrode, standard calomel reference electrode (SCE) (Hg|Hg_2Cl_2 in 3.5 M KCl, E = + 0.250 V *vs*. normal hydrogen electrode (NHE) at 25 °C) connected to the working electrode *via* the Luggin capillary electrolyte bridge and coiled platinum wire as a counter electrode.

The working electrode material is 0.6 mm thick layer of synthetic diamond, highly boron-doped with $[B] > 10^{20}$ atoms per cm^3, obtained by high–pressure chemical vapor deposition (CVD) on plate (area 1 cm^2), with low specific resistivity of 0.02 – 0.18 ohm cm. The BDD electrode *p*-silicon wafer plates were purchased from Element Six Ltd. UK. Stability of the used BDD electrode after extended anodic polarization in the strong alkaline electrolyte, 10 M KOH, was proved elsewhere by the X-ray diffraction spectra [13].

The *p*-silicon wafer plate was electrically connected to the copper plate current collector with conductive silver glue to form working electrode, which back and lateral surfaces were isolated from electrolyte with chemically resistant epoxy resin.

As produced BDD surface of the electrode was cleaned with ethanol and distilled water first and appropriately conditioned. Pre–treatment of BDD electrode by 10 cycles of potential between limits of – 0.2 V and + 2.2 V against SCE was practiced before each experiment to ensure surface reproducibility as much as possible [13].

Cyclic voltammetry and potentiostatic experiments were performed by potentiostat – galvanostat PAR 273.

Sodium chloride solution has been selected as supporting electrolyte because of its availability and low price. Solutions of 0.42 M NaCl and 0.42 M NaCl + 0.15 M sucrose were prepared from bi-distilled water and chemicals of *pro analysis* quality. The pH value of experimental solutions was adjusted with 10 M NaOH and 10 M HCl solutions.

Concentration of sucrose in the experimental solutions was determined as chemical oxygen demand (COD) by standard chromate method [14].

RESULTS AND DISCUSSION

The cyclic voltammograms of BDD electrode showed in Fig. 1 are recorded in the pure sodium chloride alkaline solution. The absence of anodic current waves at the potentials negative regarding OER, which would result from the hydrogen–terminated surface oxidation, proved the oxygen termination of BDD surface after pre-treatment [3,8,9,12,13].

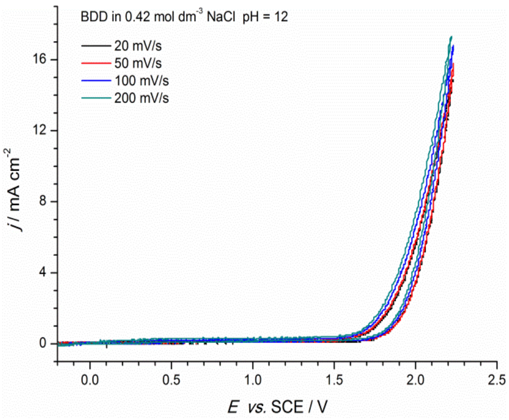

Figure 1. Cyclic voltammograms of BDD electrode in 0.42 M NaCl electrolyte, pH = 12, pre-treatment included 10 cycles of potential sweep between – 0.2 V and + 2.3 V against SCE

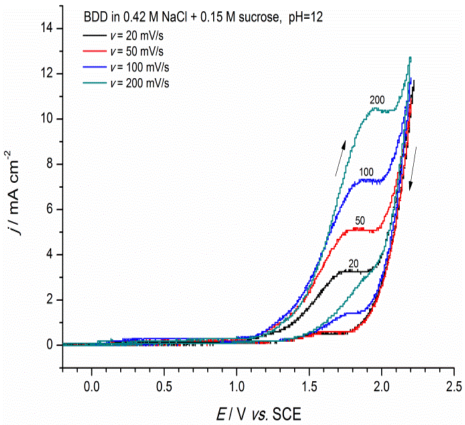

Figure 2. Cyclic voltammograms of BDD electrode in 0.42 M NaCl + 0.15 M sucrose electrolyte, pH = 12, pre-treatment included 10 cycles of potential sweep between – 0.2 V and + 2.2 V against SCE in 0.42 M NaCl

Also, on CVs presented in Fig. 1 there are no current waves of any other possible anodic processes of chloride oxidation in the potential region preceding OER in spite of the thermodynamic possibillity according to the Table 1, as a result of the higher overpotentials of the possible parallel reactions [3, 4].

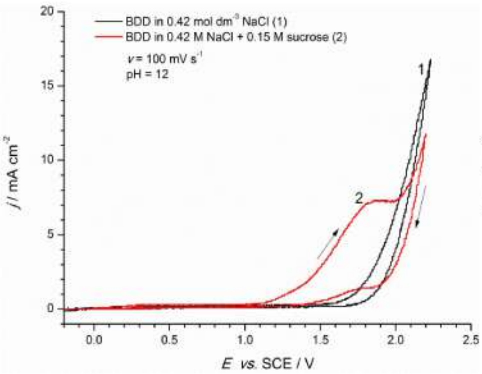

Figure 3. BDD electrode cyclic voltammograms in 0.42 M NaCl (1) and in 0.42 M NaCl + 0.15 M sucrose electrolyte (2), v = 100 mV s^{-1}, pH = 12, pre-treatment included 10 cycles of potential sweep between – 0.2 V and + 2.2 V against SCE in 0.42 M NaCl

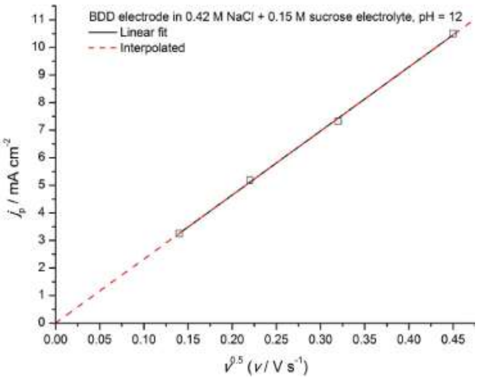

Figure 4. Dependence $j_P – v^{1/2}$ for BDD electrode in 0.42 M NaCl + 0.15 M sucrose electrolyte, pH = 12, data from Fig. 2. j_P – current density peak; v – potential sweep rate

As seen in Figs. 2 the addition of sucrose into 0.42 M NaCl alkaline electrolyte obviously provoked appearance of the new current wave on the cyclic voltammograms of BDD electrode in the potential region negative regarding OER which clearly show the direct sucrose electrochemical interaction with BDD anode. It is evident that the anodic current waves on CVs in Fig. 2 start at potentials > + 1.1 V against SCE (> 1.36 V vs. NHE), which is nearly 0.5 V negative with respect to the OER start potential + 1.6 V against SCE on the CVs in Fig.1. Also, it is seen from Fig 2 that sucrose reaction on the BDD electrode shifts OER potential more positively regarding behavior in the pure chloride solution. Such behavior would be explained by the electrochemical interaction of the adsorbed sucrose molecules with BDD electrode in the direct electrons exchange between these two parties. Although diamond surface is known as chemically inert, the electrode conditioning by anodic polarization would provoke activation of its surface by formation of C=O active sites, which enable sucrose adsorption at the BDD surface [15–21].

Table 1. Possible electrode reactions at high anodic potentials [3, 4]

Reaction	*E vs.* NHE / V
$OH^{\bullet} + H^+ + e^- \leftrightarrows H_2O$	2.80
$O_3(g) + 2H^+ + 2e^- \leftrightarrows O_2(g) + H_2O$	2.075
$H_2O_2 + 2H^+ + 2e^- \leftrightarrows 2H_2O$	1.763
$HO_2^{\bullet} + 3H^+ + 3e^- \leftrightarrows 2H_2O$	1.65
$HC1O + H^+ + 2e \leftrightarrows Cl^- + H_2O$	1.482
$C1O_4^- + 8H^+ + 8e \leftrightarrows Cl^- + 4H_2O$	1.389
$Cl_2(g) + 2e^- \leftrightarrows 2Cl^-$	1.358
$O_2 + 4H^+ + 4e \leftrightarrows 2H_2O$	1.229
$C1O_2 + e \leftrightarrows ClO_2^-$	0.954
$ClO^- + H_2O + 2e \leftrightarrows Cl^- + 2OH^-$	0.841

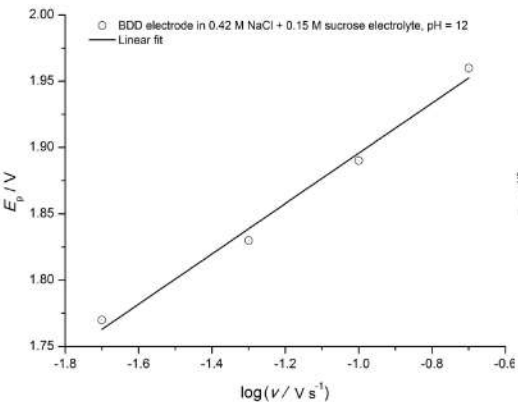

Figure 5. Dependence EP – log(v) for BDD electrode in 0.42 M NaCl + 0.15 M sucrose electrolyte, pH = 12, data from Fig. 2. EP – potential of current density peak.

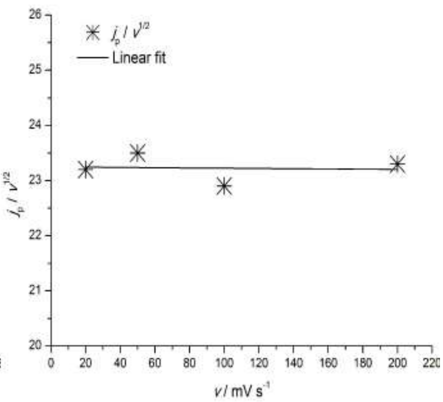

Figure 6. Dependence jP / v1/2 vs. v for BDD electrode in 0.42 M NaCl + 0.15 M sucrose electrolyte, pH = 12, data from Fig. 2

Despite the fact that cathodic current peaks related to the anodic current peaks were not observed on the voltammograms in Figs. 2 and 3, some aspects of the character of the first electrochemical step, a direct electron exchange of sucrose with BDD electrode, of the entire multistage process of the sucrose oxidation could be analyzed from the dependence of the anodic current peaks on the potential scan rate, according to procedure given in literature [22 – 24].

The dependence of the anodic current peak, j_p, on the square root of sweep rate, $v^{1/2}$, given in Fig. 4, is almost perfectly linear and its extrapolation passing through the origin, characterizes the reversible diffusion controled electrode process [22]. Also, the linear dependence E_p against log v, given in Fig. 5, characterize a reversible electrode process followed by irreversible chemical reaction, reaction type VI in reference [23]. Further, almost horizontal line of the dependence $j_P/v^{1/2}$ against v, shown in Fig. 7, characterizes an uncomplicated charge transfer reactions [23]. The sucrose electrocatalytic oxidation process would comprise virtually reversible charge transfer process in the first step, which product reacts further and probably ends by formation of a new compound. Therefore, it seems that direct (without interaction of oxygen transfer mediators) anodic sucrose oxidation at BDD electrode has a diffusion controlled kinetics which involves successive processes, similar to the sucrose electrocatalytic oxidation at the noble metals [5 – 7].

CONCLUSIONS

The possibility of the direct electron exchange between anodically conditioned BDD electrode and sucrose molecule at anodic potentials lower with respect of the OER potential is experimentally confirmed in the strong alkaline chloride electrolyte at anodic potentials > 1.1 V against SCE, near 0.5 V negative regarding OER potential. This is possible because of the high overpotentials of water and chloride oxidation on the BDD electrode in given conditions. The mediated sucrose oxidation by strong oxidative species generated at BDD electrodes would be expected at potentials higher regarding OER potential.

Acknowledgement

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THE SUCROSE OXIDATION ON BORON-DOPED DIAMOND IN THE BRINE WATER - POTENTIOSTATIC ELECTROLYSIS

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ABSTRACT

The potentiostatic electrolytic oxidation of a brine sucrose water showed partial sucrose oxidation at BDD electrode at potentials negative regarding oxygen evolution reaction (OER), while a mediated oxidation by the oxygen transfer species is probable at potentials higher regarding OER. FTIR spectra of the electrolyzed sucrose solution at potential of + 1.8 V against SCE showed incomplete sucrose oxidation with probable generation of sucronic acids. The electrolytic sucrose oxidation at + 2.5 V against SCE is twice more efficient in COD reduction regarding oxidation at + 1.8 V against SCE, which confirms electrolytic sucrose incineration to carbonate.

Key words: boron-doped diamond; sucrose; electrolytic oxidation; potentiostatic oxidation.

INTRODUCTION

The effluent waters from sugar plants contain significant amount of organic matter, mostly sucrose, available for oxidation, which consume a large quantity of oxygen from recipient waters because of the high chemical oxygen demand (COD) of 10 g dm^{-3}, which threatens water fauna and florae life, and promotes development of anaerobic pathogens. [1]

A treatment of beet sugar factories effluent water is usually biochemical, and combines aerobic and anaerobic oxidation. However, such treatment of a wastewater rich in organic matter is long term process which brings many environmental problems such as are waste necessary area requirements, risk of unpleasant odour emissions, risk of ground water contamination and intolerable massive development of algal production during vegetative period.

Electrochemical treatment of sucrose refineries effluent water would be an economical alternative process or secondary decontamination process when conventional treatment methods are inadequate to reduce pollution tolerably [1 – 3].

The nature of electrode material has strong influence on the process of organics oxidation. Some anodes favored partial and selective oxidation of pollutants (i.e., conversion), while others favored complete combustion to CO_2. Boron doped diamond because of great potential difference between oxygen and hydrogen evolution reactions is promising electrode material for the electrolytic incineration of the organics in the wastewaters [2 – 11] Oxygen-terminated boron-doped diamond reportedly has a wide window of water stability and lower background currents than hydrogenated boron-doped diamond [4 - 9]. The influence of anodic treatment on electrochemical behavior of BDD has been discussed in papers [10, 11].

A transition from C–H to C–O terminations of BDD surface induces a positive shift of flat-band voltage on BDD and increases its electrochemical activity [12].

EXPERIMENTAL

Electrochemical experiments were carried out in the standard three-electrode system consisted of highly boron-doped synthetic diamond, as a working electrode, standard calomel reference electrode (SCE) ($Hg|Hg_2Cl_2$ in 3.5 M KCl, E = + 0.250 V vs. normal hydrogen electrode (NHE) at 25 °C) connected to the working electrode via the Luggin capillary electrolyte bridge and coiled platinum wire as a counter electrode. Catholyte and anolyte parts of the electrolytic cell were separated by PTFE ion selective membrane.

The working electrode material is 0.6 mm thick layer of synthetic diamond, highly boron-doped with [B] > 10^{20} atoms per cm^3, obtained by high–pressure chemical vapor deposition (CVD) on plate, with low specific resistivity of 0.02 – 0.18 ohm cm. The BDD electrode p-silicon wafer plates were purchased from Element Six Ltd. UK. Stability of the used BDD electrode after extended anodic polarization in the strong alkaline electrolyte, 10 M KOH, was proved elsewhere by the X-ray diffraction spectra [13].

The p-silicon wafer plate was electrically connected to the copper plate current collector with conductive silver glue to form working electrode, which back and lateral surfaces were isolated from electrolyte with chemically resistant epoxy resin.

As produced BDD surface of the electrode was cleaned with ethanol and distilled water first and appropriately conditioned. Pre–treatment of BDD electrode by 10 cycles of potential between limits of – 0.2 V and + 2.2 V against SCE was practiced before each experiment to ensure surface reproducibility as much as possible.

Potentiostatic electrolysis was performed by potentiostat – galvanostat PAR 273. Sodium chloride solution has been selected as supporting electrolyte because of its availability and low price. Solutions of 0.42 M NaCl and 0.42 M NaCl + 0.15 M sucrose were prepared from bi-distilled water and chemicals of pro analysis quality. The pH value of experimental solutions was adjusted with 10 M NaOH and 10 M HCl solutions.

Concentration of sucrose in the experimental solutions was determined as chemical oxygen demand (COD) by standard chromate method [14].

FTIR analysis of the sucrose electrolyte after oxidation at BDD electrode has been done with spectrophotometer Bomem MB-100, Hartman and Brown.

RESULTS AND DISCUSSION

The electrochemical method for the mineralization of organic pollutants is a new technology and has attracted a great deal of attention recently. This technology is interesting for the treatment of dilute wastewater (COD < 5 g/l) and it is in competition with the process of chemical oxidation, which comprises using of strong oxidants. [1 - 8] The efficiencies of the direct and mediated electrolytic oxidation of sucrose on BDD electrode in alkaline chloride solution were explored by the potentiostatic electrolysis of sucrose alkaline solution at potentials negative and positive regarding OER potential, as presented in Figs. 1 and 2.

$$C_{12}H_{22}O_{11} + 13\,OH^- \rightarrow 12\,CO_2 + 25\,H^+ + 25\,e^- \quad (1)$$

The electrolysis efficiency was calculated on the base of reaction (1) and results are summarized in the Table 1. The level of sucrose oxidation in the sucrose electrolyte samples was measured as difference between the chemical oxygen demand (COD) values [14] before and after electrochemical oxidation, with assumption that the sucrose was the only oxidizable substance in the solution.

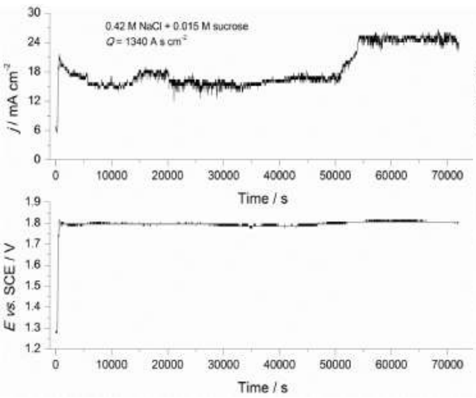

Figure 1. Electrochemical oxidation of 200 ml 0.42 M NaCl + 0.015 M sucrose, pH = 12, solution on BDD electrode at E = + 1.8 V vs. SCE

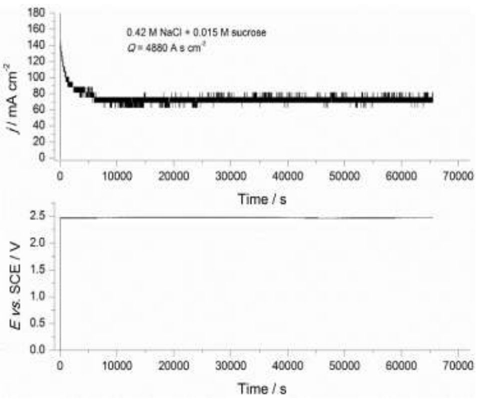

Figure 2. Electrochemical oxidation of 200 ml 0.42 M NaCl + 0.015 M sucrose, pH = 12, solution on BDD electrode at E = + 2.5 V vs. SCE

Table 1. Efficiency of sucrose oxidation at BDD electrode BDD in 0.2 dm^{-3} 0.42 M NaCl + 0.015 M sucrose, pH = 12, calculated based on Eq. (4), sucrose quantity in sample measured by solution COD*

E, V *vs.* SCE	C_s, g dm^{-3}	*Q*, C cm^{-2}	Δm^T_s, mg cm^{-2}	COD, g O_2	ΔCOD. g O_2	Δm_s, mg cm^{-2}	η
+ 1.8	5	1340	200	1.122	0.061	54	0.27
+ 2.5	5	4880	700	1.122	0.445	397	0.57

**Mean values from the three independent experiments for the each applied potential.*

C_s – starting sucrose concentration
E – BDD electrode electrolysis potential
Q – Specific passed current capacity
Δm^T_s – specific theoretical quantity of sucrose decomposition
Δm_s – specific real quantity of sucrose decomposition
$\eta = \Delta m_s / \Delta m^T_s$ – efficiency of sucrose decomposition

The results from the Table 1 show that COD of sucrose solution after electrolytic oxidation at electrode potential negative from OER potential is moderately reduced, probably because of the synthesis of some new organic compounds [4 – 8] and their oxidation by chromate in the COD determination. Electrolysis at higher electrode potential regarding OER the COD of the electrolyzed sucrose electrolyte was reduced considerably, because of the better efficiency of sucrose mineralization. The overall electrolysis efficiency is reduced because of the parallel electrode processes of water and chloride oxidation [3 – 8].

The increase of the positive potential scan positively from + 2.3 V against SCE provokes generation of the powerful oxidants, i.e. hydroxyl, chlorine and oxygen radicals, which as intermediates in the oxygen transfer could catalyze sucrose oxidation to carbonate in the process of the mediated sucrose oxidation [2, 3, 7 – 9]. The radicals, generated by water oxidation (Eq. 2) at the BDD electrode, mediate in the oxygen transfer from the water to the hydrocarbon (Eq. 3), in parallel with side reaction of oxygen evolution (Eq. 4) [3 – 12, 15 – 17].

$$\mathrm{BDD} + \mathrm{H_2O} \rightarrow \mathrm{BDD}(\bullet\mathrm{OH}) + \mathrm{H^+} + \mathrm{e^-} \tag{2}$$

$$\mathrm{BDD}(\bullet\mathrm{OH}) + \mathrm{C_{12}H_{22}O_{11}} \rightarrow \mathrm{BDD} + \mathrm{products} + \mathrm{H^+} + \mathrm{e^-} \tag{3}$$

$$\mathrm{BDD} + (\bullet\mathrm{OH}) \rightarrow \mathrm{BDD} + \tfrac{1}{2}\mathrm{O_2} + \mathrm{H^+} + \mathrm{e^-} \tag{4}$$

FTIR spectrum analyses

Products of the electrolytic oxidation of sucrose brine water solution at BDD electrode potential of + 1.8 V against SCE were analyzed by FTIR spectroscopy.

FTIR spectrum in Fig. 3 of sucrose solution recorded after the electrochemical treatment at given conditions, demonstrates incomplete sucrose decay in the process of electrochemical sucrose oxidation at BDD electrode with possible generation of new products.

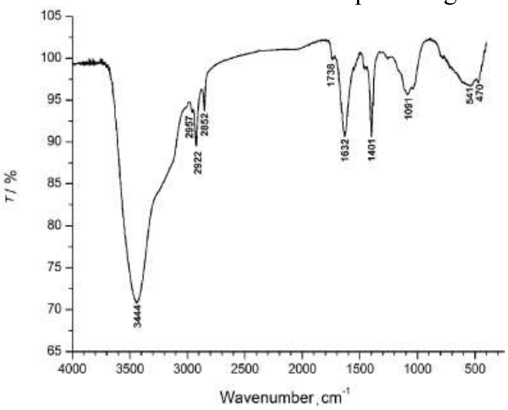

Figure 3. FTIR spectrum of sucrose solution 0.4 M NaCl + 0.15 M sucrose pH = 12 after 6 h oxidation at + 1.8 V against SCE.

The FTIR spectrum bands in Fig. 3 can be explained as follows:

a. band at wavenumber 3444.78 cm^{-1} characterize OH group vibrations, given the shape and intensity of the peak there is a lot of OH groups,
b. bands at wavenumbers 2957, 2922, 2852 cm^{-1} characterize methylene (–CH_2CH_3) groups stretching vibrations,
c. band at wavenumber 1632 cm^{-1} characterize water molecule vibration,
d. band at 1738 cm^{-1} characterize stretching of C=O bond, the vibration of a free acid [9–11, 44],
e. band at 1401 cm^{-1} may results from –OH, =CH_2 vibrations,
f. band at wavenumber 1091 cm^{-1} possible reaction product ester group C–O.

FTIR spectrum indicates that the structure of the carbohydrate has not been completely destroyed during electrolysis at the given electrode potential and that oxidation of sucrose to sucronic acids is probable [15 – 19].

This seems obvious because the characteristic FTIR spectrum bands of sucrose, given in Table 2, were not recorded in the explored solution after electrochemical treatment, which supports assumption of the partial sucrose oxidation in the given experimental conditions to its derivate.

Table 2. Predominant FTIR bands for Sugar Solutions [19]

Wavenumber (cm^{-1})	**Group**	**Peak Assignment**
924	CH=CH_2	CH_2 out-of Plane vibration
994	CH=CH_2	CH_2 out-of-plane deformation
1052	CH_x–O–H	C-O stretch
1134	C–O–C	C–O–C asymmetric stretch

Therefore, it seems that the partial electrocatalytic oxidation of sucrose solution at the BDD electrode potential lower with respect to OER probably gives monocarboxylic sucrose acids as main reaction products [4 – 5, 14].

CONCLUSIONS

The presented results of potentiostatic electrolytic sucrose oxidation confirms preposition, resulted from the cyclic voltammetry exploration [20] that the direct electrochemical oxidation of sucrose on BDD electrode in strongly alkaline chloride electrolytes is expected at anodic potentials > 1.1 V against SCE, near 0.5 V negative regarding OER potential, and lover than + 2.3 V against SCE. The mediated sucrose oxidation by strong oxidative species generated at BDD electrodes would be expected at potentials higher regarding OER potential.

FTIR analysis of the products of direct sucrose oxidation at BDD electrode showed that partial sucrose oxidation generates the new products such as are monocarboxylic acids of sucrose.

So, the direct or straight oxidation would be convenient in the processes of electro-organic synthesis from sucrose as row material, while the mediated oxidation by oxygen and its oxidative species is much more efficient in reduction of sucrose wastewaters COD.

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SILVER NANOPARTICLES AND HUMAN HEALTH RISK

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ABSTRACT

Nanomaterials have various applications, even as food ingredients. However, their effects on human health are not throughly investigated and potential health risk should be assessed. The objective of the present paper is to give brief overview of silver nanoparticles hazard characterization as well as to estimate consumer exposure through nanosilver water, intended to be used as dietary supplement. Mean content of colloidal silver in commercial samples of nanosilver water, determined by flame atomic absorption spectrometry, was 14.3 mg/l. Taking into account recommended use and toxicokinetic parameters, the amount of absorbed silver was estimated to be 0.5 µg/kg bw/day.

Key words: Silver, Nanoparticle, Toxicology, Food.

INTRODUCTION

Nanoparticles (NPs), defined as particles with diameter in the range between 1 and 100 nanometers, exhibit specific properties or behavior. The functional properties and potential toxicity of the NPs mainly depend on their physicochemical characteristics: discrete form or aggregate/agglomerate, size, shape, crystal structure or not, surface charge, solubility etc. The applications of nanomaterials are numerous and remarkably significant in human society, as they are included in many industrial processes and used as ingredients in a wide variety of products, including food, drinks, cosmetics, textiles.(1) Nowadays, the widespread application of manufactured nanomaterials causes an increase in the population exposure through a multitude of consumer products, raising questions about related health risks. It is important to emphasize that toxicokinetic parameters (absorption, distribution, metabolism and excretion) of nanoparticles appear to be different in comparison with a conventional chemical entity.(1) In general, the degree of absorption is in correlation with the size of NPs, the surface charge, hydrophobicity, and the presence or absence of surface ligands. The speed of absorption increases with decreasing particle diameter (2); consequently, if aggregation of NPs in the digestive lumen occurs, their absorption speed will decrease. The distribution of NPs after absorption differs, depending on the nature of NPs and biological system: some

NPs enter the portal circulation and the liver or lymphatic system, others are excreted in the feces and urine (3). Overall, due to the physicochemical properties of nanomaterials, their toxicokinetic and toxicity profiles cannot be inferred from data on their equivalent non-nanoforms.

Silver nanoparticles

Silver nanoparticles (AgNPs) are the most widely produced NPs, with estimated global annual production about 55 tons.(4) AgNPs have widespread use in various consumer products: bedding, washing machines, water purification, toothpaste, clothes, shoes, detergents, shampoo, filters, kitchen utensils, toys, and humidifiers.(5) The most important potential benefits of AgNPs are based on their antibiotic, antifungal and antiviral properties.(6) Increasing resistancy of microorganisms to antibiotics and reduced effectiveness of these drugs is very important concern of human society. In addition to proven efficiency against a broad range of microorganisms, AgNPs prevent the occurrence of their resistance. Therefore, colloidal silver is an important alternative to the antibiotics and usage of AgNPs as an antibacterial agent in medicine has increased lately. AgNPs may also replace antibiotics in animal feed.(7) Due to their antimicrobial properties (8), AgNPs are also added to food packaging materials (9), most often as finely dispersed particles embedded in containers and coatings.

Useful application of NPs (formation of micelles, emulsions) can be considered in the food industry, due to their large surface area and reactivity. However, ageing of the particles can lead to aggregation and agglomeration and thus cause property changes. Moreover, NPs may react with biopolymers present in food matrix: proteins, lipids, carbohydrates, nucleic acids, as well as inorganic ions and water.(10) The Woodrow Wilson database lists about 40 applications of silver in food and food-related products, most of them in food supplements. (11) Aqueous dispersion of AgNPs for oral consumption is accessible on the market.(11) Therefore, oral ingestion represents a relevant route of exposure of consumers to AgNPs. When introduced into organism, AgNPs can trigger undesirable and hazardous interactions, thereby generating toxic effects, although not yet fully understood.(12)

Toxicokinetics and toxicity of silver nanopartiles

Toxicology of silver and its compounds is well known, but when silver in the form of NPs is considered there are still gaps in both human and environmental risk assessment.(6) Silver may be absorbed via the gastrointestinal tract, lungs, mucous membranes, and skin lesions (13). With regard to the oral route of intake, some of the questions are following: to what extent the intact AgNPs enter the body or only the silver ions from the NPs are absorbed, whether they undergo changes in digestive tract, for example transformations by digestive hydrolases, whether they absorb biomolecules present in the food matrix.(14) Given the importance of the oral route of exposure to silver nanoparticles, it was of interest to investigate their fate during gastrointestinal digestion. Walczak et al. (15) studied 60 nm AgNPs and silver ions ($AgNO_3$) using in vitro model of human digestion. The study showed that AgNPs can reach the intestinal wall in their native size and composition. The absorption rate of colloidal silver after oral application can be as high as 5% (16). Once absorbed throughout the intestinal mucosa, AgNPs target the liver (17) and spleen. Most of the silver transported in blood is bound to globulins (13). In tissues, it is present in the cytosolic fraction, bound to metallothionein. (18) Silver is stored mainly in liver and skin and in smaller amounts in other organs (13). Lee et al. in 2012 (19) observed the transfer of silver from female rats to offspring after oral administration of 8 nm AgNPs, suggesting that silver crosses the placenta. The liver plays a decisive role in silver excretion, most of what is absorbed being excreted with the bile in the faeces. In mice, rats, monkeys, and dogs, cumulative excretion was in the range 90–99%. Silver retention was about 10% in the dog, <5% in the monkey, and <1% in rodents (20). In humans, under normal conditions of daily silver exposure, retention rates between 0 and 10% have been observed (13). Only limited data are available regarding the persistence of silver in the body after oral administration. The biological half-life in humans (liver) ranges from several to 50 days (18).

Despite the widespread use of AgNPs-containing products, *in vivo* toxicity data relevant for orally ingested AgNPs are rare. The best-described adverse effects of chronic exposure to silver in humans are permanent slush-grey discoloration (argyria or argyrosis) of the skin and/or eyes.(27) Based on several published studies, Gaillet and Rouanet (1) concluded that repeated ingestion of AgNPs may induce organ toxicity and inflammatory responses in mice. In some animal toxicity studies an increase of various liver enzymes was observed, indicating liver toxicity after a silver nanoparticle administration. However, liver toxicity could not be observed by histopathology.(21) Yu et al. (22) studied the potential effects of AgNPs on pregnant rats and embryo-fetal development after maternal exposure. Their findings indicated that repeated ingestion of AgNPs during pregnancy caused oxidative stress in hepatic tissues, but did not caused developmental toxicity at studied doses. Hong et al. (23) performed reproduction/developmental screening test that showed no evidence of toxicity.

The safety, health and environmental effects of nanosilver have been recently reviewed by the Scientific Committee on Emerging and Newly Identified Health Risks (SCENIHR).(21) Overall, human toxicity of both silver and nanosilver has been reported as low. While *in vitro* studies with silver nanomaterials reported cytotoxic effects, genotoxic DNA damaging capacity, and developmental toxicity; the *in vivo* studies could not confirm the same effects. *In vivo* repeated dose toxicity studies did not result in alterations in the specific immune responses; the *in vitro* studies, in contrast, reported an induction of cytokine in macrophages and natural killer cell activity. Thus, further studies on the effects of silver nanomaterials on the immune system and its functionality are needed. (21)

The mechanism(s) of AgNPs-induced toxicity are not well understood. Several published studies have established strong link between production of radical oxygen species mediated by AgNPs, the oxidative stress and cytotoxicity.(24) Kim and Ryu (25) reported oxidative stress induced by oral exposure to AgNPs. Cytotoxicity is a direct consequence of oxidative stress caused by AgNPs and release of Ag ions. Zhang et al. (26) used electron spin resonance to show that the active surface of AgNPs can directly induce the generation of free radicals. The dissolution of AgNPs into Ag ions triggers the production of hydroxyl radicals. In many studies, the release of ionic silver has been considered as the main cause of toxicity (both in humans and in the environment), however, an increasing number of studies found that this release cannot alone account for the observed toxic effects.(21) These results indicate that oxidative stress is an important factor of AgNPs toxicity.

Exposure limit

On the basis of present epidemiological and pharmacokinetic knowledge, several estimates of exposure limit (health-based guidance values) were provided for silver. According to the WHO, for the general human population a total lifetime oral intake of about 10 g of silver can be considered as the No Observable Adverse Effect Level (NOAEL), related to the sum of all exposure routes.(27) Considering a lifetime of 70 years and body weight (bw) of 70 kg, this value is expressed as 5 μg/kg bw/day. The EU considers an Acceptable Daily Intake (ADI) of 0.3 μg/kg bw/day for silver ion, but no specific exposure limits have been calculated for nanosilver.(21) In a review by Hadrup and Lam (28), a Tolerable Daily Intake (TDI) of 2.5 μg/kg bw/day for oral exposure to colloidal AgNPs was established. This TDI was calculated by dividing the NOAEL by a safety factor of 100. The NOAEL of 0.25 mg/kg was derived from significant increase of TGF in serum of mice exposed during 14 days to 22 nm silver particles.

A detailed risk assessment of nanosilver has not been performed since available information is too limited. It is strongly recommended to perform risk assessment of nanomaterials on a case-by-case basis as there are insufficient data to allow generic approaches.

MATERIAL AND METHOD

In total, ten samples of "Srebrna voda" were analyzed on colloidal silver content during 2012-2014. All samples were produced in Serbia by electrochemical process (electrolysis of silver 99.99%) in pure water (double distilled water). The samples were packed in dark glass bottles with volume size 0.5 l. The label contained the following information: nanosilver (colloidal) 15 mg/l in double distilled water, quantity in 15 ml: 0.225 mg Ag, recommended use: take 15 ml of "Srebrna voda", two to three times per day.

After dilution (1:10) and acidification with nitric acid (63%, trace element grade) to pH<2, solution was analyzed using flame atomic absorption spectrometry (Thermo Scientific iCE 3000 Series). Laboratory method performance was characterized by limit of quantification of 0.5 mg/l, precision expressed as relative standard deviation of 5.81%, and measurement uncertainty of 0.75 mg/l.

RESULTS AND DISCUSSION

Number of analyzed samples per year, arithmetic means and medians, as well as minimum and maximum of silver concentration are given in Table 1. Only concentration of silver but not size of nanosilver particles was determined. Minimum and maximum silver concentrations were 12.87 mg/l and 15.40 mg/l, respectively. The average silver concentration was 14.3±0.75 mg/l, thus confirming the content of silver declared on the product label.

Table 1. Descriptive statistics for silver concentrations measured in "Srebrna voda"

Year	2012	2013	2014
Silver concentration, mg/l	13.88	14.91	13.50
	14.13	14.41	15.40
	12.87		14.80
			15.16
			14.36
N	3	2	5
Ntot	10		
Mean, mg/l	14.34		
Median, mg/l	14.38		
Min, mg/l	12.87		
Max, mg/l	15.4		

N – number of samples

If a consumer, following the quantity and frequency of consumption recommended by the producer, takes 15 ml of silver water three times per day, the resulting intake would be 0.644 mg of silver per day (or 9.2 μg/kg bw/day for a person with body weight of 70 kg). However, given the ratio of ingested and absorbed amount of silver (20:1; 5% absorption rate), the internal exposure will be 20-fold lower, i.e. 0.032 mg per day (or 0.5 μg/kg bw/day). As a result of lifetime use (70 year or 25550 days), about 16 g of silver originating from silver water consumed as dietary supplement could be introduced into the body, 0.8 g of which could be expected to be absorbed. However, it is not likely that a dietary supplement will be consumed throughout the very long time period. Presented calculations are made to give an insight into the contribution of one specific source of exposure to AgNPs. Given the fact that there are numerous possible sources of AgNPs among us, it is not an easy task to interpret the obtained values and it is not appropriate to compare it directly to the exposure limit. Differences between the limit values set by different organizations, as mentioned above, are an additional difficulty. Nevertheless, the estimated exposure through silver water could not be characterized as insignificant, and should be cautiously taken into account in overall exposure assessment.

The European Food Safety Authority (EFSA) in 2008 expressed inability to assess the safety on silver hydrosol as a source of silver in food supplements.(29) Silver hydrosol represented an aqueous colloidal suspension of nanoparticles of silver with an average size of 0.8 nm at a concentration of 10 mg/kg or 23 mg/kg in purified water. The EFSA Panel considered that data on ionic silver cannot be used to establish the safety of silver hydrosol, while toxicological data provided for silver hydrosol were insufficient to allow hazard characterization.

CONCLUSION

The main pillars of human health risk assessment are hazard characterization and consumer exposure. Accurate characterization of hazard demands multidisciplinary investigations, and the most relevant issues necessary to be resolved in order to assess the risk associated with nanomaterials include proportion of NPs that pass through the gastrointestinal barrier, their accumulation in certain organs and biopersistence, and their long-term effects. Assessment of consumers exposure is associated with the knowledge of potential food uses and presence of NPs in foodstuffs, but data addressing these issues are scarce. The risk assessment of nanomaterials needs to include both nanospecific properties and those common to the equivalent non-nanoforms. Caution should be kept in mind when use of nanoparticles in food is considered.

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SHAPE MEMORY ALLOYS AND SOME OF THEIR MEDICAL APPLICATIONS

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ABSTRACT

Shape memory alloys – SMA are specific materials which have unusual characteristic to change their shape and return to some memorized state, according to the environment temperature. The area of usage of shape memory alloys is very large and heterogeneous. Very often, this materials are biocompatible, which enables their usage in medicine. This paper will present some basic characteristics of the shape memory alloys, different types of their transformations, and some possibilities of their medical applications.

Key words: shape memory alloys, biocompatibility.

INTRODUCTION

The possibility to return to some remembered state, i.e. shape memory effect, has been firstly noticed on the copper based alloys (Cu-Zn and Cu-Sn) in thirties years of the past century [1]. But, one of the most frequently used shape memory alloy, known as Nitinol (alloy on the basis of nickel and titanium) was revealed in the sixties years of the past century in Naval Ordnance Laboratory in USA, which is commonly assigned as the origin of the investigation in the shape memory alloys field.

The first reported and documented large usage of SMA was in 1971. for a coupling which was used to connect titanium hydraulic tubing installations in the Grumman F-14 air-craft [2]. The titanium tubes were used due to a recommendation for the lightening of the whole construction, and the main problem solved on that way was their joining with SMA coupling.

In the eighties of the past century, the significant usage of the shape memory alloys for manufacturing the valves for air-condition devices was reported in Japan. Approximately at the same time started the large usage of the shape memory alloys primarily in dental, and after that, for all other medical applications.

There is always an aspiration for the usage of new materials, which was primarily developed for the military and aircraft industry, in the medicine, for manufacturing of the compatible and functional implants, with a goal to enhance the quality of the patient's life [3].

THE SHAPE MEMORY EFFECT

The main characteristic of the SMA is their shape transformation, caused by changes in the environment temperature. Depending on the environment temperature and amount of the applied load, shape memory alloys can be present in two different crystal structures, i.e. phases [4]. The low temperature phase is martensite, while the high temperature phase is austenite, Figure 1. Solid state phase transition from martensite to austenite, and vice versa, is a key process which enables shape changing of the SMAs. This effect is called marthensitic thermoelastic transformation [5]. Starting and finishing temperatures of the martensite transformation, as well as starting and finishing temperatures of the austenite transformation depends on the physical and chemical characteristic of the alloy. There are four characteristic temperatures of the shape memory effect:

M_s – Martensite start forming temperature
M_f– Martensite finish forming temperature
A_s – Austenite start forming temperature
A_f – Austenite finish forming temperature

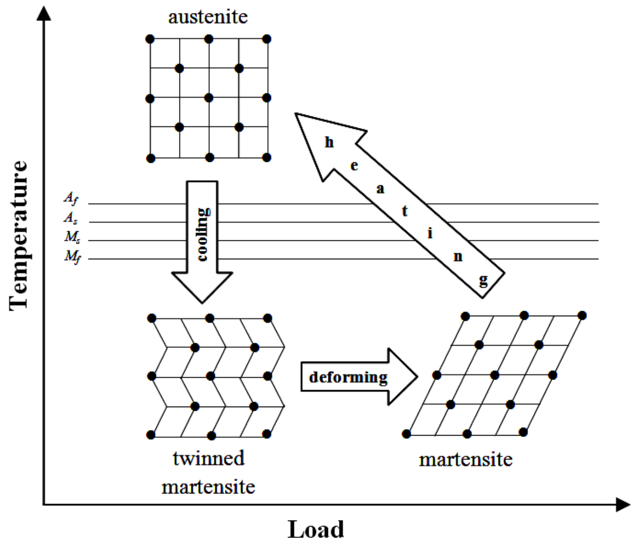

Figure 1. Austenite-martensite transformation

a) One way shape memory effect

In the one way shape memory effect material is firstly deformed at some lower temperature. Due to the one way shape memory effect, the material can return to its memorized shape by simple heating, as shown at Figure 2.

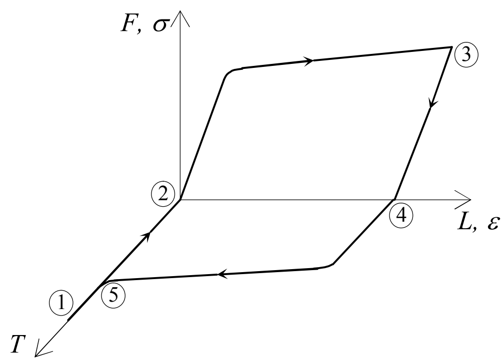

Figure 2. One way shape memory effect

At the beginning, the specimen is on the room temperature in the austenite state (point 1). The first phase is forming of the martensite by reduction of the temperature, without any loading (point 2). After that, the low temperature deforming begins, using external load – *F*, which causes changes in the specimen dimensions – *L* (point 3). After unloading, the specimen is still in the deformed state (point 4). The specimen returns to its origin, undeformed shape, by simply heating, which is followed by the transformation from martensite to austenit (point 5).

b) Two way shape memory effect

The main characteristic of this effect is changing of the materials shape by its alternately heating and cooling, without any external forces, Figure 3.

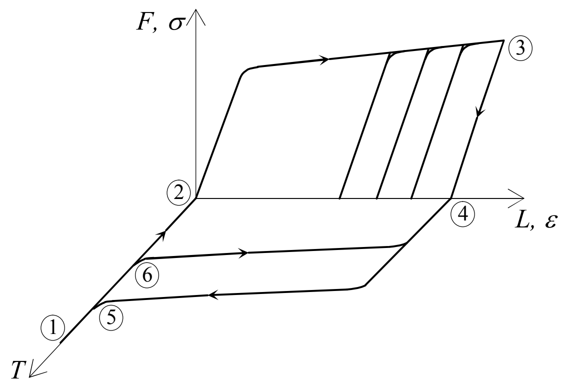

Figure 3. Two way shape memory effect

Primarily, the specimen is in the austenite state on the room temperature (point 1). Transformation from austenite to martensite takes place by cooling, without the external loading (point 2). The specimen is loading and unloading many times, on the low temperature, using external force – *F*, in order to "rememer" its deformed shape (point 3). After unloading the specimen remains in deformed shape, with changed dimension – *L* (point 4). Transformation from martensite to austenite ocurre with heating, and the specimen returns to its original, undeformed shape (point 5). But in this case, with another cooling of the specimen (point 6), without external loads, the specimen takes it's deformed, i.e. "remembered", shape (point 4). On that way, the dimensions of the specimen are changing without any external loads, only by heating and cooling.

c) Superthermoelastic effect

With loading with external forces the material is deformed. The ability of the specimen to return to its original state, after unloading is known as elasticity, and that characteristic have almost all materials. But only few materials have the ability to accept extremely large loads and return to its original shape after unloading. This characteristic is known as superelasticity or pseudoelasticity. Superthermoelastic effect includes superelastic and superthermic effect.

Superelastic effect: This effect happens at the constant temperature (Figure 4 a)). In the beginning, the specimen is in the austenite state (point 1). Loading of the specimen with external force – *F* causes changing in the dimensions of the specimen – *L*. Increasing of the external load leads to the large deformation of the specimen, followed by the formation of martensite in the interior of the austenitic phase of the material [1]. The maximum deformation of the specimen is noticed in point 3. Finally, the specimen is released and it returns into original shape, shown with points 4 and 1. This occurrence is similar to the classical elasticity, but the deformations of the superelastic materials are multiple times larger than the deformations of the classic materials.

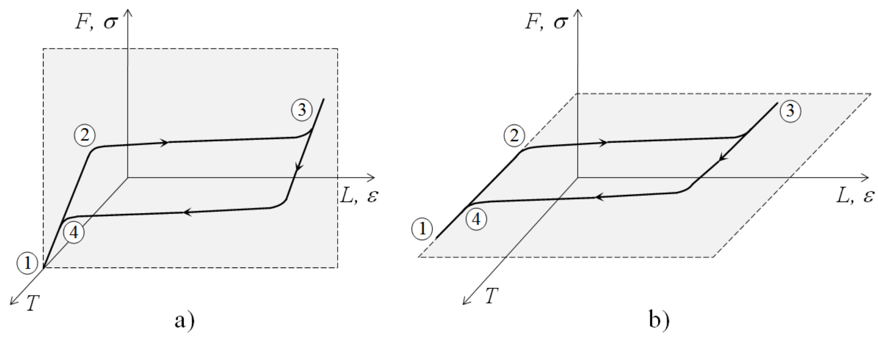

Figure 4. a) Superelastic effect, b) Superthermic effect

Superthermic effect: Unlike the superelastic effect, this effect happens during loading with the constant external force – *F*, Figure 4 b). The specimen is in the austenite state, at the begining (point 1). Decreasing of the temperature leads to the changing in its dimensions – *L*. With further decreasing of the temperature, forming of the martensite inside the austenite phase happens, which leads to the maximum specimen deforming, shown with points 2 and 3. This process is reversible, because the specimen returns to its original, undeformed shape with temperature increasing (point 4). The changes in the material shape occur with the changes in the environment temperature, similar as in the case of two way shape memory effect.

MEDICAL APPLICATIONS OF THE SHAPE MEMORY ALLOYS

Two main demands which medical implants must fulfil are biocompatibility and biofunctionality. Biocompatibility means that used implant material is non toxic, while biofunctionality provides smooth execution of all needed functions of the implant in the required period of time [6].

Applications in orthopedic surgery

Various kinds of metal plates are already widely used in orthopedic surgery. But metal plates and other orthopedic devices made from shape memory alloys provide some new possibilities. The bone healing is much better in cases when broken parts are pressed toward each other during healing. This external force can be obtained by using of SMA plates. For such a purpose SMA plates are deformed on the lower temperature, and then applied on the broken bone. After application, the body temperature causes returning on the memorized shape, providing on that way necessary force which stuck together broken parts, Figure 5.

Figure 5. SMA plate for bone fixation

Dental applications

Dental braces are medical devices that provide normal teeth growth and correction of the teeth disposition, Figure 6. The braces wires made from SMA provides necessary external forces, which shouldn't be too large because there is a danger to deform teeth, and also shouldn't be too small because they will not be able to realize main purpose. SMA braces enables constant and uniform external forces, which affects the teeth during long period of time, avoiding the need for frequent dentist interventions.

Figure 6. Shape memory alloy dental braces

*Cardiovascular application*s

Shape memory alloy devices are very commonly used in cardiovascular field, avoiding on that way the need for classic operation which requires totally anaesthesia. The SMA stents, shown on Figure 7, are very often used devices, and their application is based on the shape memory effect. After proper appliance, the stent enables constant fluid flow in the potentially dangerous zones.

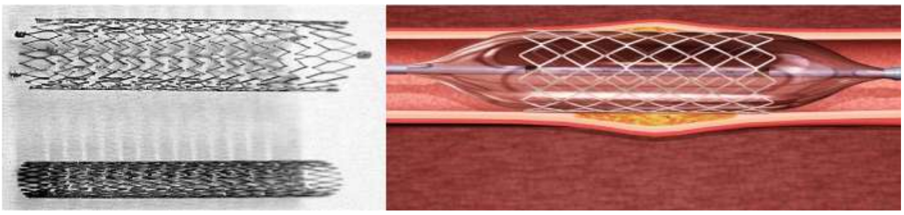

Figure 7. SMA stent and its shape after appliance

Surgery instruments and tools

The nowadays surgery requires minimal damage of the tissue, which brings the tendency toward small, extremely precise instruments and tools. The ability of the instruments made from SMA to remember complicated shapes, as well as superelastic effect, are very important characteristics that can upgrade surgical instruments. For example, the shape memory alloy basket is often used for removing kidney or bladder stones. The other shape memory alloy surgery instruments, which are often in usage, are in the form of guidewires, catheters, laparascopy instruments etc.

CONCLUSION

Shape memory alloys generally have good mechanical and physical characteristics. Their ability to remember some previous shape is widely used in almost all fields of science and engineering. Their biocompatibility is one of the advantageous characteristics which classify them into the priority class of materials for biomedical usage. In the first part of this work, one way shape memory effect, two way shape memory effect, superelastic and superthermic effects are presented. After that, some examples of the medical applications of shape memory alloys are presented.

Acknowledgments

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FEED MATERIAL QUALITY ADJUSTMENTS IN HOLCIM CEMENT PLANT FROM THE ENVIRONMENTAL PROTECTION ASPECT

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ABSTRACT

Portland cement production requires the product quality to be within the legal limits with minimum, below maximum allowed, environmental impact. This is achieved by proper adjustment of clinker production feed and fuel quality, and constant monitoring of flue gasses.

Accordingly, Holcim cement plant Popovac developed its own standard named Holcim Raw Materials Management supported by appropriate software tools.

Proper adjustment in raw material composition and fuel composition results in the achievement of environmentally acceptable composition of flue gas.

Key words: cement production, raw material quality, environmental protection.

INTRODUCTION

Mining as industrial branch covers exploitation and processing of raw materials with dominant materials being energetic, metalic, nonmetalic and construction. Production of construction materials is profitable industrial branch leaned to exploitation of stone, construction sand, cement production raw materials, industrial carbonates, quartz sands, clay etc.

Limestone, clay, marlstone and clay marl are basic feed materials for clinker production in the process of cement production. During process other materials are used, such as industrial byproducts and waste as well as other raw materials bearing aluminium oxide, iron and silica.

Apart from basic materials corrective mineral additives are also used in cement production.

Holcim (Serbia) d.o.o. cement plant Popovac provides its basic raw materials from Trešnja marlstone quarry (Fig. 1), and Čokoće limestone quarry (Fig. 2).

The deposits were additionally explored and tested for introduction of Holcim Raw Materials Management system (RMM), supported by QSO Expert (Quarry sheduling optimisation expert) [3], QuarryMaster [4] and MixOpt software tools. These tools are the foundation of successful and profitable cement production achieved through adjustments and optimization of feed material quality.

This article analyzes basic and corrective raw materials from the aspect of strategic and operative production planning. Additionally the article explains the quality control and optimization during production and presents the achieved results and predicted impact of this concept to emission.

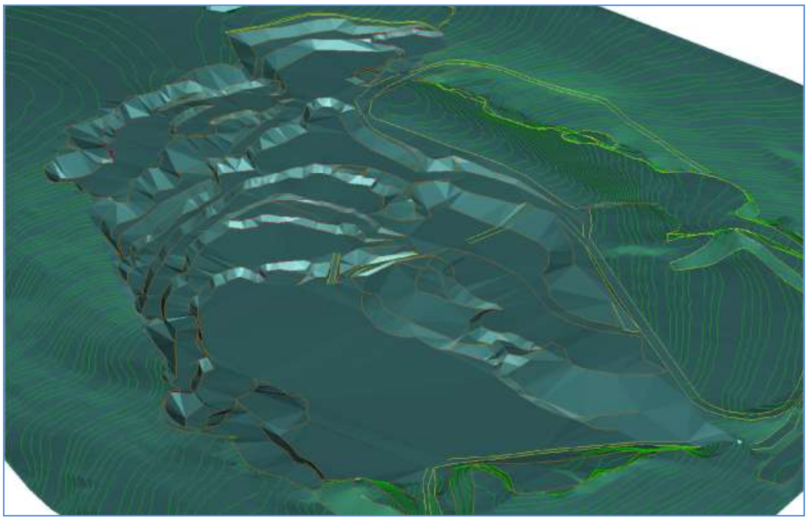

Figure 1. Trešnja quarry [1]

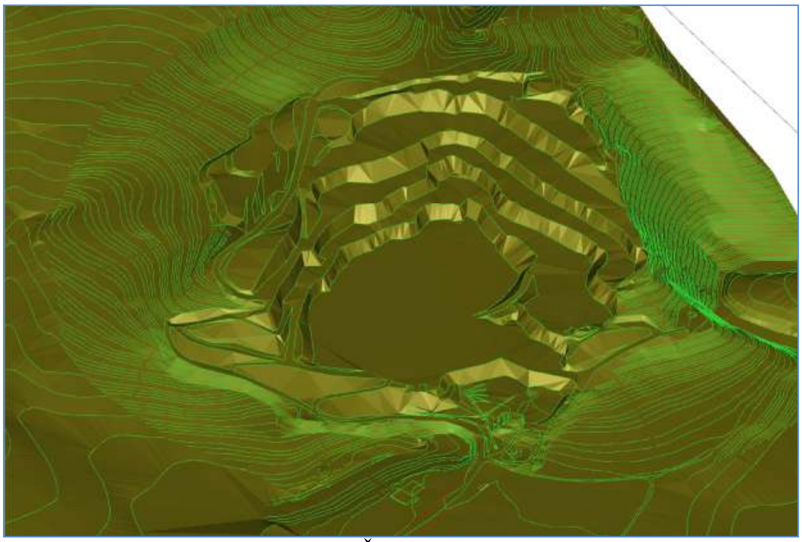

Figure 2. Čokoće quarry [1]

CEMENT INDUSTRY RAW MATERIALS

Cement production raw materials can be classified into basic raw materials and additives. Basic raw materials are mainly limestone and clays and aluminum oxide, iron and silica bearing materials provided mainly from industrial waste and byproducts.

Mineral additives are components used in clinker production (gypsum and inert materials).

Specific requirements for basic materials and additives quality are defined by clinker production raw material flour quality. It is defined by the specific oxides content and limit in content of harmful components. Harmful components are MgO, Na_2O, K_2O, SO_3, pyrite sulfur expressed as SO_3, TOC (total organic carbon), VOC (volatile organic carbon) and ammonia (NH_3).

The relations of specific oxides are expressed via silica module (SM), aluminum module (AM) and saturation degree (SZ) calculated as:

$$\mathbf{SM} = \frac{SiO_2}{(Al_2O_3 + Fe_2O_3)}$$

$$\mathbf{AM} = \frac{Al_2O_3}{Fe_2O_3}$$

$$\mathbf{SZ} = \frac{CaO}{(2{,}8SiO_2 + 1{,}18Al_2O_3 + 0{,}65Fe_2O_3)}$$

Clinker production quality demands these modules to be in the following ranges SM = (2,6 ÷ 2,8), AM = (1,9 ÷ 2,3) i SZ = (98 ÷ 103).

Allowable content of harmful components is up to 2.5 % of MgO and up to 0.7 % of SO_3.

In order to protect the environment emission factors (pyrite sulfur, VOC and NH_3) are also limited to following values:

TOC	0.13%	limit value (0.10 ÷ 0.17) %
Pyrite sulfur	0.11 % SO_3	limit value (0.08 ÷ 0.16) % SO_3
NH_3	110 ppm	limit value (80 ÷ 180) ppm

CLINKER PRODUCTION FUEL AND EMISSION PREDICTION

Clinker production requires high temperatures provided by use of appropriate fuels, both traditional and alternative. Traditional fuels are calorific coals and petrol coke with average ratio of 65% to 35%.

Alternative fuel is mechanically comminuted solid non-harmful waste after it is analyzed in order to define its composition. Alternative fuel is also called Solid Recovered Fuel, short SRF and it mainly represents industrial waste (textile, wood etc), commercial waste (non-recyclable packaging waste), sorted communal waste and other waste. The use of alternative fuels is justified by the fact that waste can be used as fuel and replace traditional fuel. Alkali – sulfate battery in clinker furnace makes it suitable for co-processing of alternative fuels since emission of SO2, VOC and NH3 do not depend on the type and the amount of fuel used.

However, for the purposes of modeling it is assumed that the fuel is the usual mix of coal and coke (characteristics in Tab. 1), in order to incorporate the affect of ash to product quality and not to emission [1].

Table 1. Average fuel characteristics

Parameter	**Unit**	**Fuel**	
		Anthracite	**Coke**
Lower calorific value	kJ/kg	27 000	32 800
Ash content	%	14.7	1.0
Sulfur	% S	0.97	4.57

Relative emission components content is defined for each block in 3D model in order to enable their content calculation in feed mix. In order to enable emission prediction 5 representative limestone samples were analyzed showing that TOC content is below detection limit of 0.07%. VOC presence in limestone was below 10 mg/Nm^3 and is considered very low.

TOC is high for all marlstone units, and tests were performed on 3 representative samples. TOC content in these samples is in the range of 0.3 % to 1.13 % and coveres the whole TOC spectrum for the entire deposit. Predicted VOC emissions for these marlstone samples are in the range of 50 to 400 mg/Nm^3, and are considered high. This prediction is used to set limit values and limit use of deposit parts.

As said, operative calculations use average values of emission components (TOC=0.13%, pyrite sulfur=0.11 % SO_3 and NH_3=110 ppm)

HOLCIM RAW MATERIALS MANAGEMENT (RMM)

In order to adjust feed quality, i.e. to manage raw materials Holcim developed its own system.

The foundation of the system is 3D block model of the deposits. Besides the standard features of block model each block has attributes defining harmful components by type and amount.

RMM also utilizes the data on fuel characteristics

Based on the data from the block model QSO Expert tool defines extraction locations in order to provide homogenous raw material for the purpose of long and mid term planning resulting in isle-like mining operations development.

QM software is short term planning and raw material optimization tool. It is a direct link between QSO Expert and the demand for the specific quality of feed material set by quality control. In this manner production planning becomes essential part of quality control. It is developed as a link between mine operations planning and feedback after the first stage of homogenization.

MixOpt optimizes the feed composition in such way that once in contact with fuel and the ash the feed composition contributes to the quality of clinker. This tool checks the scenario set by QM and accepts or corrects the ratio of basic and corrective materials upon the results of the check. The result is the achievement of required clinker quality and acceptable composition of flue gas. Scenario correction considers the changes in the amount and the quality of feed material which, in some cases, means changes in material extraction location in the mine itself.

EXAMPLE

Cement plant measures harmful components in raw materials and flue gas. The reason is to establish correlation which can then be used to plan the composition of feed material within the RMM. An overview of the flue gas harmful components values for 2014. Is given in table 2.

Table 2. Overview of the flue gas harmful components values [5]

No	Component	Quarter in 2014				Average
		I	II	III	IV	
1	SO_2	8.35 mg/m^3	7.42 mg/m^3	14.29 mg/m^3	14.44 mg/m^3	11.12 mg/m^3
2	VOC	19.83 mg/m^3	20.8 mg/m^3	22.18 mg/m^3	22.97 mg/m^3	21.44 mg/m^3
3	NH_3*	July 2014., below 0.38mg/m^3		October 2014., below 0.38mg/m^3		0.38mg/m^3

* - Ammonia measurements are performed twice a year according to regulations

CONCLUSION

Holcim cement plant hast limestone quarry Čokoće and marlstone quarry Trešnja. The quality of the raw materials is variable and in order to achieve required cement quality it is necessary to manage feed material. Besides the basic raw material feed management covers the quality of corrective additives, fuel and other additional raw materials such as gypsum. Besides the quality of cement management of feed material also influences the composition of flue gasses ensuring that all harmful components of flue gas are below maximum allowable limits. To successfully manage feed materials Holcim developed its own system named Holcim Raw Materials Management. It is supported by a set of software tools for block modeling, long, mid and short term scheduling, optimization and quality control. The principle of operation is rather simple. Upon the results of quality control of cement and composition of flue gas the system adjusts the composition of feed material. It then runs a simulation of the process with adjusted feed composition and if the simulation results are satisfactory in terms of cement quality and harmful flue gas components concentration the system accepts the adjustment. If the results do not meet the required standards the procedure repeats.

RMM system and simulations are used to perform long term mining operations scheduling, i.e. to plan the mine development, but also for short term, daily mining schedule. Data on feed – fuel mixture quality, gas emission and cement quality are continuously monitored and fed back to the system.

The result of the raw materials management is achievement of standardized cement quality and concentration of harmful components of flue gasses below maximum allowable values.

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THE IMPACT OF THE PRODUCTION AND USE OF POLYVINYL CHLORIDE ON THE ENVIRONMENT

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ABSTRACT

The paper presents the most important characteristics of polyvinyl chloride (PVC), the types of additives that are added to it to improve its properties (primarily mechanical) and its field of application. Particular emphasis is placed to how the process of production of PVC and its application affect to the environment as well as protection measures. Bearing in mind that the environment is more hazardous, is now a serious attention is paid to recycling which can be used plastic waste and thereby also reduce environmental pollution.

Key words: polyvinyl chloride, environmental protection, recycling.

INTRODUCTION

Polyvinyl chloride is more than 70 years one of the most important polymers, whose production capacity is about 20% of the total world production of polymers. Its application is extremely broad which results in the presence of large amounts of PVC waste. Therefore, serious attention is given to the rehabilitation of such waste in order to protect the environment. Environmental protection includes: preservation of clean air, land and water, removing the waste material, noise and radiation protection, use of resources, cultivating sources and so on. [1]. In the Republic of Serbia in 2009. brought the Law about waste management, which regulates the following: type and classification the waste material, planning and operators of waste management, the responsibilities and obligations of waste management, financing the waste management etc. [2]. Recycling is the set of activities which ensure the re-use of waste materials. By recycling is achieved saving of raw resources (all materials origin from the nature and has limited quantities), saving energy (no energy loss in the primary processes, as well as in transport which following that processes, and additional energy is obtained by burning materials that are not recycled), environmental protection (waste materials degrade living environment, and it is protecting by recycling) and creation of a new jobs (processes in the recycling of materials includes investment of knowledge and work, which creates the need for new working places) [1].

POLYVINYL CHLORIDE (PVC)

In the procedure of polymerization the vinyl chloride, obtained the powder from which by further processing of products we get two types of PVC: rigid PVC and soft (flexible) PVC. Rigid PVC is obtained by processing the polymer powder without special additives. It is transparent, hard, tough and difficult for processing, but very stable on the influence of atmospheric precipitation, humidity and chemicals. It is used, for example, for making window frames, casing boxes, etc. Soft PVC is obtained by processing the polymer powder with the addition of plastificators from whose share depending by its properties, also. It has weaker mechanical properties, less resistant to heat, precipitation and chemicals, compared to the hard PVC, but is more flexible, elastic and it is easier for processing. It is used for making insulators for cables, medical instruments disposable, tubes, gloves,etc. Soft PVC is transparent, and can be used to make transparent bottles and foils. Generally, it can be said that the properties of polymers are determined by their internal structure,and some of their properties are the similar like characteristics of solid crystalline bodies,while some are similar characteristics to liquids [3]. Physical and mechanical properties of hard and soft PVC and are shown in Table 1.[4, 5].

Table 1. Physical and mechanical properties of PVC

Property	Unit	Rigid PVC	Soft PVC
Density	g/cm^3	1,38-1,55	1,16-1,35
Tensile strength	MPa	40-60	10-25
Extension at break	%	30-70	250-450
Comprenssive strength	MPa	55-90	6-12
Shore hardness	-	D 65-85	A 40-100
Specific heat capacity	J/K g	0,8-1,1	1,3-2
Thermal conductivity	W/Kcm	(15-20)x10^{-4}	(13-17)x10^{-4}
Coefficient of thermal expansion	1/K	(5-10)x10^{-5}	(7-25)x10^{-5}
Temp. of coninuous use	^{o}C	65-85	50-70

Production of PVC is big, because of good mechanical and physical properties, as well as a numerous variety of application possibilities. PVC is a nonflammable, burning only in the presence of a flame and is chemically inert. Because it contains chlorine, a melting point of PVC is very high (100-260 ° C) so, in the case of fire, has the characteristic of self-extinguishing. PVC is easily decomposed at very high temperatures producing hydrochloric acid and corrosive gas. It is compatible with many additives, including fillers, plasticizers, stabilizers, lubricants, pigments, and other polymers. Figure 1 shows the share of certain additives to PVC [6]. These additives make possible to process more easily by various techniques and to obtain products with even better mechanical properties [7, 8].

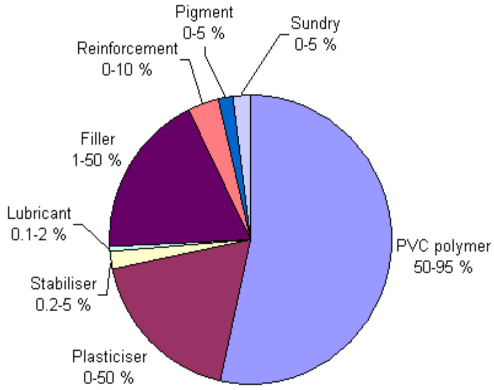

Figure 1. Proportion of certain additives in PVC mixture

During the production of PVC are formed dioxins which are among the most toxic chemical compounds, and ethylene dichloride or vinyl chloride which are in the form of gases and through the waste water discharge into the environment. Dioxins are formed as unwanted by-products, also in many other industrial processes that use chlorine, such as the production of chemicals and pesticides, bleaching of pulp and paper, and waste incineration. These are highly toxic substances in the environment, which are natural processes almost intact. Dioxins are organic compounds belonging to the group of polycyclic aromatic hydrocarbons (polychlorinated dibenzo-p-dioxins PCDD) with similar physical and chemical properties. PCDD include 75 different isomers of which the most dangerous is 2, 3, 7, 8-tetrachlorodibenzo-p-dioxin (TCDD), or simply "dioxin" [9]. The main problem in the life cycle of PVC from the manufacturing process, to the recycling process is formation the dioxine.

RECYCLING OF PLASTICS AND PVC AND PROTECTION MEASURES

Successful recycling of plastic waste began in the moment when it is developed the method for separating different polymers from mixture. Today, the research in the field of processing of waste materials is very well developed, which contributed to reducing the level of pollution of the environment. The process of recycling the waste by different composition in recent years is the most developed in Japan, by designing machines that can process it. At the beginning of 1975., in Japan was more than 20 factories, whose production capacity, annually, was approximately 40.000 tons of finished products. These products are used as a substitute for wood and concrete, because they are cheap, resistant to the high temperatures, atmospheric precipitation etc. In order to successfully processed such a waste material, it is necessary to contain 80% of the thermoplastic (PVC, polyethylene, polystyrene, nylon, etc.), and the rest may be paper, aluminum foil, sand, etc. [10]. To the recycled material, in a certain percentage can be added the new non-recycled materials, and then it can be re-processed resulting in a lower price of a definitive product. PVC waste can be treated in three ways: by recycling, incineration and storage in dumps. PVC waste can be successfully recycled;

recycling mark is 3, Figure 2. Burning must be strictly controlled due to the release of toxic substances. Disposal in landfills is the least acceptable, because PVC is not naturally degraded, so that eventually formed large deposits which is not good for the environment. However, regardless the existing difficulties in terms of PVC waste remediation, the main reasons for its wide range of applications are quality and saving energy and raw materials. For the production of PVC it is necessary 20% less energy than for the production of other types of plastic. Also, the raw material for PVC is chlorine, which is obtained by processing ordinary salt (60%). PVC is considered as material that is difficult and expensive to recycle, but the advent of new technologies solved this problem successfully. As the example of recycling PVC in Figure 2, is given a closed cycle of recycling PVC window profiles [11].

Figure 2. The cycle of recycling PVC window profiles

In order to avoid a negative impact on the environment in the complete processing of PVC we take care about additives that are added. Thus, for example, in the production of window profiles, instead of lead-based stabilizers in practice are increasingly using stabilizers based on calcium and zinc [12]. The application of new and modern technologies in the process of recycling waste plastics can reduce the level of release of toxic substances. The best example is the company "Envion" from Washington, which is operating in Maryland and converts waste plastics into synthetic oil. This technological process does not even require prior separation of plastics by type and origin [13]. Time of degradation the waste plastics is 100-1000 years. Because of that, it is necessary to implement a measure of collecting plastic separately from other waste [1]. Within the framework of regulations and planning documents of the EU, increasingly promote waste reduction, which would reduce the waste problem at the source. There is, however, a significant difference in the application of this principle in EU member states. The percentage of waste recycling ranges from 10 to 65%, and the percentage of waste disposal to landfill from 10% to 90%. The principle of reducing the amount of waste includes initiatives for the introduction of cleaner technology and comprehensive campaign to raise public awareness among the population. EU policy about waste material emphasizes the development of measures such as the promotion of cleaner production, removal of hazardous characteristics of waste treatment, the establishment of technical standards to limit the content of certain hazardous substances in products, promoting re-use and recycling of waste, the use of economic instruments, analysis of the product life cycle, development of eco-labeling system [14]. The implementation of environmental policy is based on the precautionary principle and the principle of prevention. Each activity must be planned and implemented in a manner that causes the least possible change in the environment and the least risk to the environment and human and animal health reduce the load space and consumption of raw materials and energy in construction, production, distribution and use [14].

CONCLUSION

Environmental protection is a priority task in all countries and is directly related to the degree of development of the national economy. Also, the ongoing education of the population on the importance of a healthy environment contributes to its preservation. The development of new materials and their use imposed by the question how to manage the waste generated with their processing and use. PVC is a polymer of which the production capacity and the use of constantly increasing. PVC waste can be treated in three ways: by recycling (most used), burning (must be strictly controlled due to the release of toxic substances) and stored in dumps (minimum acceptable because PVC is not naturally degraded, so that eventually formed large deposits)

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INVESTIGATION OF THE APPLICATION OF THE NATURAL AND WITH LEAD IONS CONTAMINATED ZEOLITE AS AN ADDITION IN PORTLAND CEMENT

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ABSTRACT

In presented paper results of the removal of lead ions from water solutions by the natural zeolite (clinoptilllite) and application of such contaminated zeolite materials as a supplement for standard additions portland cement are showed. In this investigations, the natural zeolite (clinoptilollite) with particle size 100% - 43 µm was used. The experiments of lead ions adsorption showed that the maximum adsorption capacity of the natural zeolite was 66 mg Pb^{2+}/g. After adsorption experiments the saturated zeolite with lead ions was used as a supplement to portland cement. Investigations of the mechanical properties of the cement with the addition, natural zeolite and zeolite saturated with lead ions showed that this material can be used as a supplement for portland cement up to 30%.

Key words: Natural zeolite, Pb zeolite, Portland cement, Flexural strengths, Compressive strength.

INTRODUCTION

Natural zeolites are crystalline hydrated aluminosilicate minerals of alkaline and alkaline earth cations, which are very widespread in nature. However, only clinoptilolite, mordenite, filipsite, chabazide, erionite, ferrierite and analcite are in sufficient amount spread in the nature so their exploitation cost effective [1]. Due to the unique properties that they have: high selective and high cation exchange capacity, high degree of crystallinity, uniform channels of molecular dimensions, a high degree of hydration and easy dehydration, low density, high absorption capacity for ions of heavy metals (lead, copper, zinc, etc.) natural zeolites found wide application:

- catalysts in many reactions,
- such as molecular sieves and cation exchangers [2]

- Adsorption of impurities in the waste water
- adsorbents for radionuclides - 137Cs [3]
- ammonia adsorbents [4,5]
- adsorbents of heavy metals ions - Pb, Cu, Zn [6]
- material for recultivation of degraded lands (ash thermal power plants, flotation tailings)
- material in pharmacy and veterinary medicine
- feed additive in veterinary medicine for the prevention of digestive problems in young animals [7].

In order to improve properties of natural zeolite (clinoptilolite), various methods of modification of the starting minerals were applied [8]. Such modified zeolites can be used as:

- adsorbent of mycotoxins that are found in animal food such as: aflatoxins, zearalenone, ochratoxin A, ergot alkaloids [2]
- tool for removing impurities from the water [9 - 11];
  weakly polar organic molecules;inorganic anions - sulfate, phosphate, chromate;
- decontaminant land-radionuclide-uranyl ion [12; 13] cesium etc.

From an environmental point of view, it is possible to use zeolites in certain ecosystems:

1 Air: adsorbent moisture, gases and unpleasant odors in the stables (NH3, CO2)
2 Water: adsorbent cations, anions, heavy metals, low polar organic molecules
3 Land: adsorbent radionuclides; tool for re-cultivation of land
4 Feed: adsorbent of mycotoxins (zearalenone, aflatoxin B1, B2 and G2; vomitoxin, ochratoxin, T-2, DAS -diacetoksiscipirenol), feed additive for the prevention of diarrhea and regulating the pH.

However, storing and keeping of once used zeolite is still not fully resolved, and very low number of studies are engaged in solving this problem. The aim of this paper is to investigate the potential use of natural zeolite (clinoptilolite) contaminated with lead ions in the cement industry as the replacement of standard additions in portland cement.

EXPERIMENTAL PART

Material. In this investigations, natural zeolite originating from Vranjska Banja, Serbia and Portland cement PC 42.5R from Beočin, Serbia were used. Chemical compositions of starting raw materials are given in table 1.

Metods. Adsorption isotherm for lead ions removal by the natural zeolite was obtained acording following procedure: 1 g of the natural zeolite was mixed with 50 ml of aqueous solution contaminated with different concentrations of lead ions (350-7200 mg/l). The suspensions were mixed 24 h, at a stirring speed of 350 min^{-1}. The initial pH was not adjusted and only was only measured and was in range from 2.8 for the maximum lead ions concentration (7200 mg / l), to 4.3 for the lowest concentration of lead ions (350 mg /l). After reaction time, suspensions were centrifuged for 10 min at 10 000 min^{-1}. Then, using the atomic absorption spectrophotometry (AAS) and the instrument "Aanalysis 300" starting and non absorbed concentrations of lead ions were determined. The amounts of adsorbed ions of lead were determined from the difference between the initial and the concentration of ions in the filtrate.

To obtain with lead ions contaminated zeolite which will be used as an addition to Portland cement, concentration of lead ions equal to the maximum adsorption capacity obtained by adsorption isotherm was used . The procedure for obtaining contaminated zeolites was:

Natural zeolite was milled to reach the grain size 100% of -43 μm, and afterwards mixed with $PbNO_3$ under following procedure: 400 g of $Pb(NO_3)_2$ was dissolved in 120 l of distilled water. Then, 3.5 kg of natural zeolite was added in lead ions contaminated water, so the concentration of lead ions in the solution was approximately equal to the maximum adsorption capacity obtained by adsorption isotherm (66 mg/g). Reaction time was 7 days with occasional mixing. After 7 days dewatering, filtration, drying and disintegration of sample was done. Finally, dry zeolite contaminated with lead ions (PbZ) was obtained. Determined adsorbed amount of lead ions was ~60 $mgPb^{2+}/g$ which is very close to the maximum adsorption capacity of natural zeolite obtained from adsorption isotherm (66 $mgPb^{2+}/g$).

Afterwards, mixing of Portland cement with zeolite: 10% (PC10Z), 30% (PC30Z), 50% (PC50Z), and 10% of Pb-zeolite (PC10PbZ); 30% of Pb-zeolite (PC30PbZ) and 50% of Pb-zeolite (PC50PbZ) in laboratory mill without balls was performed in duration of 10 minutes. On such obtained samples of cement with addition of zeolite and on starting sample (cement PC42.5R) standard physico-mechanical testing have been performed according to European Normative EN197:

- Determination of the specific surface according to Blaine (EN 196-6) (Blaine apparatus was used).
- Determination of standard consistency (EN196-3) (Vicat apparatus was used).
- Determination of the setting time of the cement dough (EN 196-3) (Vicat apparatus was used with the rod replaced by a needle)
- Determination of the compressive strength (EN 196-1).

Thusly, the following cements with additions are obtained:

PC42.5R
PC+10%-PZ = PC10Z
PC+30%-PZ = PC30Z
PC+50%-PZ = PC50Z
PC+10%PbZ = PC10PbZ
PC+30%PbZ = PC30PbZ
PC+50%PbZ = PC50PbZ

All stated cements had mass of 4000 g.

RESULTS AND DISCUSSION

Results of adsorption of lead ions from water by using natural zeolite

To determine the maximum adsorption capacity of natural zeolite for lead ions, at first adsorption isotherm was determined. This part of experiments was important, in order to define the conditions for obtaining the contaminated zeolite which will be used as an addition to portland cement.

Results of adsorption of lead ions on the natural zeolite, with particle size -43 µm are given in Figure 1. Figure 1a showed the adsorption isotherm, which is obtained as a dependence of the amount of adsorbed lead ions in mg/g vs. equilibrium concentration of pollutant in the solution after adsorption on zeolite in mg/l. Figure 1b showed dependence of the adsorption percent of lead ions vs. its initial concentration. From Figure 1a, it can be seen that, under applied experimental conditions, with increasing initial concentration of pollutants increases the concentration of adsorbed ions of lead.

The results showed in Figure 1a are fitted using the Langmuir and the Freundlich adsorption model. Mathematical forms of this two isotherms are given in equations 1 and 2.

Langmuir isotherm: $$c_{ads} = \frac{abc_e}{1 + bc_e} \quad (1)$$

Freundlich isotherm: $$c_{ads} = bc_e^{\beta}, \quad (2)$$

where c_{ads} is the concentration of the adsorbed lead ions (mg/g), c_e is the equilibrium concentration of lead ions in the filtrate (mg / l), *a is* the maximum adsorbed lead ions concentration of adsorbed per gram of adsorbent, *b* is the adsorption equilibrium constant of the surface (l /mg), and the β is factor heterogeneity and determined affinity of the adsorbent according to adsorbate.

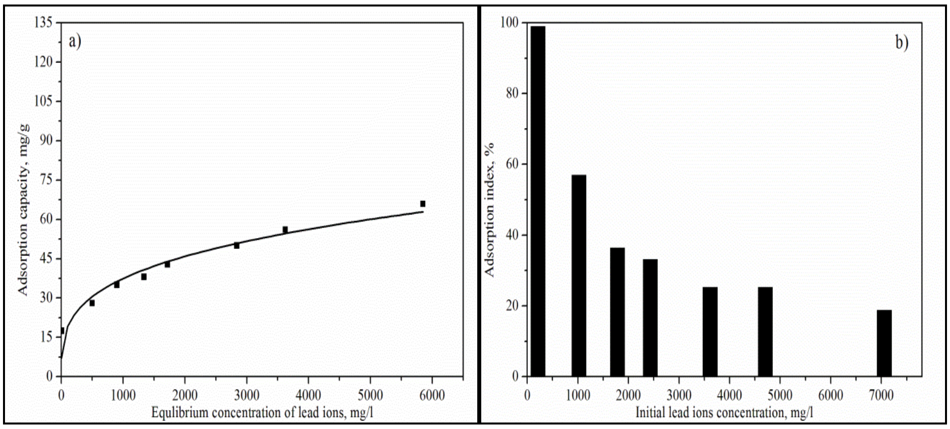

Figure 1. a) Adsorption isotherms of lead ions on natural zeolite; b) The dependency index sorption of lead in the function of the starting concentration of lead ions in solution

For results showed in Figure 1 the best fit of experimental data was obtained by the Freundlich adsorption model (r^2> 0.93) indicating a complex mechanism of binding ions lead to the natural zeolite. The maximum amount of adsorbed lead ions was 66 mg/g.

Also, we measured the pH of the suspension after the reaction time. For all initial concentrations of lead ions equilibrium pH were higher than initial, but, both, initial and equilibrium pH, decreased with increasing initial concentration of lead ions. Measuring of the equilibrium pH showed that final pH, for all initial concentrations of lead ions was lower than pH 6.0 what according to [14] mining that lead was in cationic, and dominantly Pb^{2+} form, i.e. precipitation of lead in form of hydroxide did not occur. These investigations showed that the natural zeolite (clinoptilolite) from the Vranjska banja, Serbia has a good adsorption capacity for binding lead ions from water and aqueous solutions. However, because storage of waste material (zeolite contaminated with lead ions) is still not solved, we did the second part of experiments, and investigated opportunity of using that material as an additive in Portland cement production instead of the existing standard additions.

Results of the application of the natural zeolite contaminated with lead ions as an additive in portland cement

The influence of zeolite and saturated zeolite on Portland cement quality was monitored by determining of the chemical composition, physical and mechanical characteristics.

The results of the chemical analysis of all portland cement mixes are given in the Table 1, while in the Table 2 are presented the results of physical properties of PC42.5R and PC with addition of zeolite and contaminated in various mass ratios.

As can be seen (Table 1) the content of PbO in the PbZ was 2.22. When such zeolite is added into PC in mass ratio 10 %, the 0.29 PbO is obtained (PC10PbZ). By increasing of the PbZ content in the PC, the content of PbO also increased. Thus, with 50 % content of Pb zeolite and 50 % PC 42.5R, there was 1.08 % of PbO in the PC50PbZ sample. In our previous paper [15] it was found that lead ions are connected via strong forces with natural zeolite and there is no desorption of its ions. Because of that, the Pb leaching test has not been performed in this investigation.

Table 1. Chemical composition of zeolites and portland cements

Oxide, %	SiO_2	Al_2O_3	CaO	MgO	Fe_2O_3	K_2O	Na_2O	TiO_2	SO_3	MnO	PbO	LoI
Zeolite samples												
PbZ	65.12	13.50	3.47	0.39	2.25	1.15	1.07	-	-	-	2.22	10.83
Cement samples												
PC 42.5R	24.02	6.03	59.60	2.03	1.48	0.76	0.34	0.346	3.4	0.087	0.0065	1.89
PC10Z	29.40	6.46	48.87	1.84	2.25	0.68	0.32	0.17	3.13	0.080	0.0043	6.75
PC30Z	33.11	7.89	43.73	1.64	2.23	0.81	0.45	0.17	2.70	0.066	0.0038	7.20
PC50Z	40.60	9.34	34.41	1.40	2.23	0.89	0.36	0.17	2.28	0.053	0.0033	7.92
PC10PbZ	28.10	6.71	53.87	2.00	1.58	0.82	0.55	0.646	2.80	0.084	0.29	2.75
PC30PbZ	34.83	8.02	43.66	1.91	1.57	1.04	0.71	0.346	2.68	0.071	0.72	4.44
PC50PbZ	40.75	9.54	34.98	1.80	1.53	1.01	0.88	0.329	1.88	0.054	1.08	6.16

Since the initial zeolite sample had grain size -43 μm, when this sample is mixed with Portland cement the specific surface area significantly increased what can be seen in Table 2. Standard consistency (SK, %) of all investigated cements is higher than SK of PC (29.0%), and was in the range from 31.6 % for PC10PbZ to 44.0 % for PC50FeZ.

Table 2. Results of physico-mechanical properties of the investigated cements

Sample	Fineness, %	Sp, cm^2/g	SK, %	Setting time, min	
				Start of the setting	End of the setting
PC42.5R	*0.6*	*3940*	*29.0*	*220*	*270*
PC10Z					
PC30Z					
PC50Z					
PC10PbZ	0.05	4880	31.6	190	250
PC30PbZ	0.06	6960	37.0	270	340
PC50PbZ	0.1	9840	36.8	190	250

Sample	Flexural strength, MPa			Compressive strength, MPa		
	2 days	7 days	28 days	2 days	7 days	28 days
PC42.5R	*6.4±0,8*	*8.4±0,6*	*9.6±0,8*	*33.0±0,7*	*49.0±0,8*	*61.1±1.4*
PC10Z	1.8±0,1	5.4±0,2	10.3±0,4	5.3±0,1	22.5±1,8	58.9±0.6
PC30Z	2.1±0,1	6.1±0,1	9.7±0,5	7.5±0,2	29.8±0,3	57.4±1.5
PC50Z	2.0±0,1	5.8±1,1	7.8±0,5	6.7±0,3	26.9±1,1	50.5±1.9
PC42.5R	6.4±0.8	8.4±0.6	9.6±0.8	33.0±0,7	49.0±0.8	61.1±1.4
PC10PbZ	6.2±0.4	7.5±0.7	9.2±0.2	25.2±0,8	41.2±0.9	63.3±2.1
PC30PbZ	4.3±0.1	5.9±0.2	8.5±0.5	17.0±0.4	31.3±0.7	57.3±0.6
PC50PbZ	2.4±0.1	4.2±0.6	6.9±0.3	10.0±0.6	23.4±0.1	44.9±1.5

According to the Point 17 of Regulation [15] which concerns cement PC 42.R and similar cements (according to the SRPS EN 196-3), initiation of setting time for cement PC 42.5 R must be ≥ 60 min. All investigated cements are fulfilling this condition. However, the shortest setting time (initiation and ending) is noticed in the case of PC30Z (80/100 min) and PC50Z (80/130 min). The longest setting time is obtained in the case of PC30PbZ (270/340 min), which is longer time period than PC setting time for 50 min (initiation), i.e. 70 min – end of setting.

Table 2 show values of flexural strength and compressive strength of Portland cement and cement with addition natural and saturated zeolite for 2, 7, 28 days of hydration. Based on these results it can be seen that values of flexural strength and compressive strength depend on the mass content of addition used in Portland cement. Strengths of investigated cements are decreasing with the increasing of saturated zeolite content in the PC for all investigation periods (2, 7 and 28 days). However, the decrease of the strength was after 2 days of hydration, lower for 7 days, and the lowest for 28 days.

According to the EN 197 Standard, cement marked as CAM I should have compressive strength 42.5 MPa. Compressive strengths of newly-formed cements with addition of Pb ion saturated zeolite after 28 days of hydration are mostly above these values. It can be said that all used zeolites can be applied as additives for Portland cement in the quantity up to 30 %. Namely, values of compressive strength (after 28 days of solidification) for all cements with 30 % of additive are high (PC30PbZ – 57.3 MPa and PC30Z – 57.4 MPa) in comparison with requested minimum - 42.5 MPa.

CONCLUSION

Based on the results obtained from adsorption isotherms, it can be seen that increasing of the concentration of the lead ions in the water solutions the concentration of adsorbed lead ions increased. The maximum amount of lead ions adsorbed on zeolite under certain experimental conditions was 66 mg Pb^{2+}/g.

Results of using zeolite saturated with lead ions as the addition for portland cement, instead of the more common additives, showed that this material can be used as Supplementary Cementitious Materials (SCM). Since the flexural strengths (after 28 says of solidification) for the samples obtained by addition of 50 wt. % zeolite into Portland cement are in the range 7 - 8 MPa, they can be considered as low values. The optimal mass content of zeolite or with lead ions contaminated zeolites in Portland cement should not exceed 30 %. Since values of compressive strength (after 28 days of solidification) for all cements with 30 % of additive are higher (PC30PbZ – 57.3 MPa and PC30Z – 57.4 MPa) in comparison with requested minimum - 42.5 MPa, it may be cncluded that used zeolite (lead ions saturated) can be applied as additives for Portland cement in the quantity up to 30 wt. %.

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INFLUENCE OF PARTICLE SIZE ON BIOSORPTION KINETIC PARAMETERS

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ABSTRACT

The purpose of this work was to study the particle size influence onto the biosorption kinetics of Cu (II) ions using both reaction and diffusion models: pseudo-first-order and pseudo-second-order reaction models and two types of diffusion models: intraparticle Weber–Morris and Urano-Tachikawa diffusion model. Experiments have shown that increase in particle size decreases the biosorption capacity, while the time necessary for equilibrium is increased. Results also showed that pseudo second reaction model best fits all the data. Moreover, the initial internal diffusion rate is increased by lowering the particle size of the biosorbent.

Key words: biosorption, kinetic, copper, lignocellulose waste biomass.

INTRODUCTION

The high toxicity, persistence and bioaccumulation tendency of heavy metals have been recognized as serious environmental problem worldwide [1]. The conventional methods for their removing are either too expensive for removing low concentrations of metals, giving high operational cost and high energy demand, or create large quantities of toxic sludge which request further processing [2]. In the past fifteen years, great attention has been given to the new technologies for removing heavy metal ions from contaminated water systems. One of them is biosorption, technology that use cheap, abundant, organic waste for sequestering pollutants from wastewaters, which can be defined as adsorption onto the surface of biomass through passive metal-bonding of biosorbents [3, 4]. Among the other groups of biosorbents, agricultural waste materials have proved to be efficient, low cost and renewable source of biomass that can be exploited for removing of heavy metal from water streams.

Many authors have proved that peach shell has great potential for activated carbon production, but due to relatively high cost of this conversion process, it is necessary to find cheap, cost effective adsorbents, especially in developing economies like Serbia. Because of this, we have chosen to use waste lignocellulose material originated from peach stone, obtained as by-product in food processing factory. The Cu

(II) biosorption has been chosen to investigate, since the copper is one typical ubiquitous element, often present both in wastewaters from different industries, but also in surface run-off waters [5].

Investigating the kinetic of some sorption process is very important, since the obtained parameters give information about the metal uptake rate. This rate controls the residence time of copper uptake at the solid–liquid interface including the process which might be reaction, diffusion or combined type. In order to describe the changes in the sorption of metal ions with time, various kinetic models have been used to test experimental data. These models can be divided into two main types: diffusion based models and reaction based models [6].

EXPERIMENTAL

Peach stones were obtained from "Vino Župa" Company, where they have been disposed as by product waste from their Juice Factory. After receiving, the stone samples were separated from fruit residues, washed, dried on room temperature, and kept in polypropylene bottles for further treatment. Prior to experiment, all the samples were manually crushed and separated from kernels, so for further experiments only the hard stone part was taken. The peach stones were further milled using vybro mill with rings, and the different fraction sizes were separated. All the samples were washed several times in tap water, three times in 0.01M HCl in order to eliminate surface impurities and then in distilled water until negative reaction on Cl^- ions. After that, the samples were dried at 60°C until the constant mass. Before utilization as the biosorbent, the raw peach stone particles were sieved into four fractions as a function of particle diameter d_p (μm): PS1: $d_p < 100$μm, PS2: $100<d_p<500$, PS3: $500<d_p<1000$ and PS4: $1000 <d_p<2000$ and the fifth fraction was PS5: whole stone, $d_p \sim 3$ cm.

Copper solutions was prepared by dissolving $CuSO_4 \cdot 5H_2O$ (analytical grade) in distilled water using standard flasks. The metal concentration was 50 mg l^{-1}, while the solution pH value of was adjusted to 5.0, according to our previous investigations [7], and kept constant all the time during the experiment. The pH measuring was performed using pH meter SensION+, model MM340 (Hach Lange).

The adsorption kinetics was carried out in closed flasks each containing 1.00 g of each PS sample and 100.0 ml of copper solutions. After predetermined time periods the shaking was turned off and immediately thereafter adsorbent material was decanted, aliquots were removed and diluted in volumetric flasks to determine the metal ion concentration by atomic absorption spectrophotometry. The total metal concentration in solution was determined with atomic absorption spectrophotometer (Perkin Elmer AAS Analyst 300).

The biosorption capacity q (mg g^{-1}), which represents the amount of Cu(II) ions adsorbed by the biosorbent is obtained by the following equation:

$$q = \frac{(C_i - C_e) \times V}{M} \qquad (1)$$

where C_i and C_e (mg l^{-1}) are the initial and the equilibrium metal ion concentration, respectively, M (g) is the mass of biosorbent and V (l) is the volume of the copper solution.

Various mechanisms and steps can control the kinetic in adsorption phenomena. According to literature [8], four major rate steps are generally listed:

- Mass transfer of solute from bulk solution to the boundary film
- Mass transfer of metal ions from boundary film to biosorbent surface
- Internal diffusion of solute into the interior pores of biosorbent
- Biosorption of ions onto the active sites trough ion exchange, complexation or physicochemical sorption.

The first and second steps are external mass transfer resistance steps and depend on agitation and homogeneity of solution. Assuming that the sufficient agitation is provided, the first and second step can be excluded as non-rate limiting. The fourth step is assumed to be very fast but the third one is an intraparticle diffusion resistance step and must be included in analysing the kinetic of porous materials.

In order to evaluate the kinetic mechanism that controls the adsorption process, the pseudo-first-order and pseudo-second-order models as well as two intraparticle diffusion models were tested to interpret the experimental data and explain the adsorption mechanism of the metal ion on the peach stone particles.

RESULTS AND DISCUSSION

Figure 1.shows the kinetics of the biosorption of ions of Cu(II) by PS of different sizes. As it can be seen from the figure, decrease of particle size increase the equilibrium biosorption capacity from 0.55 mg $g^{-1}$to 3.82 mg g^{-1} for PS5 and PS1 samples respectively. The kinetic curve showed that the copper removal for all PS sizes was very rapid in the first few minutes. It can be also seen from Figure 1. that increasing the particle size results in a greater time to reach equilibrium, starting from 90 min to 180 min for PS1 and PS4 respectively. In this case, the solute needs more time to diffuse to the interior of the particle. Another reason is because the smaller the particle size, the greater the specific surface area, which promotes external surface adsorption. This initial rapid kinetics for PS1 can have significant practical importance as it will ensure process efficiency and economy at the same time, allowing the smaller reactor dimensions.

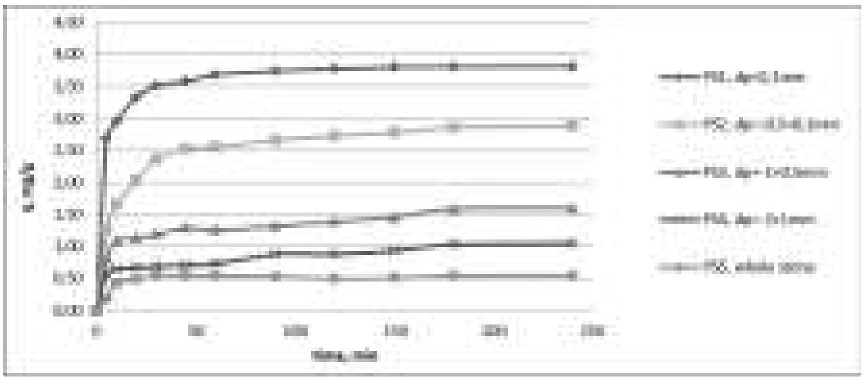

Figure 1. Biosorption kinetic for five different peach stone sizes (C_o=50 mg/l, M/V=10g/l, pH=5, T=25°C

Reaction models

The linear form of the Lagergren pseudo-first order model is described by the following equation [9]:

$$\ln(q_e - q_t) = \ln(q_e) - k_1 t \tag{2}$$

In Eq.2, k_1 (min^{-1}) is the rate constant of the pseudo first order sorption, q_t($mg\ g^{-1}$) is the biosorption capacity at time t (min), and q_e($mg\ g^{-1}$) is the value of biosorption capacity at equilibrium. The plots of ln(q_e−q_t) versus *t* gave the values of k_1 and q_e.

The pseudo-second-order equation, based on adsorption capacity at equilibrium, can be expressed by Equation 3 [10]. This model is based on the assumption that the rate-limiting step may be a chemical sorption involving forces trough the sharing or exchange of electrons between adsorbent and adsorbate [11]. The linear form of this expression is represented by Eq.3

$$\frac{t}{q} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} \tag{3}$$

where k_2 ($g\ mg^{-1}\ min^{-1}$) is the rate constant of the pseudo-second order sorption, q ($mg\ g^{-1}$) and q_e ($mg\ g^{-1}$) are the biosorption capacities at any time t and at equilibrium, respectively.

The kinetic parameters for biosorption of Cu(II) on different PS samples is given in Table1. Based on the obtained correlation coefficients, the pseudo-second-order equation was the model that furthered the best fit for the experimental kinetic data, evidencing chemical sorption as rate-limiting step of biosorption mechanism. The experimental q_e values are in good agreement with the calculated ones, which do not happen with the pseudo-first-order kinetic equation.

Table 1. Effect of particle size on the kinetic parameters in Cu (II) biosorption by PS

Particle size	q_e ($mg\ g^{-1}$)	pseudo-first order model			pseudo-second order model		
		q_m ($mg\ g^{-1}$)	k_1 (min^{-1})	R^2	q_m ($mg\ g^{-1}$)	k_2 ($g\ mg^{-1}\ min^{-1}$)	R^2
PS1	3,82	0,838	0,0235	0,971	3,88	0,084	1,000
PS2	2,88	1,31	0,0206	0,937	2,94	0,043	0,999
PS3	1,60	0,833	0,0173	0,756	1,58	0,066	0,991
PS4	1,05	0,579	0,0135	0,767	1,01	0,076	0,970
PS5	0,55	0,11	0,0060	0,687	0,52	0,807	0,999

Diffusion models

Generally, in a batch reactor with rapid stirring where external mass resistance is avoided, there is a possibility that the transport of bio sorbate from the bulk solution into the pores of the biosorbent is the rate-controlling step [12].

The possibility of intra particle diffusion was examined using the intraparticle diffusion Weber–Morris model [13] which is given by the following equation:

$$q_t = k_i t^{\frac{1}{2}} + C \tag{4}$$

Where k_i ($mg\ g^{-1}\ min^{1/2}$) is intraparticle diffusion rate constant and C is constant related to the thickness or boundary layer. If intraparticle diffusion is the sole rate-limiting step, then the plot of uptake q_t versus the square root of time ($t^{1/2}$) would result in a linear relationship and k_i values can be obtained from these plots.

Another kind of intraparticle diffusion model was proposed by Urano and Tachikawa [14]. In this model the adsorption rate is considered as very small and independent of the stirring speed, so the external diffusion is negligible in compare to the overall sorption rate. The sorption kinetics are modelled according to the following equation

$$f\left(\frac{q_t}{q_m}\right) = -\left[log\left(1-\left(\frac{q_t}{q_m}\right)^2\right)\right] = \frac{4\pi^2 D_i}{2.3d^2}t \tag{5}$$

where q_t, q_m are the solute concentration in the solid at time t and at equilibrium ($t \to \infty$) in the observed experimental conditions, d the particle diameter (m) and D_i is the diffusion coefficient in the solid ($m^2\ s^{-1}$). Linearization is carried out using the initial time of contact between 0 and 180 min.

The application of Weber-Morris model on experimental data was done and the obtained results are presented in Figure 2. It is clear from this figure that these plots gave straight lines for each sample size, but none of these lines have pass through the origin, showing that the intraparticle diffusion is not the sole rate limiting factor for the adsorption of copper. Increase in particle size leaded to decrease in initial slope of each line as well as the value of k_i, from 0,0766 mg g^{-1} $min^{1/2}$ to 0,009 mg g^{-1} $min^{1/2}$ for PS1 and PS5 respectively, indicating that smallest particles allow faster internal diffusion because its bigger porosity and surface area. At the same time, value for C decreases with particle size increase, meaning that smaller the particle of PS is, the bigger is the influence of boundary layer and external mass coefficient.

It is obvious from the Figure 2 that there can be distinguished three stages for the adsorption of copper ions. The first stage corresponds to copper diffusion from the film surrounding particles PS to the surface of the PS (external diffusion); this stage is fastest probably due to a strong electrostatic attraction between copper ions and the external surface of biosorbent at pH 5.

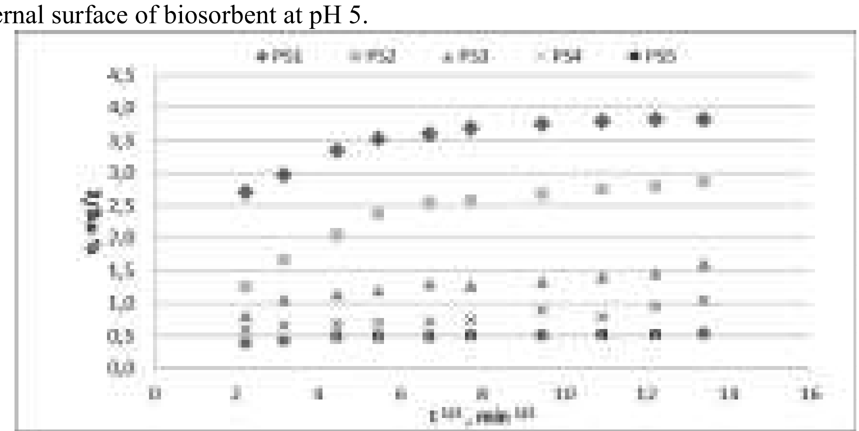

Figure 2. Intraparticle diffusion plots for Cu^{2+} biosorption on different PS sizes (C_o=50 mg/l, M/V=10g/l, pH=5, T=25^{o}C)

The second stage is a gradual adsorption stage, which can be attributed to intraparticle diffusion of copper ions through the pores of biosorbent and the k_i values should be calculated based on the data corresponding to this stage. The final stage corresponds to chemical reaction and complexation and slowest equilibrium attaining. These three stages can be better observed from Figure 3, which contains data fitting with W-M model for smallest and biggest peach stone fraction.

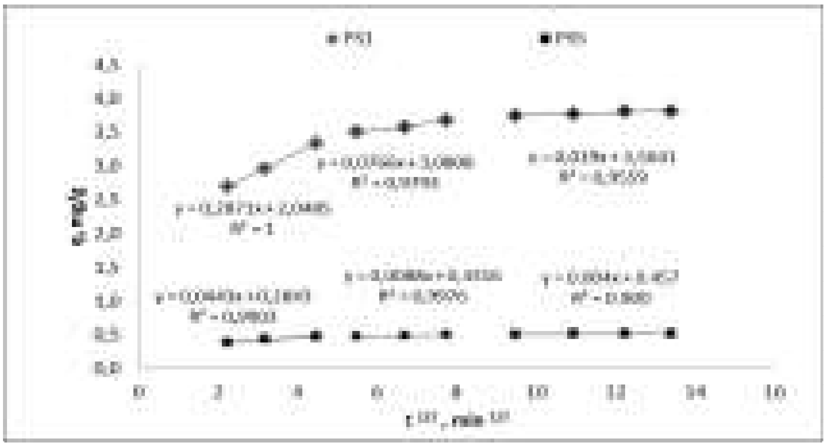

Figure 3. Comparing of trend lines for PS1 and PS5

Data fitting with Urano-Tachikawa model showed poor agreement of experimental data with expected model values: correlation coefficients for this model were 0,976 for PS1, 0,938 for PS2, 0,732 for PS3, 0,743 for PS4 and 0,725 for PS5. This trend shows decrease in R^2 with particle increase, meaning that it is harder to predict the kinetic behaviour for bigger particles. The same trend was observed for other three models. Correlation coefficients for Weber-Morris model showed much better agreements in fitting experimental data by model than Urano-Tachikawa model.

CONCLUSION

The complex mechanism of biosorption depends on the physical and chemical characteristics of the biosorbents. The influence of particle size onto the kinetics of copper biosorption has been evaluated in this paper. The amount of copper uptake (mg/g) was found to increase with decrease of particle size. The same trend was confirmed for copper uptake rate which controls the residence time of copper biosorption uptake at the solid–liquid interface. The rate of biosorption was found to conform to pseudo-second-order kinetics with a very good correlation for all particle sizes. The initial external diffusion rate is increased by lowering the particle size of the sorbent; in the same conditions the intraparticle diffusion rate is increased. Moreover, multi linearity of Weber Morris plots means that external diffusion cannot be neglected and that it must be taken in overall kinetic consideration because the overall diffusion rate involves a contribution from both mechanisms.

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MODIFIED CORN SILK AS BIOSORBENT FOR Pb(II) IONS REMOVAL FROM AQUEOUS SOLUTION

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ABSTRACT

In this work, corn silk was chemically modified by 0.5 M HNO_3 and used as biosorbent for removal of Pb (II) ions from aqueous solutions. The effect of biosorbent dosage was studied in batch experiments with 25 mL of aqueous lead solution of concentration 200 mg/L, at pH 5, 120 min of contact time and room temperature. The modified corn silk was characterized by pH_{PZC} The maximum biosorption capacity was found to be 39.5 mg/g at 0.025 g of biosorbent dosage. The biosorption capacity decreased with increasing of biosorbent dosage.

Key words: biosorption, modified corn silk, Pb(II), biosorbent dosage, pH_{PZC}.

INTRODUCTION

Industrial wastewater is considered as one of the major pollutants of the environment. Currently, heavy metal pollution has become one of the most important environmental problems. Lead is one of heavy metals and a widely used in many industries such as petrochemical, pulp and paper, electronic, refineries, mining activities, battery manufacturing, alloy and steel industries [1-4]. The wastes from these industries usually contain a large amount of lead which discharged into the environment through soils and water streams and accumulates along the food chain. It is one of the most toxic metal ions which accumulate mainly in bones, brain, kidney and muscles resulting in a high risk to human health, as high concentrations of lead will cause many diseases such as anemia, encephalopathy, hepatitis and nephritic syndrome [5]. It is therefore, very important to remove Pb(II) from wastewater before disposal.

Several conventional methods have been used for the removal of heavy metals from wastewater such as coagulation, chemical precipitation, chemical oxidation/reduction, adsorption with activated carbon [6,7]. However, these methods have some disadvantages such high operating cost and they may generate toxic sludge. Hence, from a food safety viewpoint, there is a demand for green adsorbents. Therefore, there is a growing interest in developing low-cost and high efficiency alternative technologies for wastewater treatment.

In recent years, removal of heavy metals using biomaterials as adsorbents has gained significant interest due to their high effectiveness, low cost, and simplicity. Extensive review of available literatures suggested that number of low cost natural biosorbents such as agave bagasse, rice straw, rice husk, wheat stem, olive pumice, olive stone, barley straw, coconut shell, corn cob, apricot stone, cashew nut shell, grapefruit peel [8-18] etc., have been used for the removal of heavy metal ions from wastewater. To enhance the removal efficiency and to reduce organic contents of low cost natural biosorbents, different modification techniques have been utilized by previous researchers.

The present work promotes chemically modified corn silk as non-conventional, low-cost and novel biosorbent for lead removal from aqueous solution. The main aim of this review is to reveal effect of biosorbent dosage on the biosorption of Pb(II).

MATERIALS AND METHODS

Corn silk (CS) was obtained from the local cornfields near Belgrade (Serbia) in October 2013. Collected biomaterial was milled and sieved into particle size less than 0.2 mm. Powdered CS (0.5 g) was modified in 10 ml of 0.5 M HNO_3 and the suspensions were shaken for 4 h (250 rpm) and washed until pH neutral [19]. Afterward the modified corn silk (MCS) was dried at 70°C stored and used for further experiments.

The pH_{PZC} of MCS was determined by following procedure: KNO_3 (p.a. grade) in concentration of 0.1 M was used as background electrolyte and initial pH values (pH_i) of KNO_3 solution (50 mL) were adjusted from 2 to 12 by adding small volumes of 0.1 M HNO_3 and / or 0.1 M KOH; in each initial solution 0.1 g of MCS was added and the suspensions were shaken for 24 h at room temperature, filtered through filter paper and pH of each supernatant was measured (pH_f) [20].

Lead solution was prepared by dissolving precise amount of Pb $(NO_3)_2x3H_2O$ (analytical grade) in distilled water using standard flasks. The pH value was adjusted by adding small volumes of 0.1M KOH and / or 0.1M HNO_3.

In order to study the effect of important parameters like biosorbent dosage on the biosorbent capacity of Pb(II) removal, batch experiments were performed by mixing of different amount of MCS (0.025 to 0.3 g) in 25 mL of lead solution of concentration 200 mg/L. The mixture including the lead solution and MCS were shaken during 120 min in mechanical shaker (250 rpm) at room temperature and at pH 5. At the end of the given contact time suspensions were filtered and concentration of final Pb(II) remaining in the filtrate was analysed by Atomic Adsorption Spectrophotometer (Perkin Elmer, AAnalyst 300).

Using Eq. (1) the biosorption capacity of the MCS, q (mg/g) was calculated:

$$q = (C_i - C_{eq}) \cdot V / m \tag{1}$$

where V is Pb(II) solution volume (L), m is mass of the MCS (g), and C_i and C_{eq} (mg/L) are the initial and final concentration of the Pb(II) ions in the solution, respectively.

The biosorption efficiency was determined using equation (2):

$$R\ (\%) = \frac{C_i - C_{eq}}{C_i} x100 \quad (2)$$

where C_i and C_{eq} (mg/L) are the initial and final concentration of the Pb(II) ions in the solution, respectively

RESULT AND DISCUSSION

The pH at which sorbent surface charge takes a zero value is defined as the point of zero charge (pHpzc). The experimental data are given in Fig. 1. As can be seen from Fig. 1, the plateaus of the curve $pH_f = f(pH_i)$ obtained at pH 4.35 show the pH_{PZC} of MCS. It means that at solution pH higher than 4.35, MCS surface is negatively charged and could interact with cations while at solution pH lower than 4.35, MCS surface is positively charged and could interact with anions. Since lead biosorption by the MSC was studied at pH 5, the results obtained for the point of zero charge indicated that the surface of MSC is negative at investigated pH values. Therefore, electrostatic attractions between negatively charged surface of MSC and Pb^{2+} ions could take place and contribute to biosorption [21].

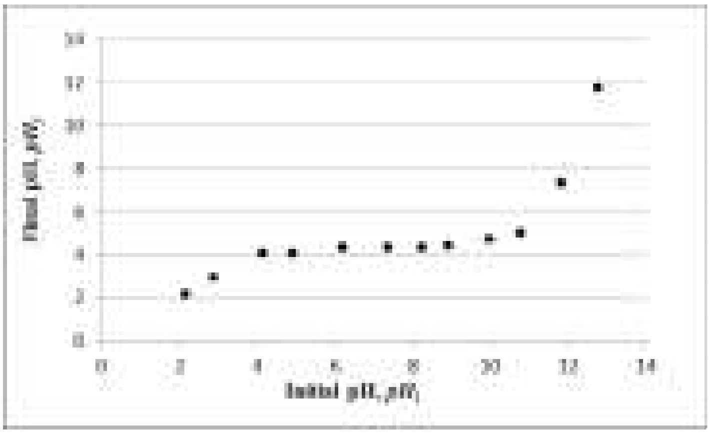

Figure 1. pH_f as a function of pH_i for modified corn silk

Biosorption of lead by modified corn silk

The effect of MCS dosage on Pb (II) ions biosorption was investigated and experimental results are given in Fig. 2.

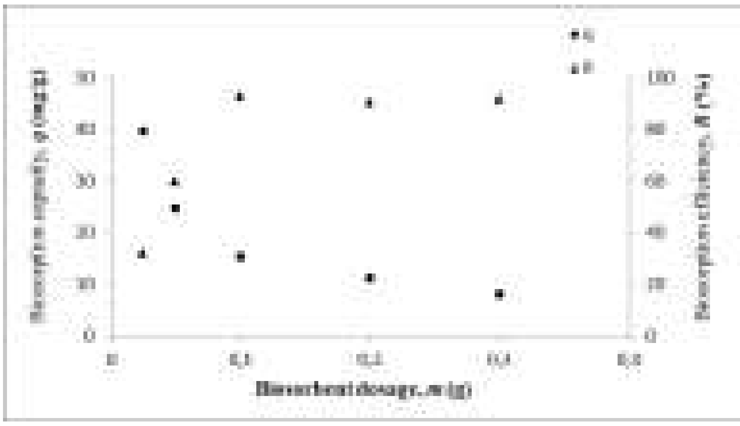

Figure 2. Effect of MCS dosage on the biosorption capacity and biosorption efficiency of Pb (II) ions (initial metal concentration 200 mg/L; pH 5, contact time 120 min and room temperature)

As can be seen (Fig. 2) when the MSC dosage increased from 0.025 to 0.30 g the biosorption capacity decreased from 39.5 to 8.17 mg/g. This phenomenon may be due to is an increasing of MCS dosage at constant Pb(II) ions concentration may cause unsaturation of the adsorption sites. At the other hand, the biosorption efficiency of Pb(II) removal increased from 32.21 to 92.99 % with an increase of adsorbent dosage from 0.025 to 0.30 g. This is due to increasing of the total number of adsorption sites available for Pb(II) ions adsorption with increase of MSC dosage [22].

CONCLUSION

The aim of this paper was to promote chemically modified corn silk as efficient, low cost and locally available biosorbent for the removal of Pb (II) ions from aqueous solutions. The results show that the biosorbent dosage is significant factor influencing the process of biosorption. When the MSC dosage increased from 0.025 to 0.30 g the biosorption capacity decreased from 39.5 to 8.17 mg/g. This study is shown that MSC can be used as an alternative adsorbent for Pb(II) ions removal from aqueous solution due to its high value of biosorption capacity.

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THE INFLUENCE OF GLASS COMPOSITION ON THE DISSOLUTION RATE

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ABSTRACT

In this paper the results of investigation of the polyphosphate glasses dissolution in acid solution at temperatures of 20, 30 and 37 °C were presented. The dissolution process in citric acid is complex and can be explained by hydration reaction and hydrolysis, leading to the disruption of phosphate chains which form the structure of glass. Mechanism of chemical reactivity of polyphosphate glasses, acting as slow release fertilizers in soil solutions was presented. The results of the dissolution experiments indicated that this glass can be used as an eco- fertilizer in soil remediation.

Key words: polyphosphate glass, fertilizer, dissolution.

INTRODUCTION

Modern civilization creates increasingly great amounts of waste and toxic substances formed in the production processes and communal management or in agriculture. The national economies are responsible for serious disturbances in the natural environment since, according to statistical data over 50% of the content of nitrogen, 50% of organic compounds and 30% of phosphorus in rivers have their source in the contaminations caused by substances eroded from the soil [1,2].

The last decades have brought a considerable progress in the field of the synthesis of new glasses for various, often unconventional applications.

The glassy fertilizers are phosphate glasses demonstrating the ability to accept in their composition the presence of a number of elements indispensable in the biological processes of the growth of plants and ability of their selective release in the soil environment in a form available for the plants. Regarding to the mineral fertilizers the dissolution of glass is a complex process which depends on several factors: glass composition, pH solution, temperature, time of reaction, etc. This process takes place in several stages and this enables that the overall time of the process can be regulated by favoring or suppressing some of these phases [3].

Earlier studies have shown that biological activity of silicate–phosphate glasses modified by addition of macroelements in the form of Mg and Ca is connected with change in the type of domains which are formed in the structure of glasses depending on the mutual proportions between the components forming their structure [4]. The presence of increasing amount of modifier in the form of Mg^{2+} cations results in the formation of domains showing the structure corresponding to that of silicates and leads to the increase in solubility of glasses. However the increase in Ca^{2+} cations content results in the formation of domains exhibiting the structure similar to that of orthophosphates which are characterized by lower solubility [5].

Iron plays an important role as a microelement that is necessary in the growth process of plants. Silicate–phosphate glasses with iron addition find application as slow release fertilizers.The FTIR results obtained indicate that the increasing amount of Fe_2O_3 and P_2O_5 in the structure of silicate–phosphate glasses causes formation of domains, whose structure changes from that corresponding to silicates to the one characteristic for phosphates [6].

EXPERIMENTAL

Two appropriate glasses batches was prepared from reagent grade raw materials $(NH_4)_2HPO_4$, K_2CO_3, $CaCO_3$, SiO_2, MgO, ZnO, Fe_2O_3 and MnO_2 in an open crucible. To minimize foaming of the melts, the crucible was slowly heated up to T=190 °C and then maintained for 3 h in order to release the gases, such as water vapor and NH_3. The melting was performed in an electric furnace Carbolite BLF 17/3 at T=1230 °C for 1 h in 200 ml open Pt/Rh crucible. The glasses was obtained by quenching the melt on a steel plate. Powder X-ray diffraction (XRD) analysis confirmed the quenched melts to be vitreous.

Characterization of the glasses

The chemical composition was determined by gravimetric and spectroscopic methods, i.e., by AAS using a PERKIN ELMER 703 instrument and UV/VIS spectroscopy using a PHILIPS 8610 spectrophotometer.

Powder X-ray diffraction (XRD) analysis was realized using a Philips PW-1710 automated diffractometer with a Cu Kα radiation tube operating at 40 kV and 32 mA. Data were collected from 5 to 70° 2θ, with a step size of 0.02° and a counting time of 1 s per step.

Leach test

Leach tests were conducted with 2% Citric acid (pH=2.31 and χ=3.103 μS/cm) which simulates the activity of organic compounds located around plant root for extraction of the useful components from soil. The glass grains size 0.3-0.65 mm was used for experiments. The samples were prepared by crushing the bulk glass in an agate mortar and then sieving it to appropriate grain size. The specific surface area of these powders was determined by Laser particlesizer Fritsch Analysette 22. After washing in distilled water and drying, 1 g of glass sample was placed into volumetric flask of 50 ml and then 2% citric acid is added. The closed flask was placed in a water bath with the determined temperature (T=20, 30 and 37 °C) and kept for the fixed time (0.5 - 720 h).

The solution from a volumetric flask was filtered and afterwards pH and the content of the present elements were determined. The rest of glass grains was dried at T=100 °C to constant mass of sample and then the mass of dissolved glass was calculated.

The measurement of pH values was performed with the pH-meter Consort, model C830P previously calibrated with appropriate standards.

Test on plants

The study was performed during 2011 and 2012 in greenhouse (Faculty of Agriculture - Belgrade). The flower selected are: a) Marigold (*Tagetes patula L*), series "Bolero"- Pan American Seed, b) domestic species of pepper (*Capsicum annum* L) "*Župska rana"*.

The polyphosphate glass BA-2 powder particle size < 0.5 mm was added in dosage: 0,1,2,3 and 5 g/l substrate.

RESULTS AND DISCUSSION

The results of chemical analysis of glasses composition presented in Table 1.

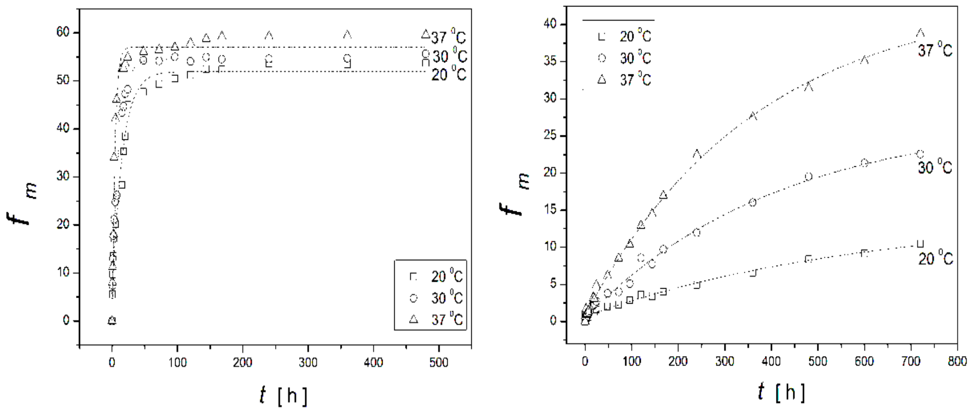
Table 1. Chemical composition of glasses

Oxide [mas %]	P_2O_5	K_2O	CaO	MgO	SiO_2	ZnO	MnO	Fe_2O_3
BA-1	62.0	23.2	7.8	3.6	1.8	1.0	0.6	
BA-2	68.0	22.0	1.6	1.4	2.9	0.8	0.7	2.6

By using the mass loss experimentally determined (Δm) and the specific surface areas of glass powders S [m^2], the normalized mass release f_m [g/m^2] was calculated. In Figure 1, the time dependence of f_m for powder samples at temperatures 20, 30 and 37 °C are shown. Fitting the experimental results yields the curve in Figure 1 that corresponds to equation (1):

$$f_m(t) = \tau \cdot r_o \left[1 - \exp\left(-\frac{t}{\tau} \right) \right] \quad (1)$$

where r_o is the starting dissolution rate, τ is a time constant and t is the dissolution time [7].



a) b)

Figure 1. The time dependence of f_m for glass powder sample particle size 0.3–0.65 mm at different temperatures for a) BA-1 glass and b) BA-2 glass

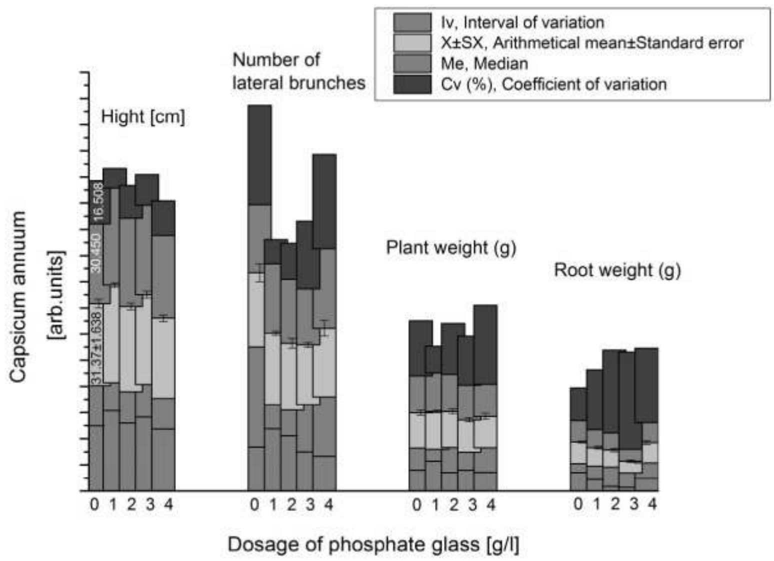
The initial dissolution rate was calculated as the slope between zero and 7 h data point at experimental temperatures, and then the time constants τ were determined using the equation (1).

Values of the dissolution rate constant k were calculated using the ratio $\tau = 1/k$. The results are summarized in Table 2.

Table 2. Rates constants k and initial dissolution rates r_o

Glass	BA-1			BA-2		
T [°C]	20	30	37	20	30	37
k [h^{-1}]	0.064	0.096	0.245	0.0016	0.0024	0.0027
r_0 [g/ m^2 h]	3.672	3.745	6.592	0.089	0.135	0.195

From the obtained rate constants and starting rates it can be deduced that the dissolution rate for the glass BA-1 is approximately ten times greater than for the glass BA-2. This can be explained by higher presence of alkalies in the glass BA-1. Also, this is a confirmation of a fact that small changes of a glass composition can drastically change the dissolution rate of a glass, which is a way of obtaining appropriate fertilizers for plants.



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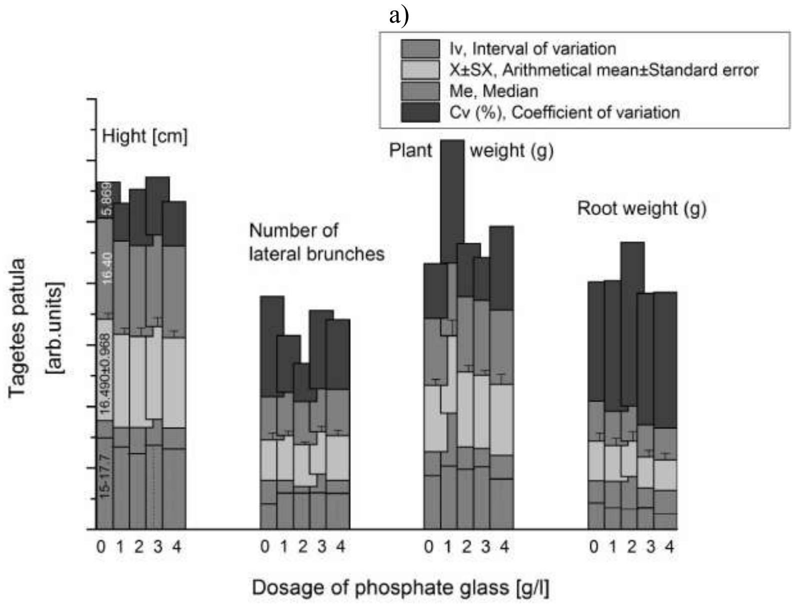

b)

Figure 3. The basic statistics indicators for the examined parameters of quality: a) pepper seedlings (Capsicum annuum L). b) marigold seedlings (Tagetes patula L) by the usage of various dosages glass

Based on parameters of development of plants examined it was determined that the glass dosage of 1 g/l is optimal. This dosage was affected significantly on increase of average height and the overground mass of the plants. In the case of pepper seedling an average overground mass determined is statistically significantly higher comparing the mass attained with glass dosage of 3 g/l. In relation to other additives for improvement of substrates (mineral fertilizers, wermicompost, etc) by addition of polyphosphate glass into substrate a better development of pepper seedlings was attained.

CONCLUSION

The results of the dissolution tests showed that this glass dissolved without back precipitation of the secondary corrosion products. The initial dissolution mass loss is linear with time. For longer reaction times the dissolution rate decreases.

The results of investigation indicated the positive effects of application of different dosage of polyphosphate glass in production of the marigold and pepper seedlings. The significant advantages can be reached: the contamination of agricultural soil is reduced and the total level of environmental protection increased.

Acknowledgment

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GEOLOGICAL CHARACTERISTICS OF ZEOLITES FROM IGROS AS RAW MATERIALS FOR USE IN VARIOUS FIELDS OF ECOLOGY

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ABSTRACT

Deposit of zeolitic tuff "Igroš" near Brus belongs to the village Igroš, which is administratively located in the area SO Brus and is about 3 km from the main road Krusevac - Brus. On the part of the field test site in Igroš the ore field "Igroš - Vidojevići", there are two ore bodies, "ore body I" and "ore body II ." In this paper are given the basic characteristics and presents of the results the latest research zeolitic tuff from deposits Igroš.

Key words: Igros, zeolitic tuff, clinoptilolite-heulandite group.

INTRODUCTION

Zeolites are group of natural and artificial inorganic compounds, which have specific physicochemical properties appropriate for industrial application. These minerals make specific group of alumosilicates within tectosilicates because of their origin, chemical compositions, structural characteristics and application. Clinoptilolite-heulandite mineral series (HEU type zeolite framework) represents economically the main group of natural zeolites. Application fields are numerous: in ecosystems (organic sulphur disposal from industrial oils, air purification from SO_2, CO_2, caesium and strontium disposal from soils contaminated with nuclear waste, in agriculture, farriery [1].

Their physical properties are: gray-white to yellow colour with limonite skins which fill-up cracks and fractures. Mineralogical composition of the zeolitic tuffs are: QUARTZ, FELDSPARS, MICA, HEU-TYPE ZEOLITES, LIMONITE, CLAY MINERALS, VOCANIC GLASS, ZIRCON, APATITE, RUTILE

GEOLOGICAL CHARACTERISTICS OF THE EXPLORATION AREA

The earliest Cretaceous sediments in the schist represent a high degree of metamorphism, mostly of sedimentary origin, transformed to amfibolitic facies. Diabase-chert formations (J2,3) was found at the south-western part of the terrain around Mosut, Igros and Sljivovo. Diabase and spilit (ββ) belong diabase-spilite-albitofirse formation. Neogene sediments were deposited in a complex tectonic depression known as the Moravian trench.

RESULTS OF THE RECENT RESEARCH

By Geozavod-Geological Institute of Serbia in 1999 on the deposit of zeolitic tuffs "Igroš" were conducted detailed geological research, in order to obtain data for the preparation of studies on reserves. For this purpose, the following works were done shooting and making situational plan in scale 1: 1,000, on an area of 2 hectares, making exploration wells, drilled 5 exploratory wells total piece 24.50 m. In 2008, the continued geological exploration at the mine field "Igroš-Vidojevic" on ore bodies I and II [2].

Geological operations

Geological research on the ore field "Igroš-Vidojevic" established two ore bodies, "ore body I" and " ore body II." By exploratory drilling completed in 2008 on two ore bodies have been dug 17 wells total meterage 299.0 m. Zeolitic tuff layer extends from the northwest to the southeast and can be monitored with interruptions over the length of 1.1 km.

Field mapping and exploitation works on the "ore body I" it was found that a layer of zeolitc tuff provides north-south direction and can be traced about 170 m along the strike and the decline in average about 50 m. Zeolitic tuff layer is interstratified in the Miocene-pliocene series shale green clay that make up the floor of clay and brown and green sandstones, which form the roof is. Zeolitic tuff layer is light gray to white colour average thickness of 1.64 m, with the general provision of the north-south and secondary statistical fall toward the north at an angle of about 4°.

Mapping the terrain in "ore body II" has been found that a layer of zeolitic tuff on the direction northwest-southeast and can be traced for a length of approximately 300 m and after the fall of about 100 m. Zeolitic tuff layer is interstratified in the Miocene-pliocene series of green clay, marl, shale brown clay that make up the floor of the conglomerate, shale brown clay and marl that make up the roof is. Zeolitic tuff layer is light gray to dark gray. By exploration drilling, investigating and recording notch open profile is determined zeolitic tuff layer with average thickness of 1.82 m, with the general provision of the north-south-southeast and secondary statistical drop in the northeast angle of 10°.

Laboratory examinations

Mineralogical and petrographical analyses

Deposits of zeolite tuffs are genetically related to volcano-sedimentary rocks. Tuffs rich in minerals HEU-type were created in marine and lacustrine sediments of the Senonian or Neogene age. The genesis of these zeolite tuffs related to the processes of diagenesis of volcanic glass. The mere lake environment had a significant impact on the formation and diagenesis minerals heulandite series. Grossly, mainly white to whitish yellow color, with frequent limonite scum. Mineralogical composition of zeolite tuffs test deposits is as follows: quartz, feldspar, mica, limonite - goethite, chlorites, volcanic glass, clay minerals, zeolite minerals, carbonate minerals group. As accessory minerals present are zircon, apatite and rutile.

Igros zeolite tuff deposit - The matrix of this tuff is hyalclastic with porous texture. Quartz grains are also well-preserved with typical angle-like forms and sharp edges. Feldspar minerals that are partially altered are mostly presented with plagioclase minerals. Zeolite minerals that are needle-like forms and very small dimensions are mainly distributed in matrix (up to 10μ). Biotite is dominant mica mineral, which is primary, while muscovite (sericite) is mainly as secondary mineral. Biotite is partially altered. Products of its alterations are iron-oxides and hydroxides (mostly limonite and goethite). Accessory minerals, apatite and zircon are regularly breezy and without any marks of alteration. Presence of plant fossils is quite frequent.

- X-ray tests: A sample of zeolite was examined by X-ray powder diffraction (powder). In the analyzed sample showed the presence of the following minerals: zeolites clinoptilolite heulandite-type, quartz, feldspar, mica. The most common minerals are zeolite, and feldspar and quartz, far less present. Mica are present in the track. From feldspar minerals are dominantly represented plagioclase. Semiquantitative share of crystalline phases (minerals) is as follows: zeolites than 80%, ≤ 10% feldspar, quartz <10%. Advanced semiquantitative analysis was very difficult because the proportion of the amorphous (glassy) phase is relatively high. The diffraction pattern of the test sample is given in the appendix to the report [3], [4], [5]

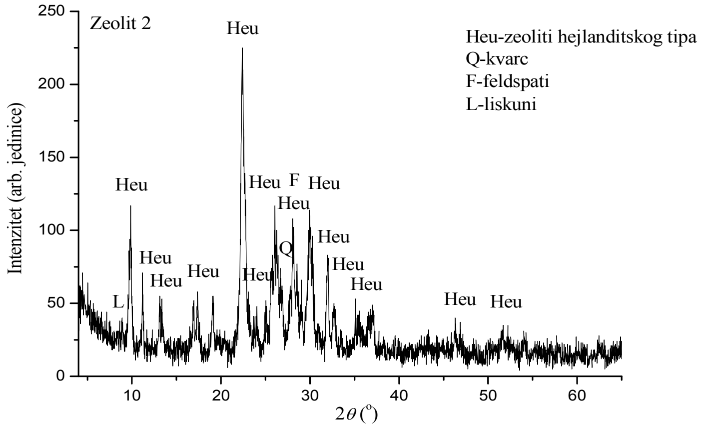

Figure 1. Diffractogram of zeolite powder sample Igroš

Chemical analyses

Based on the determination of cation exchange capacity to "ore body I" values obtained indicate that there is only one variety of zeolitic tuff terminology defined as zeolitic tuff. The average value of cation exchange capacity of the zeolites in the "ore body I" amounts to 166.9 mEq / 100 g.

Based on the analysis of the results of cation exchange capacity to "ore body II" observed two varieties of zeolite tuff: zeolitic tuff and tuff with zeolite. The average value of cation exchange capacity for zeolitic tuff is 137.85 meq / 100 g. The average value of cation exchange capacity for tuff with zeolite is 99.33 mEq / 100 g. According to the standards that are accepted in the "Institute for Technology of Nuclear and Other Mineral Raw Materials" from Belgrade, zeolitic tuff, that could be used (modified) for obtaining mineral adsorber mycotoxins as feed additive should have a value of cation exchange capacity ≥130 mEq / 100 g.

The average value of cation exchange capacity of zeolitic tuff with "ore body I" and " ore body II is 152.38 meq / 100 g. The average cation exchange capacity of 152,38 meq / 100 g indicates the potentiality of separated layers zeolitic tuff as high-quality raw materials for obtaining mineral adsorber mycotoxins.

The quality of mineral resources zeolitic tuff "ore body I" is given in Tables 1-2.

Table 1. The silicate analysis samples of zeolitic tuff "ore body I"

Elements	SiO_2	Al_2O_3	FeO	Fe_2O_3	CaO	MgO	TiO_2	Na_2O	K_2O	P_2O_5	G. Ž.
Content in %	62,30	12,59	0,23	1,20	4,08	1,94	0,22	0,70	0,63	0,016	15,65

- The average value of cation exchange capacity (KKI) amounted to 166.9 mEq / 100 g.
- clinoptilolite mineral content - heulandite in tuff is approximately 90%.

Table 2. Content of heavy metal of samples zeolitic tuff "ore body I"

Elements	Co	Cr	Pb	Zn	Mn	Sb	Sn	Cd	Cu	Ti	As
Content in ppm	14,5	2,4	20,2	33,5	149	51,0	12	1,20	38,4	142,5	0,08

The quality of mineral resources "ore body II" is presented in Tables 3-5.

Table 3. Silicate analysis of samples zeolitic tuff "ore body II"

Elements	SiO_2	Al_2O_3	FeO	Fe_2O_3	CaO	MgO	TiO_2	Na_2O	K_2O	P_2O_5	G. Ž.
Content in %	62,23	13,06	2,63		3,53	2,14	0,23	1,31	0,68	0,017	14,05

- The average value of cation exchange capacity (KKI) is 137.85 meq / 100 g.
- clinoptilolite mineral content - hejlandite in tuff is approximately 85%.

Table 4. Table 2.Content Heavy metal in the samples zeolitic tuff "ore body II"

Elements	Co	Cr	Pb	Zn	Mn	Sb	Sn	Cd	Cu	Ti	As
Content in ppm	13,6	24,2	20,2	43,1	107,8	45	12,5	1,1	24,7	123,9	0,2

Table 5. Silicate analysis of samples tuff zeolite "ore body II

Elements	SiO_2	Al_2O_3	Fe_2O_3	CaO	Na_2O	K_2O	G. Z.	G. Ž.
Content in %	63,67	12,72	3,38	2,43	1,93	1,27	3,90	8,13

-The average value of cation exchange capacity (KKI) amounts to 99.33 meq / 100 g.
- clinoptilolite mineral content - haulandite in tuff is approximately 50%.

Technological examinations and field of application of zeolitic tuffs

Earlier long-term technological and industrial test the zeolitic tuff with same or comparable quality by experts ITNMS shown that it can be successfully applied in different fields of agriculture and the economy in general:

- micronized tuffs are added to a concentrated food for livestock and poultry, and in this way reduces the impact of toxic substances are present in an intensive cattle diet,
- production of organomineral fertilizers on pig farms, the absorption of ammonia from air and water by zeolitic tuff and tuff subsequent disposal of such arable land from the release of ammonia and enrichment of nitrogen,
- since zeolitic tuffs have the ability to absorb and release water, can be applied to the soil gravel composition of greater permeability, to prevent rapid drying of soil and leaching (relating) useful substances from the same,
- recultivation of degraded land-tailing example coal mines Stavalj near Sjenica is, by experts ITNMS has successfully rehabilitated by using zeolitic tuff,
- for cleaning the waste water, production of micronized materials and granulate based on zeolite tuffs,
- production of means for filtration and funds for environmental conditions, according to the patents of scientists of the Institute-ITNMS from Belgrade
- application in industry and special paper industry using fine abrasives and many other application areas.

CONCLUSION

On the territory of the Republic of Serbia within the sedimentary deposits, there are several basins in which the isolated occurrences and deposits of zeolitic tuffs, which are economically very important mineral raw material. Tray of zeolitic tuff "Igroš"near Brus belongs to the village Igroš, which is administratively located in the area SO Brus and is about 3 km from the main road Krusevac - Brus.

Exploration drilling, exploratory digging and making exploitation floors is determined zeolitic tuff layer average thickness of 1.64 m, with the general provision of the north-south and secondary statistical fall toward the north at an angle of about 4 °. Mineralogical composition of zeolite tuffs test deposits is as follows: quartz, feldspar, mica, limonite - goethite, chlorites, volcanic glass, clay minerals, zeolite minerals, carbonate minerals group. As accessory minerals present are zircon, apatite and rutile.

In the deposit zeolitic tuff and tuff with zeolite "Igroš-Vidojevic" in two ore bodies I and II were established balance geological reserves of B + C1 categories of zeolitic tuff and tuff with zeolite in the amount of 35,712 m3 or 50,817 t. The average value of cation exchange capacity of zeolitic tuff with "ore body I" and ore body II" is 152.38 meq / 100 g. The determined quality of mineral resources allows its use in different applications: for the production of micronized mineral supplement animal feed premixes and concentrates, then in the agricultural, plant production (slow acting fertilizers, reclamation of acid soils, improving water-physical properties of the soil, storage of seeds, fruits and vegetables), in virtually all industries (production of cosmetics industry beer and wine), and daily life (removal odors and filtering drinking water, etc.).

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OBTAINING FILLERS BASED ON LIMESTONE FROM DEPOSIT "RISTOVA PONTA" – ULCINJ, FOR APPLICATIONS IN VARIOUS INDUSTRIES

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ABSTRACT

Paper presents results of investigations of using limestone as filler. Micronization methods, granulometric composition, oil and water absorption and degree of whiteness were investigated, and chemical and thermal analyses were performed.

Physico-chemical properties classified, by quality, this limestone for use as filler in the following industries: paints and coatings; rubber and plastic; glass; foundry; sugar, metallurgy and paper production. Due to low degree of whiteness and high content of MgO, heavy metals, and biogenic elements this limestone cannot be used in folowing industries: pharmaceutical and cosmetics, in fertilizers, in production of cattle feed and for neutralization of acidic soils.

Key words: limestone, filler, industrial use, standards.

INTRODUCTION

Republic of Montenegro has big reserves of limestone in coastal area and in south of the territory [1]. Even though deposits are huge, limestone is mainly used in construction as construction stone, and to some extent as architectural stone [2]. Since calcium carbonate as filler is much more expensive than construction stone, relevant institutions of Montenegro initiated investigations of the possibility of using limestone as filler [3]. On the basis of the obtained results it was evaluated whether it can be used as filler in accordance with standards (SRPS) in various industry branches [3-6].

"Ristova Ponta"-Ulcinj deposit consists of carbonate sediments, mostly limestone ones, and less dolomitic sediments. Ore reserves are estimated at about 2,500,000 t of limestone [1]. The aim of investigations presented in this paper was to determine the possibility of using raw material as filler in various industry branches.

EXPERIMENTAL

Materials and methods

Starting limestone sample used in investigations was from "Ristova Ponta" - Ulcinj deposit. First, its specific volumetric weight (density) and granulometric composition were determined. Its density was measured by pycnometer with xylol as fluid, granulometric composition was determined by Tyler screen [7]. Granulometric composition of the micronized sample was determined by sieve size 63 µm, classification on Cyclosizer and Bach elutriator. Limestone filler quality was determined by chemical analysis. Thermal (DT/TG) analysis of the sample was performed using Netzsch-Simultaneous Thermal Analysis- STA 409 EP device, with heating speed of $\Delta T = 10\ ^0C/min$, in temperature interval from 20 to 1000 ^0C. Degree of whiteness was determined by whiteness meter, according to MgO 100% standard.

Investigation of physical properties of starting sample

Specific volumetric weight of the starting sample is $\gamma = 2{,}679\ g/cm^3$.

Table 1. Granulometric-composition of the initial sample Ristova Ponta- Ulcinj

Size class, [mm]	M, %	↓∑M, %	↑∑ M, %
+ 22,2	/	/	
-22,2 + 19,1	/	/	
- 19,1 + 15,9	3,68	3,68	100,00
- 15,9 + 12,7	9,48	13,16	96,32
- 12,7 + 9,52	17,23	30,39	86,84
- 9,52 + 7,93	7,88	38,27	69,61
- 7,93 + 5,0	13,83	52,10	61,73
- 5,0 + 3,36	14,99	67,09	47,90
- 3,36+ 2,38	4,74	71,83	32,91
- 2,38+ 1,6	5,98	77,81	28,17
- 1,6+ 1,19	4,91	82,72	22,19
- 1,19+ 0,63	6,63	89,35	17,28
- 0,63 + 0,4	2,93	92,28	10,65
- 0,4 + 0,3	1,69	93,97	7,72
- 0,300 + 0,200	1,62	95,59	6,03
- 0,200 + 0,000	4,41	100,00	4,41
Input	100,00	/	/

Based on data from the table is drown a diagram of particle size distribution shown in Figure 1, for samples of limestone Ristova Ponta. In Figure 1, shows the direct curve of particle size distribution and cumulative curves and average sample of outflow and flow limestone deposits "Ristova Ponta"-Ulcinj. From the intersection of cumulative curves average outflow and flow determined that the average diameter of the sample of limestone d_{50} = 5.42 mm, and upper size limit of the sample was 15.32 mm**.**

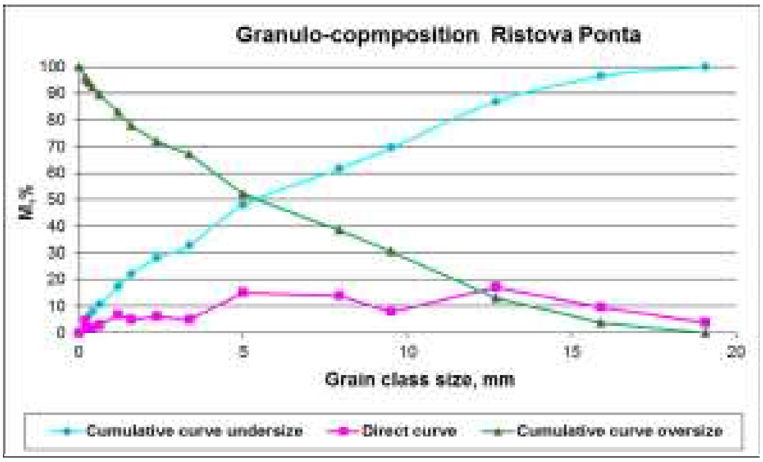

Figure 1. The curves of particle size-composition of the starting sample "Ristova Ponta"-Ulcinj

Technological investigations

For investigations of the possibility of using limestone as filler in various industry branches limestone was micronized, and thus obtained product were subjected to the following physico-chemical characterization:
-chemical analysis, thermal (DT/TG) analysis, determination of granulometric composition, degree of whiteness and absorption of oil and water.

Determining granulometric composition of micronized sample

Table 2. Granulometric composition of grinded sample Ristova Ponta

Size class [μm]	M, %	↓ΣM, %	↑Σ M, %
+ 63	25,33	25,33	100,00
-63+44	4,48	29,81	74,67
-44+33	7,02	36,83	70,19
-33+23	5,08	41,91	63,17
-23+15	3,66	45,57	58,09
-15+11	3,66	49,23	54,43
-11+5,7	35,54	84,77	50,77
-5,7+0	15,23	100,00	15,23
Input	100,00	/	/

Granulometric composition of the micronized products showed that upper size limit is about 90 μm, and that the finest class -5.7 μm content is around 15 %.

Determining the degree of whiteness

Whiteness was assessed on three samples of the limestone from deposit "Ristova Ponta", and the result is shown in Table 3.

Table 3. The degree of whiteness the limestone samples

No	mark of the sample	whiteness according MgO– 100%
1.	Ristova Ponta-1	86.30
2	Ristova Ponta-2	85.60
3	Ristova Ponta-3	86.10
	Average value	86.00

Determination of absorption water and oil

In order to determine absorption water and oil are also used three samples of the limestone from deposit "Ristova Ponta", and the results are shown in Tables 4 and 5.

Table 4. Absorption of the oil of samples of limestone

No.	mark of the sample	absorption of the oil, %
1.	Ristova Ponta-1	13,92
2.	Ristova Ponta-2	14,05
3.	Ristova Ponta-3	14,06
	Average value	14,01

Table 5. Absorption of the water of samples of limestone

No	mark of the sample	absorption of the water, %
1.	Ristova Ponta-1	19,01
2.	Ristova Ponta-2	19,17
3.	Ristova Ponta-3	19,13
	Average value	19,1

Thermal (DT/TG) analysis

Results of thermal (DTA/TG) analysis of the micronized sample "Ristova Ponta" limestone are presented as a diagram in Figure 2.

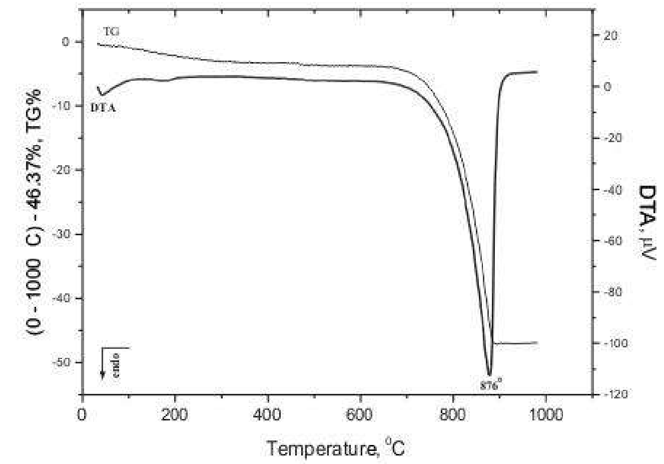

Figure 2. DTA/TG diagram of "Ristova Ponta" limestone sample

In Figure 2 are presents the TG and DTA diagrams of the initial sample of limestone. DTA diagram (Figure 2.) shows endothermic peak with maximum at 876 ^{0}C, which is attributed to phase transformation of calcite ($CaCO_3$) into CaO, according to the following reaction:

$$CaCO_3 \rightarrow CaO + CO_2 \quad (1)$$

This phase transformation is accompanied by weight loss of 46.37% (TG diagram, Figure 2) in the temperature range from 650 ^{0}C to 900 ^{0}C.

Chemical analysis

Results of chemical analysis of the micronized limestone with contents of main components and damaging components are presented in Tables 6. and 7.

Table 6. Chemical composition of main components of limestone sample

Comp.	CaO	$CaCO_3$	CO_2	MgO	Fe_2O_3	Al_2O_3	R_2O_3
Cont., %	54,75	97,72	43,50	1,04	0,0388	0,021	0,0258
Comp.	SiO_2	K_2O	Na_2O	TiO_2	P_2O_5	LOI	
Cont., %	0,064	0,0066	0,0244	<0,02	<0,005	43,63	

Table 7. Chemical composition of damaging components of limestone sample

Comp.	Cu	Mn	S	P	Ni	Cr	Mo
Cont., %	8ppm	35ppm	<0,01	<0,0025	19ppm	4 ppm	<50 ppm
Comp.	Sb	Pb	Cd	pH	Fe solu.	As	Hg
Cont., %	<25 ppm	25 ppm	2ppm	9,07	0,0340	/	/

Results of physico-chemical characterization of "Ristova Ponta" limestone sample and the required filler quality (Standards) lead to conclusion that this limestone is of good quality. Namely, its $CaCO_3$ content is high- 97.72%, and $MgCO_3$ (2,18%) and silicates (SiO_2 0.064%) content low. However, relatively high content of heavy metals was found, above all Cu (8 ppm), Mn (35 ppm), Ni (19 ppm) and Cd (2 ppm).

RESULTS AND DISCUSSION

Limestone filler quality for each industry branch is defined by appropriate standards or requirements of manufacturers who use limestone as raw material in their production cycle. Limestone quality requirements are defined as content of useful and damaging components, i.e. as chemical composition, as well as the necessary size class.

Evaluation of "Ristova Ponta" limestone filler quality based on chemical composition

According to the results presented above, limestone from "Ristova Ponta" – Ulcinj deposit can be used in the following industries:

- in industry of paints and coatings; it is among high quality raw materials in accordance with market and standard requirements (SRPS B.B6.032);
- in rubber and PVC industry; it satisfies the highest quality standards and market requirements (SRPS B.B6.031);
- in paper industry, because its relatively low whiteness degree it satisfies A, B and C quality class in accordance with market and standard requirements (SRPS B.B6.033)
- in foundry industry; it belongs to the highest class I in accordance with market requirements imposed by standard (SRPS B.B6.012);
- in sugar industry; due to the increased MgO content it is in quality class II in accordance with market and standard requirements (SRPS B.B6.013);
- in metallurgy; it is in the highest class I in accordance with market requirements imposed by standards (SRPS B.B6.011);
- in production of glass; due to the increased MgO content it is in quality category IV and V in accordance with market requirements imposed by standards (SRPS B.B6.020);

Limestone from "Ristova Ponta" – Ulcinj deposit cannot be used:

- in pharmaceutical and cosmetics industry because its low whiteness degree relative to market requirements defined by standard (SRPS B.B6.034);
- for production of mineral fertilizers because of the increased MgO content, which is strictly defined by manufacturer's requirements (Azotara Pančevo).
- in production of cattle feed because of the increased content of heavy metals Pb and Cd, which is very strictly defined for this use ("Official Gazette of the Republic of Serbia" 31/78, 6/81, 2/90, 20/00);
- for neutralization of acidic soils; because of the increased content of MgO, and K_2O as biogenic element and heavy metals, Cu, Pb, Ni and Cd, the contents of which are very strictly defined ("Official Gazette of the Republic of Serbia" 60/2000).

Evaluation of "Ristova Ponta" – Ulcinj limestone filler quality based on users' requirements for the necessary raw material size (fineness)

Some industries require finely micronized limestone, while others require raw material of larger particle size, sometimes even coarse. Following industries use ground and micronized limestone:

- for paints and coatings industry; A quality 99.5% of - 20µm, B quality 97% of - 20µm and 0.01% of + 44µm;
- rubber and PVC industry requires for A and B quality raw material to be 99.5% of -45µm, while for C and D quality upper limit limestone size is 45µm; for glass industry
- for paper industry for all quality categories (A, B and C) the required fineness is 100% of -45µm, where for A quality 75% of -10µm, for B quality 80%, and for C quality the required fineness is 95% of -10µm and 90% of -2µm; rubber and PVC industry requires for A and B quality raw material to be 99.5% of -45µm, while for C and D quality upper limit limestone size is 45µm;
- for glass industry, since "Ristova Ponta" limestone corresponds to quality IV and V according to its chemical composition, there is predefined granulometric composition for these quality classes, subdivided into six subclasses in size range from -1+0.1mm;

Following industries demand larger sizes and coarse limestone:

- for foundry industry, raw material should be size -50+30 mm, with class – 30 mm content up to 5%<;
- for sugar industry, limestone is to be classified into six subclasses in size range from -215+63mm, with maximum fine content in each subclass up to 8%;
- metallurgy uses limestone consisting of five subclasses in size range from -70+0.1mm.

CONCLUSION

Limestone from "Ristova Ponta"- Ulcinj deposit according to its physico-chemical properties belongs to high quality carbonate raw material with high content of $CaCO_3$ of 97.72%, and low content of $MgCO_3$ of 2.18% and silicates (SiO_2 0.064%). It meets the requirements of standards for using calcium carbonates as fillers in industry of paints and coatings; paper industry, glass industry, rubber and PVC industry; foundry industry; sugar industry and metallurgy. According to market demand and standards it belongs to high quality raw material in industry of paints and coatings, rubber and PVC, foundry industry and metallurgy However for sugar industry and glass production it does not conform to standards. Because of increased MgO content "Ristova Ponta" limestone cannot be used in fertilizers industry. Due to low whiteness degree (86,0%) limestone "Ristova Ponta"cannot be used in in pharmaceutical and cosmetics industry. Due to high content of MgO, heavy metals Ni (19 ppm) Pb (25ppm) and Cd (2 ppm), as well as biogenic elements Cu (8 ppm) and K_2O (0.0066%), "Ristova Ponta" limestone cannot be used in production of cattle feed and for neutralization of acidic soils.

Obtaining of wide range of fillers for various industry branches would provide products which are more expensive per mass unit than products that have been used until now up to 10 times.

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BEHAVIOR OF THE Ag43Cu37Zn20 ALLOY IN AERATED SODIUM CHLORIDE SOLUTION

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ABSTRACT

Cadmium–free silver brazing alloys are suited filler materials for joining ferrous and non–ferrous metals and alloys, which could replace materials containing cadmium in brazing alloys, except for aluminum and magnesium. The use of cadmium is restricted because of its inherent toxicity. Behavior of Ag43-Cu37-Zn20 alloy, which has the same composition as BS1845:1984 Ag5 commercial brazing alloy, in a medium similar to see water is of importance for such potential use. Electrochemical and microscopic techniques have been used for these investigations.

Key words: Brazing alloys, Ag-Cu-Zn, Corrosion, Cyclic voltammetry, FESEM.

INTRODUCTION

Brazing filler metals based on silver are widely used in various industries, but they usually contain cadmium as an alloying metal. But, the use of cadmium is restricted all over the world due to its toxicity. AgCuZn alloys or multi–component alloys based on them can reach the properties of Ag based brazing alloys containing cadmium. Three-component alloy of Ag-Cu-Zn system with the content of 43 mass % Ag, 37 mass % Cu and 20 mass % Zn was chosen for investigation because this composition corresponds to the commercial BS1845:1984 Ag5 alloy [1]. Detailed investigations of electrochemical behavior of various ternary alloys are rare, but it is commonly correlated with microstructure of the alloy [2, 3]. However, a general theory of electrochemical behavior for the multicomponent alloys is not available.

For the investigated alloy two–phase structure in solid state is suggested. As the phases are nearly binary systems, their electrochemical properties are comparable with the corresponding Ag–Zn and Cu–Zn alloys.

A general theory of the alloy polarization behavior of binary alloys was first proposed by Pickering [4]. In his study both types of the alloys, Ag–Zn and Cu–Zn, are noticed as prone to dealloying. Detailed electrochemical characterization of Ag–Zn alloy in chloride solutions has not been reported in literature. On the contrary, there are numerous publications on the electrochemical behavior and corrosion resistance of copper–zinc alloys (brasses) in near neutral chloride solutions [5–14].

Anodic behavior of brass is similar to the copper and polarization curves of brasses, particularly α-brasses, show strong similarity to those of pure copper [5, 15]. Preferential dissolution of Cu and Zn from Cu reach (fcc) phase in chloride solutions is observed in previous works [16, 17]. It is generally accepted that the anodic dissolution of unalloyed copper is activated by complexation and is influenced by chloride concentration [18–21]. Models for the anodic polarization response of copper in acid chloride solution can equally be applied to neutral and weak alkaline chloride media where Cu_2O may be favored over the deposition of CuCl [15, 23, 24]. However, zinc from the brass could cause the redeposition of copper on the surface. Despite the many studies, the reaction mechanism at different potentials still needs to be clarified.

The aim of the present work is to study and discuss electrochemical behavior of Ag43-Cu37-Zn20 alloy in aerated sodium chloride solutions. Electrochemical measurements were used and complemented by surface analytical techniques.

EXPERIMENTAL

All three metals of the alloy for electrode preparation were of minimum purity of 99.99%. The alloy was prepared by two consecutive steps of ingot metallurgy method, melting in a laboratory electric furnace and casting in a graphite mould. The obtained ingot was machined into cylinders with 7.14 mm diameter. It was subjected to homogenization annealing at 600 °C for 24 h in nitrogen atmosphere and has been slowly cooled for the next 8h to the room temperature in the same protective atmosphere. Finally, specimen was mounted in polytetrafluoroethylene (PTFE) mould. The chemical composition (in wt. %) of the alloy used in the present study was 43.5% Ag, 37.7% Cu, 18.8% Zn, and trace amounts (less than 20 ppm total) of Pb, Fe, Sn, Ni as analyzed by inductively coupled plasma atomic emission spectroscopy. The chemical composition was according to BS1845:1984 Ag5 standard.

All solutions were prepared with ultra pure water of resistivity of 18.2 MΩ cm^{-1} and analytical grade chemicals produced by Merck (Germany). The test solution, 3.5 wt. % NaCl, was prepared by dissolving 35.000 g of NaCl in 1000 ml glass flask to the total mass of the solution of 1000.00 g. pH value was adjusted to pH = 6.7 ± 0.2 by dropwise addition of 0.1 M NaOH solution.

Electrochemical studies were carried out using open circuit potential measurements, polarization measurements and cyclic voltammetry. The measurements were conducted in a conventional three-electrode glass cell. The working electrode was the cylindrical alloy electrode embedded in PTFE with active surface of 0.40 cm^2, whose potential was controlled against the saturated calomel reference electrode (SCE). Platinum sheet (2 cm × 1 cm) served as a counter electrode. Before all measurements, the alloy sample was polished with a series of grit (from 600 to 2000) SiC papers and then using 0.3 μm alumina grit paste. The electrode was thoroughly washed with double distilled water, cleaned with ethanol and degreased with acetone and finally rinsed with ultrapure water and dried with purified nitrogen. All experiments were carried out at a temperature of 25 ± 0.5 °C. Software and hardware used for electrochemical measurements was developed at the University of Belgrade, Technical Faculty in Bor [25]. The hardware consisted of a PC, AD/DA converter (PCI-E 20 428 produced by Burr-Brown) and an analog interface. The application software for electrochemical measurements and data acquisition is based on LabVIEW 8.2 platform.

The working electrode was immersed in the solutions and in each case, a potential of −1.5 V was applied for 2 min to reduce surface oxides and allowed to stabilize for at least 30 min. Following a stabilization at open circuit potential (OCP), measurements of linear polarization and Tafel plots were performed. For linear polarization (LP) measurements, a sweep from −20 to +20 mV versus OCP at a sweep rate of 0.1 $mV \cdot s^{-1}$ was used and the polarization resistance (Rp) was measured from the slope of η versus j curve in the vicinity of corrosion potential. Tafel plots, ± 0.20 V versus OCP were recorded using a scan rate of 0.1 mV/s to obtain corrosion potentials and corrosion current densities. Potentiodynamic curves were recorded starting from −0.2 V versus OCP up to +1.0 V with scan rate of 1 mV/s. Voltammetric experiments were run from cathodic potentials in the anodic direction without allowing the sample to stay in free corrosion. Before every potentiodynamics tests, electrode has been held on the starting potential of measurement for 2 min. Cyclic voltammograms were recorded at potential scan rate from 5 mV/s to 20 mV/s, in the potential range from −0.8 V to +0.6 V and −1.5 V to +0.8 V.

The surface of the alloy and corrosion products was studied using a field emission scanning electron microscope (Tescan FEG FESEM model: Mira 3 operated at 20 kV). Chemical composition of the alloy surface and products on the surface was determined using energy dispersive X-ray spectroscopy (EDS). EDS detector was Oxford Instruments model: X-Max SDD.

RESULTS AND DISCUSSION

The investigated alloy shows two phase structure: silver–rich Ag α-phase (Ag) and copper–rich Cu α-phase (Cu). Composition of the phases can vary with solidification regime and heat treatment. SEM micrograph of the annealed Ag43Cu37Zn20 alloy presented in Fig. 1 shows homogeneous dispersion of the (Cu) phase (dark) within an (Ag) phase (bright) and partially developed two phase lamellar structure in remaining dendrites. Relatively fast melt cooling in the graphite mould has promoted dendritic solidification. Degradation of the dendrite structure after the homogenization (24 h) annealing at the 873 K is obvious but it remains in some parts of the sample surface as can be noticed in Fig. 1.

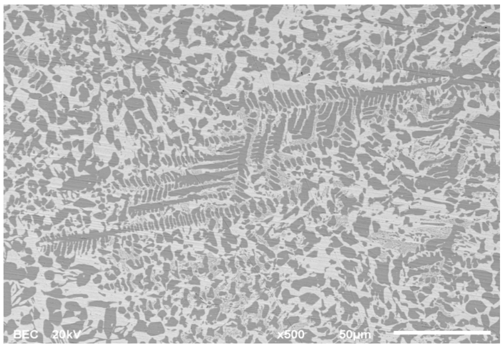

Figure 1. SEM micrograph of the annealed Ag43Cu37Zn20 alloy

The current–potential curve recorded by cyclic voltammetry (CV) at a scan-rate of 20 mV/s for the Ag43Cu37Zn20 alloy in aerated neutral NaCl solution is shown in Fig. 2. The scan is performed in anodic direction in the potential interval from −0.8 V to +0.6 V.

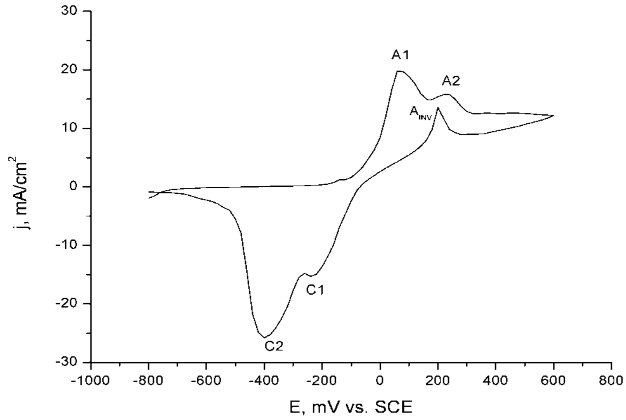

Figure 2. Cyclic voltammogram for the Ag43Cu37Zn20 alloy in aerated neutral NaCl at a scan-rate of 20 mV/s

The forward scan exhibits sharp anodic peak (A1) at the potential of +0.07 V. It is followed by another peak (A2) at +0.22 V and with current plateau from +0.28 V until start of reverse scan at +0.6 V. Current became anodic (positive) at approximately −0.28 V. It is just above corrosion potential, as should be expected (open circuit potential (OCP) was −0.248 V for naturally aerated solution). Sharp rise in current was observed from −0.18 V with the appearance of current step from about −0.16 V to −0.15 V.

The slope of the ascending part of the peak A1 suggests diffusion controlled process. Dissolution of zinc can be expected as the parallel reaction to the copper dissolution as the possible reactions corresponding to the peak A1. In the neutral chloride solutions under the anodic polarization the zinc is complexed with chloride ions according to electrochemical reaction [26]:

$$Zn + 4Cl^{-} \rightarrow ZnCl_4^{2-} + 2e^{-} \quad (1)$$

Mechanism of anodic copper dissolution by chloride complexation can be expressed as [27-30]:

$$Cu + Cl^{-} \leftrightarrow CuCl_{ads.} + e^{-} \quad (2)$$

$$CuCl_{ads.} + Cl^{-} \leftrightarrow CuCl_2^{-} \quad (3)$$

the overall reaction being:

$$CuCl_2^{-} + e^{-} \leftrightarrow Cu + 2Cl^{-} \quad (4)$$

Copper redeposition is due to the chemical reactions [26, 31]:

$$2CuCl_2^{-} + Zn \rightarrow 2Cu + ZnCl_4^{-} \quad (5)$$

$$2CuCl_2^{-} + Zn \rightarrow 2Cu + Zn^{2+} + 4Cl^{-} \quad (6)$$

Dissolution-precipitation mechanism is in accordance with appearance of the polarization curve [32].

Region of the peak formation is in the area of the $Ag \rightarrow Ag^{+} + e^{-}$ reaction equilibrium potential, in chloride solutions:

$$AgCl + e \leftrightarrow Ag + Cl^{-} \quad (7)$$

$$E(AgCl/Ag) = +0.223 - 0.0592\log[Cl^{-}], \text{ V vs. SHE} \quad (8)$$

and for the 3.5% NaCl solution with a(Cl^{-}) of 0.41, equilibrium potential is +0.245 V vs. SHE or +4 mV vs. SCE. It is right at the peak potentials but it is not certain that the reaction is occurred in that time since the whole (Ag) phase is cathodic protected by more active (Cu) and in its own phase by zinc. Reaction (7) or further complexation with chloride ions to $AgCl_2^{-}$ or $AgCl_4^{-}$ is possible at higher potentials.

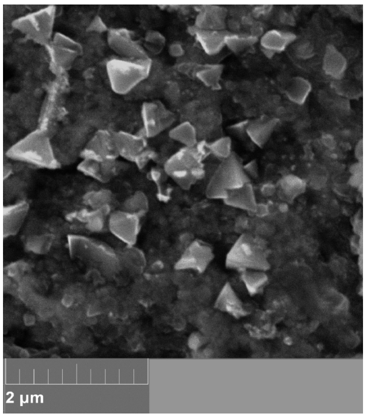

Figure 3. SEM micrograph of the Ag43Cu37Zn20 alloy sample after potentiostatic polarization at +0.25 V for 5 min, darker part of the surface film, magnification of 71,100 x

The surface on the electrode was examined after potentiostatic polarization at +0.25 V for 5 min by SEM and EDS analysis. Micrographs in Figures 3 and 4 show that the surface is covered with the very heterogenic layer. Two characteristics formations are observed, dark and bright features. Typical SEM image of the darker part of the film is shown in Figure 3. At the level of surface of ~ 10–1000 pm^2 (25 pm^2 in Figure 3) homogeneously distributed crystals on the surface of the film are observed. Among the numerous crystals of irregular shape, those with tetrahedral structure are particularly recognized. CuCl has this structure, although octahedral Cu_2O and hexagonal ZnO could have similar appearance. XRD and EDS analysis [32] revealed the prevailing presence of the CuCl.

Very different structure is observed in the areas of brighter parts of the film - agglomerated nano sized white grains with some microsized irregular shaped particles (Fig. 4). But, EDS analysis revealed similar Cu and Cl content which indicates CuCl existence in the white grains, too. Zinc is in the smaller fraction and could be in the form of oxide or hidroxychlorides. High fraction of the silver especially when smaller part of the cluster is analyzed (single white grain) suggests that the grains are precipitated silver nanoparticles with spherical or irregular shape depending on the size. Oxygen in both analysis is in the high percentage but it should not be connected with the Ag_2O considering applied potential insufficient for the reaction of the formation, pH value of the solution, concentration of chlorides and the zinc content. Size of the single grains is in the range of tens nm. It was supposed that some of them were formed by chemical reactions.

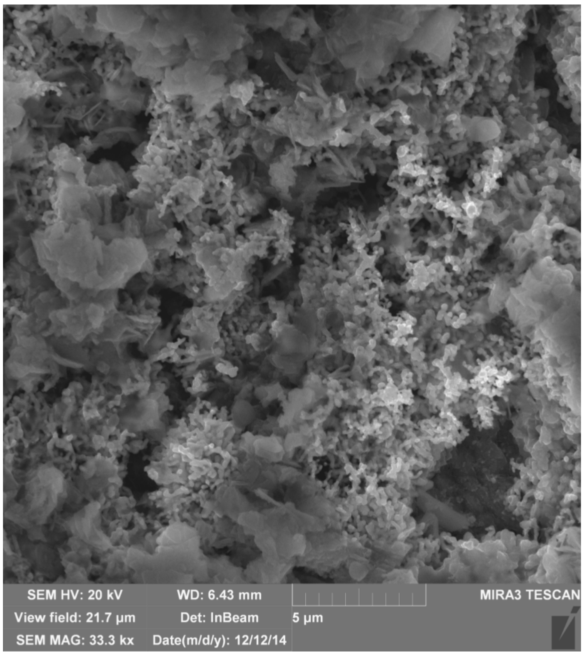

Figure 4. SEM micrograph of the Ag43Cu37Zn20 alloy sample after potentiostatic polarization at +0.25 V and for 5 min, brighter part of the surface film

CONCLUSIONS

Results of electrochemical measurements as well as surface analysis of electrochemical behavior of Ag43Cu37Zn20 alloy in 3.5% wt. NaCl lead to the conclusion that a porous film forms in aerated solution during anodic polarization. Copper rich (Cu3Zn) phase exhibits simultaneous Cu and Zn dissolution followed by formation of the complex multilayer film. XRD shows that it consists of CuCl and zinc hydroxichlorides with small amount of Cu_2O, probably formed in the pores of the film. Silver rich phase exhibits strong dealloying, dominantly dezincation. Redeposition of silver over Ag solid solution is indicated by XRD and SEM/EDS.

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THE ADSORPTION OF Cu^{2+} AND Ni^{2+} IONS FROM SYNTHETIC SOLUTIONS USING LOW COST BIOSORBENT WHEAT STRAW

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ABSTRACT

The paper presents the results of adsorption of Cu^{2+} and Ni^{2+} ions from synthetic solutions using wheat straw as a biosorbent. Change in the initial pH value during the adsorption of Cu^{2+} and Ni^{2+} ions was monitored. Kinetic studies indicated that copper and nickel adsorption followed the pseudo-second order model. The maximum adsorption capacity of 5 mg g^{-1} was achieved for Cu^{2+} ions, while the adsorption capacity for Ni^{2+} ions was 2.5 mg g^{-1}. The presented results show that wheat straw can be used as a cheap biosorbent for the adsorption of copper and nickel ions from aqueous solution.

Key words: adsorption; wheat straw; copper ions; nickel ions; biosorbent.

INTRODUCTION

Due to the complexity of the problem associated with the metal removal and recovery from wastewaters, numerous technologies for the metal removal and recovery from such sources were considered in the past. Many of them are established and marketed, while some others are still under research and development [1-5].

Different processes of treating wastewaters give different removal efficiencies. Besides the existing of conventional technologies for the purification of wastewaters from metal ions, considerable attention has been paid recently to bio-sorption processes [6].

Since the first reports on biosorption, great efforts have been made to prepare efficient, effective, and economic biomaterials and apply them for wastewater treatment [7].

The major advantage of biosorbents over the conventional adsorbents, besides their acceptable effectiveness in reducing the concentration of metal ions to a very low level, is their availability and a low price, since they are waste-or- by-products of agricultural, food or timber industry, with low or even no economic value.

The aim of this study was to investigate the adsorption ability of wheat straw to adsorb copper and nickel ions that appear most frequently in mine waters.

EXPERIMENTAL

Materials and methods

For the adsorption experiments, the synthetic solutions of Cu^{2+} and Ni^{2+} ions were used with constant initial concentration of 0.2 g dm^{-3}. Solutions were prepared dissolving corresponding sulphate salts (p.a. purity), in distilled water. From this solution lower initial concentrations were then prepared, depending on the experiments that should be carried out.

Wheat straw was used as an adsorbent in this study. The adsorbent was firstly sieved through a set of laboratory sieves and the sieve fraction (-1 + 0.4) mm was used in the adsorption experiments. Dry wheat straw were weighed, then this weight was rinsed with 200 ml of distilled water, dried again at 90 ^oC and used for further characterization or in the adsorption experiments. No chemical pretreatment of wheat straw has been performed. The concentration of considered heavy metal ions during experiments was determined using a PerkinElmer - 403 atomic adsorption spectrophotometer, while the pH value was measured by using the pH-meter WTW inoLab–720.

In order to determine the content of alkali and alkaline earth metals, as well as the other inorganic substances in the adsorbent structure, a measured amount of wheat straw (58 g) was firstly dried, in order to determine the straw moisture in it. The moisture percent was 7.23 %. The straw was then burnt and kept for 1 hat 815^oC, to oxidize the whole organic carbon to CO_2. After cooling the residual part, its mass was weighed and the percentage of ash in the wheat straw was then calculated. It was 6.2 % based on the initial mass, i.e. 6.63 % based on a dry mass of the straw. The ash was then analyzed and its chemical composition is presented in Table 1.

Table 1. Chemical composition of the wheat straw ash

Compound	SiO_2	CaO	K_2O	P_2O_5	Al_2O_3	MgO	Fe_2O_3	SO_3	Na_2O	TiO_2	MnO	Other
Content,%	36.36	6.83	28.62	3	0.29	3.25	0.57	16.12	4.14	0.017	0.11	0.69

The adsorption of Cu^{2+} and Ni^{2+} ions onto wheat straw– Experimental procedure

Adsorption experiments were carried out in laboratory beakers each equipped with a magnetic stirrer in order to maintain the straw in suspension. The stirring speed was kept constant in all experiments at 300 min^{-1}. The chosen sieve fraction of wheat straw rinsed previously with 200 ml of distilled water was used for the adsorption experiments. As the aqueous phase, single ion synthetic solution of the chosen ion, with the initial concentration of 200 mg dm^{-3}, was used. The mass of 1 g of the wheat straw was contacted with 50 ml of this solution for different contact time. After a certain contact time, the suspension was filtered and the filtrate was analyzed on the residual metal ion content, as well as the amount of alkali and alkaline earth metals. From the mass balance, the adsorption capacity was determined, as well as its change with the process time. During the adsorption, change of the solution pH value with time was also monitored. All experiments were performed at ambient temperature.

The adsorption capacity and its change with the process time were then calculated by using the equation (1):

$$q(t) = \frac{C_i - C(t)}{m} V \qquad (1)$$

where: q(t) – mass of adsorbed metal per unit mass of adsorbent (mg g^{-1}); C_i and C(t) are the initial and actual concentration of metal at time t; V- volume of the treated solution (ml); m – mass of adsorbent (g).

RESULTS AND DISCUSSION

Change of the pH value of solution with the process time during adsorption of Cu^{2+} and Ni^{2+} ions

Monitoring the changes in pH values during the adsorption experiments with the process time it was obtained dependence shown in Fig. 1

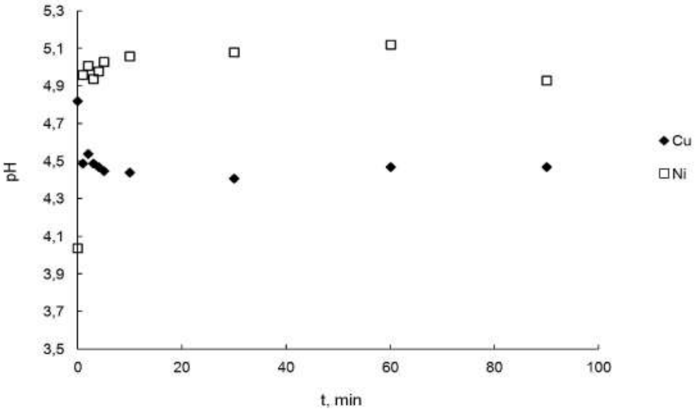


Figure 1. Change of the solution pH value with the process time during adsorption of Cu^{2+} and Ni^{2+} ions

Figure 1 presents a change of the solution pH value with time at the adsorption of Cu^{2+} and Ni^{2+} ions. It is seen in Figure 1 that when adsorbing Cu^{2+} ions the pH value rapidly drops down at the very beginning of the process, reaching a constant value in the next 30 minutes of process time. Based on the curves shape for the adsorption of Cu^{2+} ions, it was supposed that a very quick decrease in the initial pH occurs due to the releasing of H^+ ions in the aqueous phase as a result of the deprotonation of hydroxyl functional groups existing in the molecular structure of straw. During this initial period, metal ions are being exchanged with H^+ ions. The change of the initial pH value with time, when the adsorption of Ni^{2+} ions occurs is quite different. It can be seen in Figure 1 that the pH value starts increasing from the beginning of the process, reaching a constant value after 30 minutes. In this case, the increase in the pH value can be attributed to a simultaneous adsorption of Ni^{2+} and H^+ ions from the solution, resulting in a competition between Ni^{2+} and H^+ ions for the active spots in the molecular structure of straw.

Kinetics of adsorption

Kinetics of metal ion adsorption onto biosorbents has been considered by many scientist and several kinetic models were suggested [9-11]. Since the earlier findings including ours [7-8, 12-13], about the adsorption kinetics using wheat straw, led towards the pseudo-second reaction order, in this series of experiments the initial concentration of metal ions kept constant and equal 200 mg dm^{-3}, only a change of the adsorption capacity with the process time was monitored. The adsorption was terminated after 90 minutes assuming that this period is long enough for establishing the process equilibrium [8].

To describe the kinetics of adsorption of Cu^{2+} and Ni^{2+} ions onto wheat straw, the second order kinetic model of adsorption was used, described by the following equation:

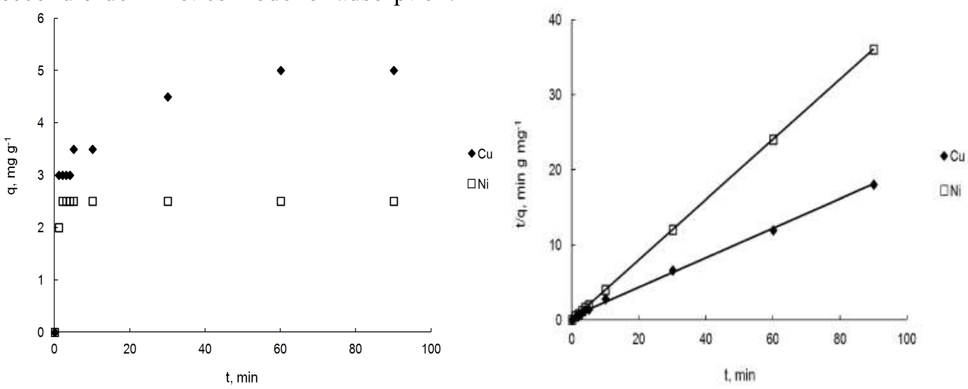
$$q(t) = \frac{q_e^2 k_2 t}{(1 + q_e k_2 t)} \tag{2}$$

where: q_e – is a mass of adsorbed metal per unit mass of adsorbent (mg g^{-1}) at equilibrium, k_2 – is the adsorption rate constant for the second order kinetic model (mg g^{-1} min^{-1}).

Rearrangement of eq. (2), leads to its linear form, as follows:

$$\frac{t}{q(t)} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \tag{3}$$

The change of adsorption capacity with time is shown in Figure 2a. In the first 5-10 minutes of a process, adsorption takes place quite rapidly; the capacity increases with time, reaching a maximum value (5 mg g^{-1} for copper ions, and 2.5 mg g^{-1} for nickel ions). Linearizing the curve from Figure 2a by plotting t/q(t) against the process time gives a straight line with a very good fitting with the pseudo-second order reaction model for both metal ions, as shown in Figure 2b. The regression coefficient is close to unity for both metal ions, confirming a good fit of the experimental results with the considered second order kinetics model of adsorption.



a) *b)*

Figure 2. a) Change of adsorption capacity with process time; b) pseudo second orderkinetic model

CONCLUSIONS

The results presented in this paper shows, that wheat straw can be successfully used for the adsorption of copper and nickel ions from aqueous solutions. During the adsorption of Cu^{2+} ions, a decrease in pH value occurs due to the deprotonation of hydroxyl functional groups present in the molecular structure of straw and as well as the released H^{+} ions into the solution which, together with Ca^{2+} ions from the molecular structure of straw by the ion-exchange mechanism, are exchanged with Cu^{2+} ions. An increase of pH value of the solution during the adsorption of Ni^{2+} ions indicates that there is a simultaneous adsorption of H^{+}, competing with nickel ions for active spots on the wheat straw internal surface.

The kinetics of adsorption was relatively fast, reaching equilibrium after 30 minutes of the adsorption process in the case of Ni^{2+} ions, and after 60 minutes in the case of Cu^{2+} ions. Kinetics of adsorption was modeled by a pseudo-second order kinetic model showing very good fitting with experimental data.

The maximum adsorption capacity of 5 mg g^{-1} was achieved for Cu^{2+} ions, while the adsorption capacity for Ni^{2+} ions was 2.5 mg g^{-1}. The obtained results show that wheat straw can be used as a cheap biosorbent for the adsorption of copper and nickel ions from aqueous solution.

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PYROLYSIS OF LIGNOCELLULOSIC BIOMASS

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ABSTRACT

Limitations and exhaustions of energy sources (e.g. fossil fuels) have resulted in taking major steps in sustainable plans for rational using of resources that exist today and finding new, alternative energy resources. Biomass is renewable energy resource which can be grown where climatic conditions are appropriate. Bio-oil as one of the major products obtained from the pyrolysis of lignocellulosic biomass has a number of industrial applications. After upgrading it is possible to use bio-oil as fuel for transport. Pyrolysis temperature is the main factor that affects the transfer of heavy metals in the volatile fraction of pyrolysis products.

Key words: pyrolysis, lignocellulosic biomass, bio-oil.

INTRODUCTION

World is facing many economical and environmental problems related to the application and consumption of energy. As a result of significant growth of population and rapid industrial and economical development, the consumption of energy is increasing despite high energy prices and many negative impacts on the environment.Limitations and exhaustions of energy sources (e.g. fossil fuels) have resulted in taking major steps in sustainable plans for rational using of resources that exist today and finding new, alternative energy resources [1,2].

Significant environmental pollution is the result of the consumption of fossil fuels (oil, coal, natural gas). Burning of fossil fuels releases harmful gases (CO, CO_2, NO_x, SO_x, CH_4) which are linked to the global warming[3].

BIOMASS

Biomass is any organic matter derived from plants. It includes phytomass and zoomass [4].Biomass is renewable energy resource which can be grown where climatic conditions are appropriate [5]. Biomass includes agricultural and forestry residues, aquatic and marine biomass and wastes (municipal solid waste, municipal sewage sludge, animal, industrial and urban organic waste, ect)[5,6].

Main polymers of biomass are cellulose, hemicelluloses and lignin[7]. Biomass usually contains 40-50 wt.% cellulose, 20-40 wt.% hemicellulose and 10-40 wt.% lignin. Besides these polymers, biomass is made of inorganic material (ash) and extractives[8]. Cellulose is linear polymer composed of D-glucopyranose linked with β-1,4glycosidic linkage[9].Hemicellulose is branched polymer composed of pentoses, hexoses and/or urgonic acids[10]. Lignin consist of aromatic polymers (synthesized from phenylpropanoid precursors) and inhibits absorption of water through cell wall [9,10].

BIOFUELS

Biofuels are gaseous or liquid fuels derived from renewable materials such as biomass. Biofuels include "first" and "second generation biofules". Raw material for making first generation biofuels is sugar, starch and vegetable oil. Their production has impact on the food supply [11].Non-edible lignocellulosic biomass can be used as feedstock for production of second generation biofuels[12-15]. There are also "third generation biofuels" and "fourth generation biofuels" which are made from algae and vegetable oil, respectively[16].

METHODS FOR CONVERSION OF BIOMASS

Processes for converting biomass to energy and fuels can be divided on thermochemical and biochemical[17].Biochemical conversion uses enzymes and microorganisms for conversion of biomass, while heat is used for thermochemical conversion[3].

Combustion, pyrolysis, gasification and liquefraction are main thermochemical converion processes [18].Combustion (the burning of biomass in air) is used to convert chemical energy from biomass into heat, mechanical power or electricity. This process is performed at temperature around 800-1000°C[19].Gasification is production of gaseous fuels from solid fuels at temperature range of 800–1300°C. Main product, producer gas, is composed of H_2, CO, CH_4 and other impurities such as CO_2, nitrogen, sulfur, alkali compounds and tars[5].Oxygen is widely used gasification agent. Beside it, steam, air, CO_2, O_2 can be used as well [3].This process can be viewed as a special form of pyrolysis which is performed at higher temperatures for production of gas (syngas). Direct liquefraction is performed at low-temperature and high pressure for breaking down biomass into small fragments in water or another solvent[18].Thermochemical decomposition of biomass in the absence of oxygen is called pyrolysis [20]. Main products of pyrolysis are gas, liquid and char[21]. Depending upon operating parameters (temperature, vapor residence time, size of feed particles, rate of biomass heating, sweeping gas flow rates, mineral matter contents, and initial moisture), characteristics of biomass and pyrolysis type, the obtained amount of products vary. Gaseous and char products are dominant at higher and lower temperatures, respectively[22].Pyrolysis liquid product is called pyrolysis oil or bio-oil, [23].CO_2, CO, CH_4 and H_2do not condense during cooling and they represent gas products, while solid product (char) is made of carbon, oxygen and hydrogen [3].

TYPES OF PYROLYSIS

Pyrolysis can be divided into conventional slow pyrolysis (carbonization), fast pyrolysis and flash pyrolysis. This classification is based on the operating conditions[24].

Pyrolysis that is performed on temperature from 400–600°C with heating rate of 0.1–1°C/s and residence time from minutes to hours is called slow pyrolysis[25]. Charcoal, the main product, can be used for domestic cooking, as raw material for production of different chemicals, activated carbon, absorbents, ect[21].

Fast pyrolysis involves high liquid yield [25]. Decomposition of biomass happens very quickly and mostly vapors and aerosols are generated, as well as some charcoal and gas[26]. The essential features of a fast pyrolysis process for producing liquids are:dry feedstock (less than 10%), small particles (less than 3 mm), short hot vapor residence times of typically less than 2 s to minimize secondary reactions, carefully controlled pyrolysis reaction temperature of around 500°C to maximize the liquid yield for most biomass,very high heating rates, rapid removal of product char to minimize cracking of vapors andrapid cooling of the pyrolysis vapors to give the bio-oil product[25, 26-28]**.**Typical yields of bio-oil, char and gaseous products of 60–70%, 12–15% and 13–25%, respectively[29]. Bio-oil obtained this way is considered as second generation bio-fuel [30].

Flash pyrolysis is used for production of solid, liquid and gaseous product and with this process yield of 75% of bio-oil can be achieved[31].

Table 1 represents ranges of main operating parameters for pyrolysis and relative distribution of products [31, 32].

Table 1. Range of the main operating parameters and products distribution for pyrolysis processes[31, 32]

Pyrolysis process	Solid residence time [s]	Heating rate [K s^{-1}]	Particle size [mm]	Temperature [K]	Product yield (%)		
					Oil	Char	Gas
Slow	450-550	0,1-1	5-50	550-950	30	35	35
Fast	0.5-10	10-200	<1	850-1250	50	20	30
Flash	<0.5	>1000	<0.2	1050-1300	75	12	13

Besides these three types of pyrolysis there are also:flash hydro-pyrolysis, solar flash pyrolysis, ultra-rapid (ultrafast) pyrolysis, hydropyrolysis, vacuum pyrolysis and methano-pyrolysis. However, the researches for producing bio-oil by vacuum flash pyrolysis, microwave assisted pyrolysis, and plasmapyrolysis are recently reported[6, 33].

APPLICATION AND UPGRADING OF BIO-OIL

Bio-oil (main product of fast pyrolysis) is composed of polar organics (about 75-80 wt%) and water (about 20-25 wt%)[27]. These compounds are derived from cellulose, hemicellulose and lignin depolymerization and fragmentation[34]. Organic compounds include acids, alcohols, aldehydes, esters, ketones, phenols, lignin-derived oligomers, furans, alkenes, sugars, nitrogen components, guaiacols, syringols, miscellaneous oxygenates[6, 35]. Inorganics in bio-oil are: Ca, Si, K, Fe, Al, Na, S, P Mg, Ni, Cr, Zn, Li, Ti, Mn, Ln, Ba, V, Cl, etc[6].

Some industrial application of bio-oil are combustion fuel in boiler, combustion in diesel engines, transportation fuel (after upgrading), production of anhydro-sugars, chemicals, adhesives [35].

Bio-oil has a higher water content (15-30 wt.%), low and corrosive pH (<3), higher oxygen content (35-40 wt.%) and lower heating value (HHV of 16-19 MJ/kg) compared with petroleum heavy fuel oil[18]. Much lower heating value of bio-oil compared with that for fossil fuel is because of many oxygenated compounds in bio-oil and significant portion of water[32].

Current techniques used for bio-oil upgrading are: hydrogenation, hydrodeoxygenation, catalytic pyrolysis, catalytic cracking, steam reforming, supercritical fluids (SCFs), emulsification and esterification [35, 36].

INFLUENCE OF PYROLYSIS TEMPERATURE ON YIELDS OF BIO-OIL

Many researchers studied pyrolysis of rapeseed (*Brassica napus*L.)[37-40], rapeseed cake[41-43], straw and stalk of the rapeseed plant[44], sunflower (*Helianthus annuus*L.) pressed bagasse[45-49], agricultural residues of sunflower[50], corncob (*Zea mays* L.)[51-55]and corn stover[56].Fig. 1 represents maximum bio-oil yield from pyrolysis of different biomass.

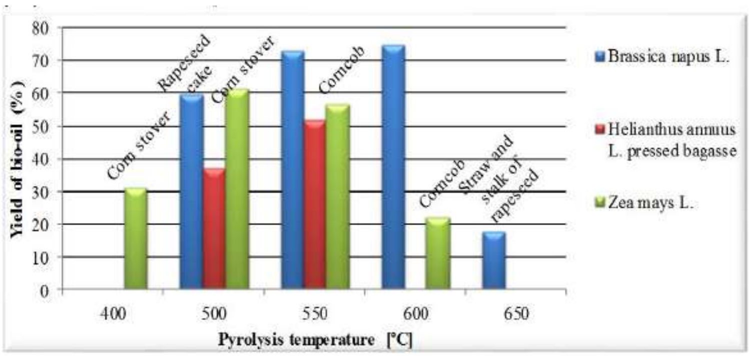

Figure 1. Maximum yield of bio-oil obtained by pyrolysis of different plant material

PYROLYSIS AS A TECHNIQUE FOR TREATING HEAVY METAL CONTAMINATED PLANT MATERIAL

Many concerns are associated with phytoremediation, such as handling and disposal of the biomass enriched with heavy metals. Result of combustion of biomass is volatilization of heavy metals, and this is why other techniques (like pyrolysis) should be explored.Advantages of this method are: reduction of volume and weight of heavy metal contaminated biomass; energy recovery; production of char/ash which contains heavy metals [57].Pyrolysis experiments were made on different biomass contaminated with heavy metals [57-61]. Table 2 represents these results.

Table 2. Heavy metal behavior (presence in obtained bio-oil)after pyrolysis of different biomass

Metal	350°C	400°C	450°C	500°C	550°C	600°C	Plant material	Ref
Cd	ND	/	ND	10 %**	ND	40 %**	Sunflower	[57]
	<1 ppm	ND	0.7%	ND	13%	ND	*Salix fragilis*– stems and leaves	[59]
	0.2%	ND	3.2%	ND	10.5%	ND	*Salix fragilis* – stems with hot-gas filter	[60]
Cu	<5 ppm	ND					*Salix fragilis*– stems and leaves	[59]
Pb	<1 ppm	ND	/	ND	/	ND	*Salix fragilis* – stems and leaves	[59]
	<1.9%	ND	<1.9%	ND	3%	ND	*Salix fragilis* – stems with hot-gas filter	[60]
Zn	ND	/	ND	/	ND	<1%*	Sunflower	[57]
	< 1%	ND					Willow - leaves and branches	[58]
	0.2%	ND	<1% **	ND	0.4 %	ND	*Salix fragilis*– stems and leaves	[59]
	0.5%	ND	0.2 %	ND	0.5 %	ND	*Salix fragilis* – stems with hot-gas filter	[60]

"/" –no detectable concentration of heavy metals; ND- no data; * – gaseous fraction; ** – non- and condensable pyrolysis fractions; ***- mixture of stems and leaves (filter experiments)

CONCLUSION

The economic development of many countries around the world has increased the need for alternative energy sources due to the lack of fossil fuels (limited quantity; greenhouse gas emissions that cause global warming) and the increase in fuel prices. Biomass is considered to be one of the alternative energy sources that seems to be the most promising because it does not contribute to a net increase in CO_2 levels in the atmosphere and contains small amounts of sulfur, nitrogen and ash.

Bio-oil as one of the major products obtained from the pyrolysis of lignocellulosic biomass has a number of industrial applications. After upgrading it, it is possible to use bio-oil as fuel for transport.

The best scope for obtaining bio-oil from rapeseed, sunflower and corn is from 500-600°C. The maximum yield of bio-oil of rapeseed (*Brassica napus*L.) of 75% was achieved at a temperature of 600°C, rapeseed cake gave 59.7% of bio-oil at 500°C, and from the straw and stalk of rapeseed was obtained 18% of bio-oil at 650°C. The maximum yield of bio-oil (52.1%) from the sunflower pressed bagasse (*Helianthus annuus* L.) was obtained at a temperature of 550°C, and sunflower oil cake gave 48.69% of bio-oil on 550°C. The agricultural residue of the sunflower gave the maximum yield of 30% ofbio-oil at 550°C. The maximum yield of bio-oil from corn cobs (*Zea mays* L.) was achieved at a temperature of 500°C and it was 61%, and at a temperature of 550°C was obtained 56.8% of bio-oil, while for the corn stover gave the maximum yield of bio-oil of 61.6% at 500°C.

Pyrolysis temperature is the main factor that affects the transfer of heavy metals in the volatile fraction of pyrolysis products. Copper, lead and zinc are retained in the solid fraction of pyrolysis products in the temperature range of 350-600°C, while cadmium shows volatility at temperatures over 450°C and its volatility increases with increasing temperature.

Acknowledgments

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IMPACT OF SELECTION OF MINING UNDERGROUND METHOD OF ORE DEPOSITS ON THE ENVIRONMENT

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ABSTRACT

The selection of underground excavation method of mineral deposits, which does not carry the risk for environmental factors within the mining area to the territory where deposit is developed, may be carried out by using the methodology of profit analysis, that can be achieved by applying of particular variants of the applicable methods. The selection of the most suitable variant of the underground excavation method of solid mineral ore, is performed based on the highest possible profit (lucre \$/t), which is realized in particular variant, after deduction of damage \$/t which are caused on the mineral resources deposit and ecological environmental factors by the application of that variant of excavation method,

Key words: Underground excavation methods, environmental protection, profit making.

INTRODUCTION

In the context of discussing the influences of underground methods of obtaining solid mineral raw materials on living environment, should be considered:

1. Impact of applied mining method of obtaining deposits on utilization of deposits and obtained ore depletion and thereby on preservation of natural asset that is non- renewable, i.e. on damages (costs of preparation and enrichment of ore), originating from that [1].
2. The impact of mining method on profit per ton of ore produced and damage to living environment, (reduced to a ton of ore produced), which is caused to overall value of natural environmental factors of the environment and deposits [2].
3. Threats to environmental factors: the earth's surface, surface and ground waters and air within the exploitation field and wider area [3].

When we start from the assumption that the underground excavation of mineral raw materials by applying the method of filling the cavities, reduces damages to the deposits of mineral raw materials, because by use of these methods deposits are better utilized, without the impoverishment, protects the Earth's surface within the exploitation field from deformation and subsidence, as well as the facilities on the and removes solid waste by storage in Excavation Sites, and not to the earth's surface, then all damages arising from the application of other methods of underground mining deposits converts into profit.

If this benefit-profit per ton of excavated ore is higher than the cost of filling empty dugs with a appropriate burden material, then for excavation of mineral raw material deposits should be applied excavation method of back filling of the excavated area.

COMPARISON OF UNDERGROUND EXCAVATION METHODS BASED ON THE INCOME BY EXPLOITATION AND ENVIRONMENTAL DAMAGES

Mathematical models for comparison of underground excavation methods based on possibly profit at excavation of mineral raw material deposits and environmental damages, are performed on the detailed analysis of the influence of mining methods on environmental factors, by valorization of these damages and their reduction to the costs ($ / t) of mineral raw materials reserves which shall be exploited. In the case where possible mining methods of deposits can provide the same production capacity of the mine and on the same cost of excavation and taking out, then their comparison can be executed based on the income D ($/t), the value of ore reduced by the: costs of production, damages to deposit, ecological factors in the environment and land reclamation, which mine has to pay.

$$D = \frac{1-g_i}{1-o_i}(C_D - S_{Di} - U_i), \ (\$/t)$$

where are:

D - profit per ton of ore obtained in the mine, ($/t)

C_D - Mine value of ore by withholding of costs for preparing and melting

S_{Di} - costs of the mining production at applied i-th mining method, ($/t)

g_i - loss coefficient of ore in deposits of i-th method in parts of the unit

o_i - obtained ore impoverishment coefficient when applying i-th method

U_i - Increase of costs of obtaining and ore when applying the i-th mining method due to contaminating of land, buildings, water and other mineral raw materials and taxes for occupied land.

In cases of using the method with the roof caving, it is necessary to define the limits of the impact of exploitation of deposits on the earth's surface and on objects in mining field and compensate owners of land and buildings, and thus exploitation field is free for use for the purposes of mine. The cost of releasing the exploitation field is determined by the formula:

$$U_1 = \frac{\sum p_{zi}C_{zi} + \sum O_b C_{oi} + \sum p_{zo}C_{zo}}{Q_r} \cdot \frac{1-O_i}{1-g_i}, \ (\$/t)$$

where are:

p_{zi} - area of i-th categories of land to be purchased by,

C_{zi}- price of i-th categories of land,

O_b- type and quantity of objects to be relocated or purchased by,

C_{oi}- price per unit of objects,

p_{zo}- area of land that will be out of use due to the takeover,
C_{zo}- tax which will mine pay for occupied land.

Due to the settlement of roof all water from area of exploitation field, regardless of drains and streams diverted, enters into the mine, so it could be expected an increased inflow of surface atmospheric waters, in proportion to the surface of exploitation field and mean annual rainfalls. Therefore costs of mine drainage are increased.

$$S_o = \frac{P_p \cdot (P_d - P_e)}{1000} \cdot \frac{1{,}1 \cdot \rho g H C_e}{1000 \eta Q_{god}}, \quad (\$/t)$$

where are:

P_p - catchment area of the subsidence trough, (m^2)
P_d- mean annual precipitation, (mm/m^2)
ρ - density of water, (kg/m^3)
H - depth of water pumping,
C_e - price of electricity, ($/kW)
η - coefficient of power utilization
Q_{god} - annual ore production, (t/god.)
P_e - average annual amount of water that evaporates from exploitation field.

Excavation methods with protective pillars for preservation of environment, and with back filling of digs between them by solidifying mud, have higher losses of ore with minimal impoverishment but by their application can be protected living environment in the limits of exploitation field. Getting ore using excavation method with back filling of stope is more expensive for the value of stope filling and damage due to falling behind of ore in protective pillars. If the value of protected objects higher than values of stope filling and damages due to loss of ore in protective pillars, then it is justified the application of mining methods with filling of excavation area.

Storage of flotation tailings also endangers the environment, so from that aspect is better to perform its storage in empty chambers of stope. This achieves recirculation of waste tailings. Cost of tailings pumping and storing on flotation tailings on the surface can be equal to the costs of filling in of stope. This does not additionally encumber production of concentrate.

Arrangement, geometry and revenue yield of excavation at both mining methods can be so selected that remain identical: way of opening, development, ventilation, drainage, and transport and export of ore, so then the costs of obtaining of ore are identical. Differences remain in the domain of utilization of deposits, impoverishment of ore, filling in of stopes and endangering of living environment.

Profit at application of mining method with roof caving D_1 or when applying mining method with leaving the protective pillars for protection of roof from subsidence and filling in of stope D_2 or mining method with siltation of stope by solidifying stowage D_3, and full utilization of deposits, shall be determined according formulae:

$$D_1 = \frac{1-g_1}{1-o_1}(C_D - S_{D_1} - U_1), \quad (\$/t)$$

$$D_2 = \frac{1-g_2}{1-o_2}(C_D - S_{D_1} - O), \quad (\$/t)$$

$$D_3 = \frac{1-g_3}{1-o_3}(C_d - S_{D_3} - O), \quad (\$/t)$$

$$S_{D_1} = S_D + S_o; \quad C_{D_2} - S_D + S_z; \quad S_{D_3} = S_D + S_z + S_c$$

In addition to the well-known designations, the others are:

S_D - costs of opening and development, mining, transport and export of ore,
S_o - cost of additional drainage,
S_z - cost of pumping and the silting up of stope,
Sc - additional costs for making the solidifying stowage.
O(0)-the cost of protecting objects and living environment have the value (0)

For excavation of deposits shall be selected method of underground excavation which generates the longest exploitation life of deposit and the largest profit: D_i (max), and that can be a filling method.

Example:

In order to illustrate the impact of environmental protection at the selection of mining method may serve an example from the practice:

The ore body with copper content in the ore m=0,6% and ore reserves Q_R=623. 000.000 t, spreads to a depth of H=1000 m. During the exploitation of ore body mining method with roof caving will be realized losses coefficient of ore g_1=0,35 and impoverishment O_1=0,2. Above the deposits will form sag, with area of P_p=11,6 km^2.

Within the sags there are objects to be relocated, a land redeems and pays taxes every year for the occupied land, for: railway and tunnel - 19 229.031,00 \$, settlement 4 535 187 000 \$, asphalt road 3.615.023,50 \$ and relocation of the cemetery 373,869,95 \$, deviation of stream 70. 225,35 \$, purchase of land 338.461,5 \$. Average precipitation in the area are P_d=720 mm/m^2 per year.

Reduced costs, damages for endangering the environment, on ton of ore: Objects and land acquisition 0,048 \$, taxes for occupied land 0,025 \$, additional cost of drainage So=0,14 \$.

$$U_1 = [0{,}048 + 0{,}02 + 0{,}14]\frac{1-0{,}2}{1-0{,}35} = 0{,}256, \quad (\$/t) \text{ exported ore.}$$

In the case of exploitation of deposits using chamber -pillar method with siltation of excavated area, costs of environmental protection (U=O) do not appear. Appears cost of siltation of stope, which in the world practice is S_z=0,2 \$/t, which can be reduced for costs of disposal of flotation tailings. Loss coefficient ore $g_2$is 0,55, and coefficient of impoverishment is O_2=O.

In order to apply solidifying stowing, it would be achieved better utilization of deposits at the subsequent obtaining of pillars, so the loss coefficient of ore would be g_3=0,2, coefficient of impoverishment O_3=0,1 and costs of adding a binding agent S_c=0,2 \$/t.

The value of ore C_D is treated differently depending on the obtaining of certain metals from polymetallic ore. In this way the lowest value of ore in mine is determined, after deduction of expenses of melting and flotation, in obtaining only copper in the amount of 5,125 \$/t. In obtaining the other metals from ore, its value is 10,39 \$/t [2].

The costs of obtaining of ore are limited by the request of mine at 7 \$/t.

Based on these data it is possible to calculate profit and loss in the application of different methods of mass excavation of ore (at affordable metal prices on the market for copper higher than the minimum in the past period of XX century), C_D=2.500 \$/t) as:

1. Excavation with the roof caving
   a) only at the utilization of copper D_1=0,812 [5,12-7-0,256] = -1,73 \$/t loss
   b) at the utilization of other metals D_1=0,812 [10,39-7-0,256] = 2,54 \$/t profit
2. Chamber -pillar excavation with siltation of stopes
   a) utilization of only copper D_2=0,45 [5,12-7-0,2] = - 0,9 \$/t loss
   b) utilization of other metals D_2=0,45 [10,39-7-0,2] = 1,43 \$/t profit
3. Excavation using siltation of chambers by solidifying stowing and subsequent obtaining of pillars
   a) utilization of only copper D_3=0,88 [5,12-7-0,4] = - 2,006 \$/t loss
   b) utilization of other metals D_3=0,88 [10,39-7-0,4] = 2,63 \$/t profit

CONCLUSION

Full utilization of deposits without impoverishment of ore and all metals from ore profit can be made even at obtaining of poor deposits. In doing so positive, and the higher profit, can be realized by using mining method with the siltation of excavation area solidifying stowing with addition of cement. In doing so, it extends the life of the mine and achieves savings in environmental protection.

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PREVENTION, RISK AND INSURANCE OF MINING PRODUCTION SYSTEMS

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ABSTRACT

The choice of protection strategy of accidents and in relation to them, damage in the mine, can be successfully carried out applying the theory of games, elaborated in the literature for operational research. Based on it may be chosen an alternative: installation of protective systems as a preventive measure against hazards of damages in the mine or Insurance of the mine of those damages at the insurance company. For optimal selection of strategy for protection against damages which may originate from any form of manifestation of risk from certain natural hazard, it is necessary to know the probability of the occurrence of that danger.

Key words: probability of risk manifestation in the mine, size of damage, strategy selection.

INTRODUCTION

The risk, at the beginning of the third millennium, is taken for the serious economic technical, public and political concept and used in many situations, almost as a term TENDER or TRANSPARENT with different meanings. It has its own market, its market value, sellers and buyers or users [1].

Those who invest in prevention to reduce the risks of damages or ensure someone's risk, expect profit, which in turn means that it is more important to identify risk and manage it, rather than to insist on the reduction and elimination of risk "at any cost". That is in any case a new management philosophy with complex systems. If the company is trying to completely eliminate the possibility of damage by installing protective devices of high probability of reliability and efficiency, therefore to declare unnecessary to ensure the devices or systems, and requires insurance with a small premium amount, it can reach a zone of high investment needs in prevention and safety of system. In this case should be applied management towards risk.

It is known that the insurance company expects profit from operating insurance of capital equipment. The Company has an interest in insurance premiums to be as low as possible and shall endeavor to show high probability of reliability of its production system for preventive investment in safety equipment. Therefore, between the insurance company and the entrepreneur must find common ground in the form of the matrix game with zero (nearly zero) sum (risk). This will happen when both players have an alternative:

I player - entrepreneur with alternatives a_i, which can be expressed by cost of equipment without security protection, or with safety protection, accompanied by a certain probability of safety, i.e. risk (hazard) from potential dangers, with the prices of equipment and installations.

II player - insurance company (it may be the designer) with alternatives b_j responsible for suppression of risks from possible potential damage of the insured (or payment of premiums on risk to equipment and installations) in the the case of manifestation of potential danger.

The company strategy based only on the assumption that with insurance the production system will realize increased profits is wrong, because they will have to pay high insurance premiums, and in case of an accident, get the minimum value of written-off funds and will not be able to launch a new production. This is why in the loss are both, the entrepreneur and the insurance company. The optimal strategy for eliminating the risk in order to make profits, for entrepreneurs and for insurance companies, is continuous improvement and reduction of risks in the production system by installing of protective screens; in this case we can reduce the risk for both players by proportional reduction of the amount of premiums. Below we provide a method of selection of strategy of risk protection from potential hazards in mines, in what should participate insurance companies with their professional services.

SOURCES OF RISK IN MINES AND EXPLOITATION DESIGN

To solve problems in choosing strategy for protection from accidents in mines, successfully can be applied game theory in the field of operational research. Based on it may be chosen a range of alternatives for suppression of any kind of manifestation of certain natural hazard.

Accident in a mine and damages at the equipment and installations is caused by manifestation of a source of danger, due to which damage occurs of mining structures, interruption of production or losses of human lives. Sources of accidents in mines may be different, but the most common are:

Cave-ins of a large scope and rock bursts,
Flashes of water or slurry materials,
Blasts of explosive systems,
Mine's endogenous or exogenous fires,
Breakthroughs of toxic and asphyxiating gases from their collectors [1].

The probability of the risk of an accident sources depends on the way of its manifestations. If a source of accidents does not manifest in the layer, then the probability of danger from that source is zero, and therefore investments in the system of protection are not required (could be zero a_o=0). If a source of danger manifests with the probability of danger p>0,3 (first degree), then the system of protection from manifestation of this source of danger and investments for its installation and maintenance are adequate to the first and basic degree. These investments will have a value which can be conditionally marked with $a_1=1$. (I group of costs in dinars.). If a source of danger manifests with the probability of danger $p_1>0,5$ (second degree of danger) then, to ensure safety from accidents is necessary more perfect protection system whose price of application will be higher $a_2=2$ (II group of costs). If a source of danger manifests with the probability of danger $p>0,8$ (third degree of danger) hen to ensure safety from accidents is necessary to install more comprehensive and more perfect protection system, for whose operation costs are of a third size $a_3=3$ (III group of costs).

Design of deposit exploitation is performed based on the available geological data about deposit and data on assessment of possible ways of certain natural potential hazards manifestation. In the project of security should be adopted optimal solution that requires minimal investment and maintenance costs of the system of protection from certain natural potential hazards, and which provides maximum safety of that accident. If adequate protection system is not provided there is a risk that an accident occurs with all the consequences that it brings, including mining accidents followed up with human victims.

SELECTION OF PROTECTION STRATEGY AGAINST POTENTIAL DANGERS IN THE MINE

A preventive protection strategy against accidents from a source of danger is defined as the set of all alternatives which designer disposes in making decisions. He can plans decisions (alternative) taking into account all the possible ways of manifesting some natural potential hazards that may occur during deposit exploitation, and they can be encouraged by technical factors of exploitation. The set of alternatives and their prices, which designer may select will be denoted by $A_i=/a_0, a_1, a_2,...a_m/$, and the set of alternative ways of expressing the natural potential hazard, and related with it the costs for procurement, installation and use of a protection system of high probability and reliability is denoted by $B_j=/b_0, b_1, b_2,...b_n/$. Based on these data, could be defined a simple dot matrix game, In which I player is designer of protection system, and II player is natural potential danger (source of accidents) with its probability of manifestation and necessary costs for suppression of risk from accidents, which depend on the probability of manifestation and the ways and extent of damage in the manifestation of danger. The matrix of system costs for protection from accidents is shown in Table 1.

Table 1. The matrix of system costs for protection from accidents C/ai;bj/

Ways of manifestation of natural potential hazard					
category of deposit		0	I	II	III
The probability of accidents occurrence p_i		0	0,3	0,5	0,8
The cost of security B_j protection costs		b_0	b_1	b_2	b_3
Strategy of designers in selection of protection and prices A_i (depends on estimated amount of damage)	a_o a_1 a_2 a_3	0:0 1:0 2:0 3:0	0:1 1:1 2:1 3:1	0:2 1:2 2:2 3:2	0:3 1:3 2:3 3:3

The strategy can be counted, or rigorously determined and thus each illogicality in determining excluded [2]. Choosing these arguments which are under the control of the designer depend on the assessment, damage that may occur in the manifestation of accident, his logic and reasoning. On that way, will be able to adopt one strategy versus estimated or the actual way of danger manifestation, dominant or not. Result of efficiency and dominance of a particular strategy is learned only when the exploitation of deposits, or part of the deposit, for which the project is being worked, completed or when an accident occurred, and then on its outcome can not affect.

For a strategy which is selected is said to be a zero-sum game price if, at the end of the game, the player who got the game equals the loss of a player who has lost the game. No player can not completely, but only partially, influence on the outcome of event. In the case when only one player can influence the outcome of event, while the other player is without influence, game is reduced to a game of one person. If designer of the security system has a number alternatives which are marked with A/a_0, a_1, a_2, ...a_m/ with the outcome price $C/a_i/$ then it may be requested an optimal alternative in a way that C/a'/>C/ai/ for all values a_i. When both player have selected alternatives then the price for player I is C/a_i, $b_j/$, for player II is C'/a_i; $b_j/$, where $C/a_i;b_j/=-C'/a_i$; $b_j/$. The value of the gain is equal to the RISK - C'/a_i; $b_j/$.

When objects and installations of mines are ensured from damage with insurance companies, then mine pays the insurance premium during the period of the facility duration, depending on the price of the buildings and installations and probability "a priori" of manifestation of natural potential risks to their destruction. Aggregated values of paid premiums for certain probability of danger,"B_j" should be approximately equal to the values of investments in protective screens to achieve the adequate probability of security "A_i". Determining the value of monthly premiums for insurance of buildings and installations from potential danger from destruction is defined by the formula:

$$Pm = \frac{p_{(\Delta t)} D}{12 \Delta T}$$

where are:

Pm - monthly premium (din/month),

P(Δt) - probability of the insured event occurrence during the insurance period ΔT year.

D - insured value or extent of possible damage expressed in RSD, B_j=/b_0, b_1, b_2,...b_n/.

ΔT - period of insurance, at long-term insurance.

Between the price for chosen alternative of protection from accidents a_i and necessary protection, depending on the way of manifestation of natural potential hazard, b_j, there is a difference $R=/a_i-b_j/$. It represents a saving on security, or risk with selection of strategy, i.e. system for providing security that an accident or damage will not occur.

The value of the damage that would occur due to emergence of accidents may be higher than the risk (usually higher), and at death of humans it is irrecoverable. Matrix for pricing strategies of safety and risk with conditional values $R_i = \lfloor a_i - b_j \rfloor$; [$a_i$=0, 1, 2, ...m]; [$b_j$=0,1,2,..n], are given in Table 2.

Table 2. Matrix of price groups of security and risk

Possible damages / The cost of selected system	b_0	b_1	b_2	b_3
a_0	0	-1	-2	-3
a_1	1	0	-1	-2
a_2	2	1	0	-1
a_3	3	2	1	0

a_i - price of alternatives protection by installing a protective screen, which is chosen by designer
b_j - price of insurance premiums for insurance for system insurance period due to the way of manifestation of natural potential hazard.

If certain natural hazard does not appear in deposit b_j o, then it is logical that it is unnecessary to invest in the protection system, so the response of designer is a_i o. There are no investments or risk. If designer does not know the way of manifestation of certain hazards, but he knows that it will be manifested, then he can choose the strategies a_1, a_2, a_3. If the chosen strategy is a_2 with price 2 (second group), and way of manifestation of damage occurs with b_1, then the designer overestimated the opponents, so it is much invested (2), and gets (1). If the risk is manifested with b_2, then the strategy selected is with a value of zero, so this is the optimal strategy. If the danger is manifested with the request for investments in the protection system to the level b_3, then it was selected with the risk whose price group is R=/2-3/=-1. The emergence of risk suggests that an accident may occur, because the manifestation of danger will not be revealed on time. Is it worth to risk depends on whether the damage from accident will be is less or greater than the risks. If the damage from accident is less than risk, then it's worth to risk.

To the ways of manifestation danger b_j can join the probability of frequency qi>0, known from practice /if in Z mine: zero, first, second and third mode of manifestation of danger occurs z_0, z_1, z_2, z_3 times, than $q_0 = z_0 / Z$, $q_1 = z_1 / Z$, $q_2 = z_2 / Z$, $q_3 = z_3 / Z$ /, then we can define n-dimensional vector Q/q_0, q_1, q_2, q_3/ for distribution of probability of occurrence, where is $\sum q_i = 1$. The frequency of choice of certain strategies / protection system / by designers also can be represented with m dimensional vector P=/p_0, p_1, p_2,..., p_m/, where p_i>= 0, and Σp_i=1. /i=0, 1, 2,...,m/.

Price for strategies is then given by $C / PQ / = \sum p_i q_i a_{ij}$. The expression indicates that there are optimal strategies $P_x Q_x$ such that:

$$C[P_x Q_x] = \min P \max QC[P\,Q] = \max Q \min P\, C*[P\,Q]$$

Choosing the strategy can take a form of one procedure, and it can be a series of procedures with the new information at each stage. The procedure of strategy selection, i.e. protection system is based on the matrix in table 1 represents the normal form of simple matrix game, but positional or dynamic games include the new information at any further step.

Selection of strategies through the matrix can be transformed into a linear programming problem. The general formula of linear programming task, which is best suited for this purpose, is the following:

$$F[x] = C_1 x_1 + C_2 x_2 + ... + C_n x_n$$

At the restrictions:

$$a_{11}x_1 \quad + \quad a_{12}x_2 \quad + ... \quad + \quad a_{1n}x_n > b_1$$
$$a_{21}x_1 \quad + \quad a_{22}x_2 \quad + ... \quad + \quad a_{2n}x_n > b_2$$
$$a_{m1}x_1 \quad + \quad a_{m2}x_2 \quad + ... \quad + \quad a_{mn}x_n > b_n$$

Where are:

Elements $a_{ij} = R > O$, (value of risk or price of the investment in insurance)

Xi - alternative mark

Inequalities are given in columns.

It is always possible to find such a constant size of d which will, when added to each element of the matrix, give a new matrix, in which all elements are positive. When the matrix structure remains unchanged, but its value differs by a constant amount d in relation to the previous. A pair of optimal strategies in the initial matrix is the same as a pair of optimal strategies in the new matrix.

If $P = [p_0, p_1, ... p_m]$ is optimal strategy by designer, then for any clear strategy, depending on the mode of manifestation of certain natural hazards, which indicates price with bj, is valid known relation: $C / p * b_j / > V$. V - the value of variants [j=0, 1, 2, ...,n].

Developed form of this relation is given in the form of inequalities in columns

$$a_{11}p_1 \quad + \quad a_{21}p_2 \quad + ... \quad + \quad a_{m1}p_m > V$$
$$a_{21}p_1 \quad + \quad a_{22}p_2 \quad + ... \quad + \quad a_{m2}p_m > V$$
$$a_{1n}p_1 \quad + \quad a_{2n}p_2 \quad + ... \quad + \quad a_{mn}p_m > V$$

Based on these relations can be obtained solutions p_1, p_2, p_m, and given system of equations can be written in the form:

$$a_{11}p_1 / V \quad + \quad a_{21}p_2 / V \quad + ... \quad + \quad a_{m1}p_m / V \quad > \quad 1$$
$$a_{1n}p_1 / V \quad + \quad a_{2n}p_2 / V \quad + ... \quad + \quad a_{mn}p_m / V \quad > \quad 1$$
$$x_i = p_i / V \qquad i = [1, 2, m]$$

Considering that $p_1+p_2+...p_m=1$, is obtained $x_1+x_2+...+x_m=1/V$

The designer wants to choose such a set of values p_1, p_2,..., p_m and V (The value of variant) that will meet the previous inequality by (p_i), while at the same V being as less. This is identical to the statement that the designer wants to determine a set of values x_1, x_2,..., x_m, which satisfy a set of inequalities given by the columns of the matrix 1.

$$\begin{array}{ccccccccc}
a_{11}x_1 & + & a_{21}x_2 & +.. & + & a_{m1}x_m & > & 1 \\
a_{12}x_1 & + & a_{22}x_2 & +.. & + & a_{m2}x_m & > & 1 \\
a_{1n}x_1 & + & a_{2n}x_2 & +.. & + & a_{mn}x_m & > & 1
\end{array}$$

Inequalities ensure that the function $F_{[x]}=1/V=x_1+x_2+...+x_m$ obtain the minimum value. In the given example, it is possible to form four inequalities with four unknown x_i whose solution is easy to find [2].

CONCLUSION

Based on the analysis of possible ways of manifestation of certain natural potential hazards, possible systems of protection against emergence of accidents and costs of their use, it is possible to select the optimal strategy for protection against accidents, i.e., such a protection system that will require minimal cost and ensuring the maximum security. Only after the introduction of preventive protection in production systems and determining the probability of its safety should be approached to insurance at insurance companies, in order the insurance premium is less. Simplifying the problem to the task of linear programming, solution can be obtained by using the "simplex" method and programs contained in the computers.

Acknowledgements

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THE INFLUENCE OF BENZOTRIAZOLE ON POTENTIOSTATIC OXYDATION OF AgCu50 ALLOY IN PRESENCE OF CHLORIDES

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ABSTRACT

Potentiodynamic and potentiostatic method have been used to investigate electrochemical behavior of AgCu50 alloy. Investigations have been performed in 0.1 mol dm^{-3} NaOH + 0.1 mol dm^{-3} NaCl in absence and in the presence of benzotriazole in concentrations ranging from 0.00005-0.01 mol dm^{-3}. Seven current peaks appear on all anodic potentiodynamic curves. Potentiostatic polarisation was conducted at 620 mV vs. SCE during 100 s at the temperature of 25^0C. Stationary current densities on potentiostatic curves decrease with the increasing of concentration of benzotriazole in the electrolyte. After the potentiostatic oxidation electrode surface was monitored using optical microscopy. Microphotographs confirm the presumption that, beside the CuBTA and AgBTA film, in the presence of BTA copper and silver oxides are formed, but in a quantity which could be neglected.

Key words: Corrosion, AgCu50 alloy, benzotriazole, electrochemical oxidation, CuBTA, AgBTA film.

INTRODUCTION

Organic substances are widely used for corrosion protection of pure metals and alloys in different environments. Among them, the efficiency of employing azoles for corrosion protection of copper and its alloys is widely investigated [1, 2]. The most commonly used corrosion inhibitior for copper and copper alloys from the azoles group is benzotriazole (BTA). Protective efficiency of BTA in some environment could be explained with the inherent characteristics of BTA compound. BTA appears in three different forms depending on the solution pH [3]. In strong acids it exists as $BTAH_2^+$, in neutral media and weak alkalines it presents as a neutral molekule BTAH, while in strong alkalines it is in a form of BTA^- ion.

It was found that BTA is an anodic corrosion inhibitor for copper, where the mechanism of influence comprises chemisorption on copper surface, governed by Langmuir adsorption isotherm [4,5], followed with forming of Cu(I)BTA complex [3, 6, 7]. In alkaline media in presence of chloride ions and benzotriazole, besides CuBTA film, copper oxides and copper chlorides are formed [2].

Based on available literature it could be supposed that in alkaline media in presence of chloride ions and benzotriazole AgBTA complex is formed in parallel with oxides and chlorides of silver [4].

EXPERIMENTAL

The experiments were carried out in a system consisting of an electrochemical cell and hardware interface for computerized control and data acquisition. In a standard three-electrode electrochemical cell, the working electrode was AgCu50 alloy, whose potential was controlled against saturated calomel reference electrode (SCE). Platinum foil served as a counter electrode. The computerized controll (National Instruments card, NI-6251) and data acquisition software (LabVIEW 8.2 platform), fully developed by Technical Faculty in Bor [8], was used to run the electrochemical experiments.

AgCu50 alloy was investigated in 0.1 mol dm^{-3} NaOH + 0.1 mol dm^{-3} NaCl in absence and in presence of benzotrizole (0.00005 mol/dm^3 – 0.01 mol/dm^3) of p.a. quality using cyclic voltammetry and potentiosatic method at 25^0C. Anodic polarisation curves have been recorded in a potential range from -1 V vs. SCE to 1 V vs. SCE with a scan rate of 20 mV/s. Potentiostatic curves have been recorded on 620 mV vs. SCE. After potentiostatic oxidation, the electrode surface was characterized by optical microscopy.

RESULTS AND DISCUSSION

Anodic polarisation curves for the AgCu50 alloy in 0.1 mol dm^{-3} NaOH with the addition of 0.1 mol dm^{-3} NaCl with the absence and with the presence of 0,00005-0,01 mol dm^{-3} BTA with the scan rate of 20 mV s^{-1} are presented in Figure 1.

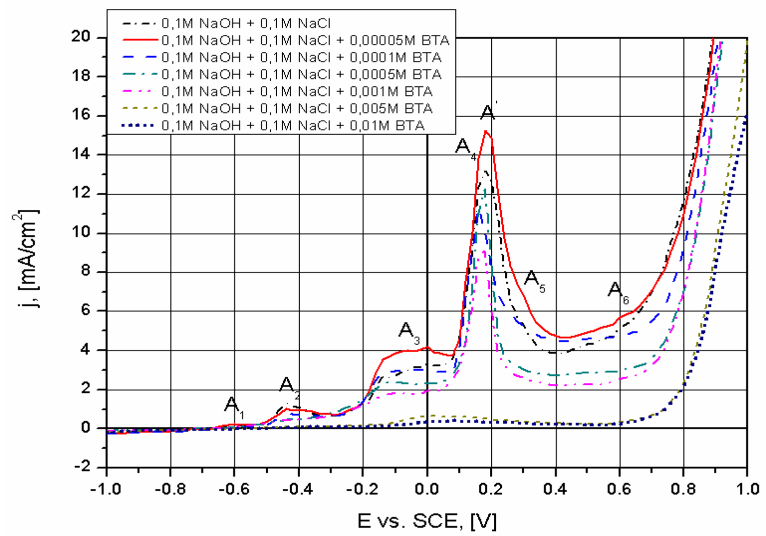


Figure 1. Anodic polarisation curves for AgCu50 alloy in 0.1 mol dm^{-3} NaOH with the presence of 0.1 mol dm^{-3} NaCl without and with the addition of BTA in concentration range of 0.00005-0.01 mol dm^{-3} with the scan rate of 20 mV s^{-1}

Analysis of the anodic polarization curves from Figure 1 leads to the conclusion that chloride ions have very active influence on the alloy corrosion in presence of BTA in some investigated concentrations. BTA itself has an activating corrosion effect when its concentration is 0.00005 mol dm^{-3}. Anodic current peaks have lower current density values for all BTA concentrations higher than 0.0001 mol dm^{-3}, that proves the effectivness of BTA as a corrosion inhibitor. From the diagram it also can be concluded that BTA in concentrations higher than 0.001 mol dm^{-3} fully protects electrode surface in spite of the presence of chloride ions.

Based on diagrams constructed by Tromans [9] and a fact that the solution pH equals 12, it can be concluded that benzotriazole in investigated system is present in the form of BTA$^-$. So, further conclusion is that protective film made of CuBTA and AgBTA is formed by the following reactions [10]:

$$Cu_{(Ag\text{-}Cu)} + BTA^-_{\ aq} \rightarrow (Cu_{(Ag\text{-}Cu)}\text{-}BTA)_{ads} + e^- \quad (1)$$

or

$$(Cu_{(Ag\text{-}Cu)}\text{-}H_2O)_{ads} + BTA^- \rightarrow (Cu_{(Ag\text{-}Cu)}\text{-}BTA)_{ads} + H_2O_{aq} + e^- \quad (2)$$

On places at the surface richer in silver, protective film will be formed by the following reactions:

$$Ag_{(Ag\text{-}Cu)} + BTA^-_{\ aq} \rightarrow (Ag_{(Ag\text{-}Cu)}\text{-}BTA)_{ads} + e^- \quad (3)$$

or

$$(Ag_{(Ag\text{-}Cu)}\text{-}H_2O)_{ads} + BTA^- \rightarrow (Ag_{(Ag\text{-}Cu)}\text{-}BTA)_{ads} + H_2O_{aq} + e^- \quad (4)$$

Because of the presence of chloride ions, following reactions for copper and silver from the alloy can be expected:

$$Cu_{(Ag\text{-}Cu)}\text{-}Cl^-)_{ads} + BTA^- \rightarrow (Cu_{(Ag\text{-}Cu)}\text{-}BTA)_{ads} + Cl^- \quad (5)$$

$$(Ag_{(Ag\text{-}Cu)}\text{-}Cl^-)_{ads} + BTA^- \rightarrow (Ag_{(Ag\text{-}Cu)}\text{-}BTA)_{ads} + Cl^- \quad (6)$$

At the same time, oxides of silver an copper are formed on uncovered places. It should be emphasized that in the presence of BTA, both silver oxides Ag_2O and AgO are present, but mechanism of formation of Ag_2O is changed in compare with the mechanism without the presence of that inhibitor. Silver and copper oxides keep growing until the whole electrode surface is covered with CuBTA and AgBTA complexes [10].

POTENTIOSTATIC METHOD

Potentiostatic measurements are performed on 620 mV vs. SCE during 100 s. This potential correspond to the current peak A_6 on anodic polarisation curves. Obtained polarisation curves are presented in Figure 2.

It can be seen from Figure 2 that the current densities in 0.1 mol dm^{-3} NaOH + 0.1 mol dm^{-3} NaCl solution are higher then current densities recorded without the presence of NaCl on the whole flow of potentiostatic curves. With the addition of 0.0001 mol dm^{-3} BTA in 0.1 mol dm^{-3} NaOH + 0.1 mol dm^{-3} NaCl solution current densities are almost equal for both solutions till about 16 seconds; after that, current densities are lower in compare with those obtained in presence of chloride ions, but higher than the current densities obtained under the same conditions in 0.1 mol dm^{-3} NaOH.

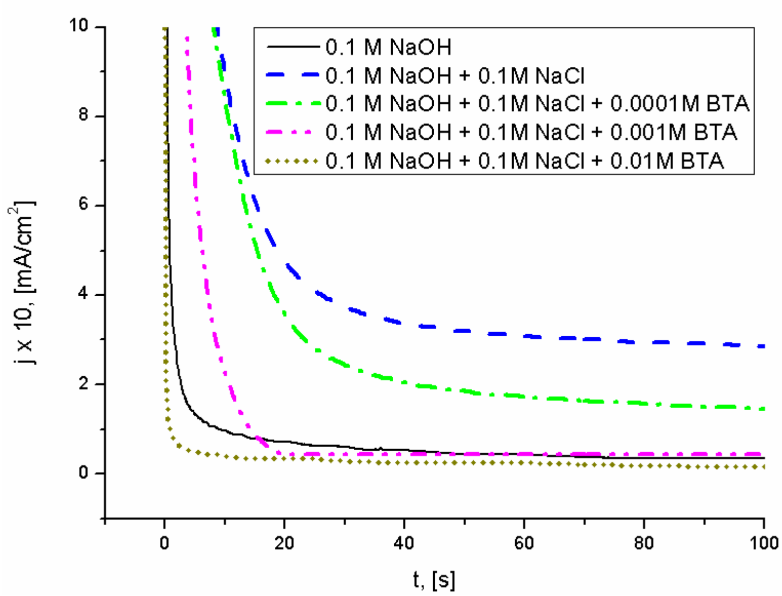
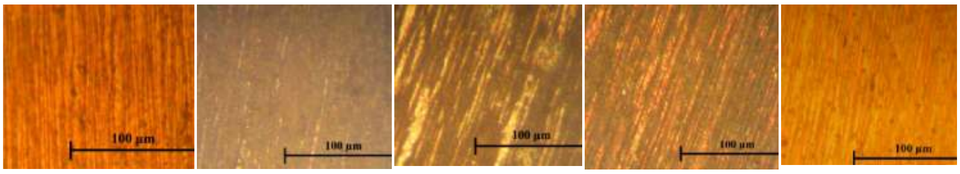


Figure 2. Potentiostatic curves for AgCu50 alloy in 0.1 M NaOH + 0.1M NaCl on E = 620 mV vs. SCE at different concentrations of BTA

When concentration of BTA is 0.001 mol dm^{-3}, potentiostatic curve shows that, after switching on, current density drops fast and in the first couple seconds reaches stable value. In presence of 0.01 mol dm^{-3} BTA current density, after initial sharp drop, reaches the value that is lower than current density recorded without the presence of chloride ions and remains constant until the end of measurement. This points out that Cu(I)BTA and AgBTA a film which protects the alloy from oxidation is formed.

Characterization of the surface of the alloy is performed with optical microscopy after potentiostatic treatment of the alloy first in pure 0.1 mol dm^{-3} NaOH and then in the same solution with the addition of chloride ions; finaly, same potentiostatic treatment and characterization are performed when, beside NaOH and NaCl, BTA in different concentrations was present in electrolyte. Potentiostatic polarization is conducted at 620 mV vs, SCE during 100 s. Microphotographs of surface of the treated electrodes are presented in Figure 3 (a, b, c, d i e).



a) b) c) d) e)

Figure 3. Microphotographs of surface of AgCu50 alloy after potentiostatic treatment on 620 mV vs. SCE during 100 s: a) in 0.1 mol dm^{-3} NaOH; b) 0.1 mol dm^{-3} NaOH + 0.1 mol dm^{-3} NaCl; c) 0.1 mol dm^{-3} NaOH + 0.1 mol dm^{-3} NaCl + 0.0001 mol dm^{-3} BTA; d) 0.1 mol dm^{-3} NaOH + 0.1 mol dm^{-3} NaCl + 0.001 mol dm^{-3} BTA; e) 0.1 mol dm^{-3} NaOH + 0.1 mol dm^{-3} NaCl + 0.01 mol dm^{-3} BTA

On the microphotography obtained after the potentiostatic treatment in 0.1 mol dm^{-3} NaOH (Figure 3a) a dark phase that originates from copper and silver oxides can be noticed on the surface. With the addition of chloride ions in concentration of 0.1 mol dm^{-3} (Figure 3b), on the surface appears a green phase that originates from copper chloride, and a small quantity of white phase that comes from silver chloride. Dark phase originating from copper and silver oxides appears, too.

When benzotriazole is added in concentrations from 0.0001 to 0.01 mol dm^{-3} (Figures 3c, 3d and 3e), it adsorbes on the alloy surface forming CuBTA and AgBTA complexes that protect the alloy from corrosion. The microphotographs show that the quantity of chlorides and oxides on the surface decreases with the increasing of BTA concentration in solution, proving protective role of BTA.

CONCLUSION

On anodic polarization curves recorded for AgCu50 alloy in 0.1 mol dm^{-3} NaOH with the addition of chloride ions, one additional current peak appears that is not present on voltammograms recorded without the presence of chlorides. The presence of Cl^- ions in alkaline solutions intensifies anodic processes on AgCu50 alloy leading to the higher peak current densities. Increasing of concentration of chloride ions also causes the increasing of the peak heights. Benzotriazole, the known corrosion inhibitor for copper yielded to slow down of processes which take place on AgCu50 alloy during anodic polarization in presence of Cl^- ions. At the lowest investigated concentration of 0.00005 mol dm^{-3}, BTA acts as an activator of corrosion processes. That confirms the rule that inhibitors should be added in enough high concentration, which has to be established by experiments, to give a positive effect on corrosion slow down. Anodic reactions decrease when concentration of BTA is higher than 0.0001 mol dm^{-3}, but the biggest influence is achieved with concentrations higher than 0.001 mol dm^{-3}.

Inhibition effect is a consequence of formation of a protective film on the surface of the alloy. That film consists of adsorbed CuBTA and AgBTA complexes formed by the reactions of copper and silver with BTA^- particles. Also, current peaks are shifted to more positive values and current densities reach values almost zero values at high BTA concentrations. Copper and silver oxides also are formed until the whole electrode surface is covered with protective complexes.

Potentiostatic measurements show that the mechanism of inhibition with BTA depends on its concentration in electrolyte. Optical microscopy confirms that in the presence of BTA, beside CuBTA and AgBTA film, oxides and chlorides of copper and silver appear in a quantity that can be neglected.

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Zn-Al-BASED ECOLOGICAL ALLOYS AND THEIR APPLICATION IN ELECTRONICS

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ABSTRACT

The improvement of lead-free solder alloys for high-temperature applications is vital to meet growing demands for reliable replacements for lead-containing alloys. Several candidate alloys have been proposed as alternative solders to high-temperature high-lead solders. None of them, however, can fulfill all the requirements to replace the current high-lead solders. The development of lead-free solders has become a major concern to the researchers in electronic industry. This paper provides a short review of recent research on Zn-Al-based ecological high-temperature alloys with different additional alloying elements.

Key words: Lead-free solder, Zn-Al-based ecological alloys, high-temperature alloys.

INTRODUCTION

Lead was until lately a universally used element in many components of the electronics industry. It appears in solder materials, coatings soldered on printed circuit boards, pins and the ends of boards. The commonness of the electronic equipment which accompanies almost every aspect of our lives is 8 million tons of waste per year in EU countries. As a result of the wastes, corrosion toxic lead compounds were passing into groundwater and contributing to environmental pollution. Harmful effect of lead on human health is well known - its accumulation in the body causes disorders in the nervous and reproductive systems, the delays in neurological and physical development, anemia and hypertension [1].

Health and environmental issues

In the 90's of the last century Japan and the U.S. initiated research on the replacement of typical PbSn solders. Among the countries of the European Union breakthrough came about 10 years later, along with two directives of the European Parliament and the Council: RoHS (2002/95/EC) - on the restriction of the use of Certain Hazardous Substances in electric [2, 3] and electronic equipment and WEEE

(2002/96/WE) - on waste electric and electronic equipment [4]. Although the RoHS legislation was adopted in 2006 to eliminate lead and other toxic materials from electronic assemblies, high-lead-content solders were exempt from the legislation. The high-lead-content-solder exemption appears to be offered primarily for die-attach applications and will be phased out in many products by 2017 unless renewal requests are submitted and accepted.

Performance characteristics of high-temperature solders

Sn-Pb solders for metal interconnections have a long history, dating back 2000 years. This solder and the alloys developed with it have long provided and continue to provide many benefits, such as ease of handling, low melting temperatures, good workability, ductility, and excellent wetting on Cu and its alloys [5]. There are strict performance requirements for solder alloys used in electronics. In general, the solder alloy must meet the expected levels of electrical and mechanical performance, and must also have the desired melting temperature. The properties of solders that are of importance from a manufacturing and also long-term reliability perspective are summarized in Table 1[6].

Table 1. Important properties of high-temperature solder alloys [6]

Properties relevant to manufacturing	Properties relevant to reliability and performance
Melting/liquidus temperature	Electrical conductivity
Wettability (of copper)	Thermal conductivity
Cost	Coefficient of thermal expansion
Environmental friendliness	Shear properties
Availability and number of suppliers	Tensile properties
Manufacturability using current processes	Creep resistance
Ability to be made into balls	Fatigue properties
Copper pick-up rate	Corrosion and oxidation resistance
Recyclability	Intermetallic compound formation
Ability to be made into paste	

With the miniaturization and increasing power of power electronics, high temperature operation has become a serious issue. As a response to the growing demand of high temperature operation, next generation power semiconductors such as SiC and GaN, and packaging materials such as AlN and Si_3N_4 have been developed for application at temperatures in excess of 300°C [7]. The development of a high temperature solder that can function at an ambient temperature above 300°C is expected to enable significant improvements in power electronics. For a solder alloy design, it is necessary to consider: melting temperature in the range of 260°C to 400°C; softness to maintain a joint structure by relaxation of thermal stress; small volume expansion at reflow treatment that does not break a package; sufficient workability to be thin wires or sheets; good electric conductivity; good thermal conductivity; good mechanical properties, especially fatigue resistance; air tightness not to break vacuum package; fluxless; no alpha ray emission [8]. To meet these requirements, only a few candidates exist for high temperature lead-free solder application, including Au-(Sn, Si, Ge), Bi-Ag, and Zn-Al based alloys. Since Au and Bi based alloys have several serious problems such as their high cost, formation of a massive intermetallic compound and brittle nature [7], Zn-Al based alloys are thought to be a good choice.

Zn–Al-BASED ECOLOGICAL ALLOYS

Zn–Al alloys

Zn–6 wt.% Al with a eutectic melting point of 381°C is a very interesting candidate for high temperature applications. The binary phase diagram of Al–Zn system [9] contains no intermetallic compounds, as seen in Fig. 1. Zn–Al alloys are already used as high-temperature solders for various applications, especially in die-attaching process [10]. Despite the low cost, there are several disadvantages when considering the use of Zn–Al alloys as high temperature solder. Firstly, Zn is a corrosive metal and this may strictly limit the lifespan under typical service conditions. Secondly, these alloys display relatively poor wetting behavior due to the high oxygen affinity of both Zn and Al. Lastly, it has been found that the Zn–Al eutectic shows a fine dendrite microstructure which makes the alloy very hard and brittle when compared to the high lead content solders [11-13]. It is interesting to note that the alloy is somewhat brittle while it becomes super plastic in a specific alloy microstructure with the composition [7]. Many researchers have discussed methods to develop the properties of Zn–Al solder alloys, and one of most effective way is adding a third element such as copper, magnesium, tin, gallium or germanium, the melting temperature decreases below 350°C [7, 12, 14-24]. The addition of a third element increases the formation of massive intermetallic compounds and increasing hardness and brittleness, so the problems of Zn–Al solder are not yet fully resolved [8].

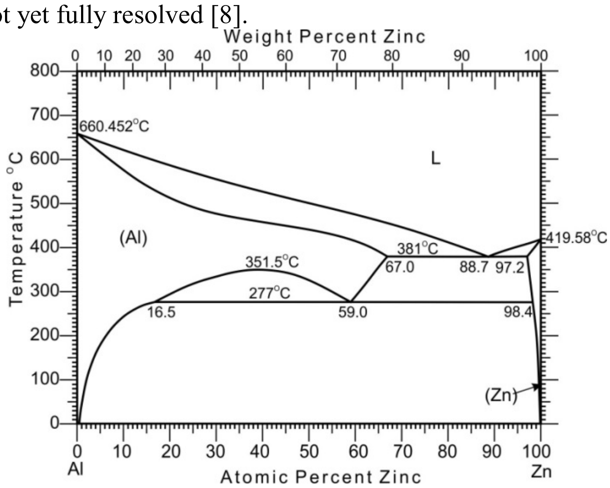

Figure 1. Binary phase diagram of Al–Zn [9]

Zn–Al–Cu alloys

Zn-(4-6)Al-(1-5)Cu solders developed for ultra-high temperature applications is investigated by Kang et al. [25]. The solder was designed to have a liquidus temperature between 382-402°C. It has to be admitted that the wettability of Zn–Al is relatively poor compared to the high lead solder due to the oxygen affinity of Zn and Al. However, according to Kang et al.'s report [25], the increase of Al content from 4.0 wt.% to 6.0 wt.% relatively improved the spreadability and electrical resistivity of Zn–Al, and also the hardness and tensile strength with the α/η eutectic/eutectoid. Also Zn-4Al-(2-3)Cu were proposed as a new class of high temperature solders by Kim et al. [7]. As the Al and Cu contents increased, the eutectic phases increased which is associated with the increase in Vickers hardness and tensile strength, and with the decrease in elongation. The increase in the Al content improved the solderability expressed as a spread ratio [7].

Zn–Al–Sn alloys

The microstructure of the Zn-6Al-xSn alloys studied in work of Yang et al. [24], contains Zn primary phase, Zn-Al structure, Sn-Zn eutectic structure, and Sn-Zn-Al peritectic structure. The wetting angles of the solder were all below 30%, indicating the diffusion between liquid solder and copper was sufficient to contribute very good wettability on Cu substrate; moreover, Cu_6Sn_5 compound formed at the interface [24].

Zn–Al–In alloys

The aim of work of Gancarz et al.[26] is to study temperature properties of alloys based on Zn-Al eutectic with small additions of indium and their wetting behavior on Cu and Al substrates. It was found that small additions of indium to Zn-Al eutectic decrease its melting temperature, increases electrical resistivity and coefficient of thermal expansion value. Wetting angles on Cu and Al substrates of liquid Zn-Al eutectic-based alloys containing up to 1.5 at.% of In is decrease with increasing concentration of In [26].

Zn–Al–Ge alloys

Chih et al. [27] and Haque at al. [28], in ther study's, Zn-Al-Ge alloy solder wire was used for Si die attachment on Cu substrate in an automatic die attach machine. The formation of three IMC layers such as β`-CuZn, γ-Cu_5Zn_8 and ε-$CuZn_4$ were observed at the solder Cu substrate interface. Wetting on Cu substrate was found better at higher die attached temperature which is closed to the maximum operating temperature of the Si die. Voids were found in the solder which were more in number at higher die attach temperatures. Die shear strength was found to be higher at the die attached temperature of 390°C (22.3 MPa) as compared with those obtained at 370-380°C (15.5-17.4 MPa). Accordingly to their investigation the main applications for Zn-Al-Ge solders within the electronics industry are for advanced packing technologies, e.g. die-attach and ball grid array (BGA) solder spheres, chip scale package (CSP) and multi-chip modeling (MCM) [27, 28].

Zn–Al–Ga alloys

Accordingly to investigation made by Rettenmayr et al.[10], Balanovic at al. [19] and in scope of COST Action MP0602 [29], based on the criteria of thermodynamics (phase diagram extrapolations) and mechanical behavior (flow curves), it is possible to select the Zn-Al-Ga alloy as best meeting the requirements concerning melting range necessary for die attach and mechanical properties.

Zn-Al-Mg-Ge alloy

By adding both Mg and Ge to a Zn-Al alloy solder, the melting point can be lowered by a certain level and, at the same time, it is possible to ensure the rolling-workability and to improve the oxidation resistance [30].

Zn-Al-Mg-Ga alloy

Comparative studies of die attach properties such as wetting, void and die shear strength was made by Haque at al. [22, 31] during Si die attachment with Zn-AI-Mg-Ga high-temperature solder on bare Cu lead-frame and Ni metallized Cu lead-frame. Wetting on bare Cu lead-frame was found better as compare to Ni metallized Cu lead-frame. On the other hand, more voids were found using bare Cu lead-frame as compare to Ni metallized Cu lead-frame. Die shear strength of Zn-AI-Mg-Ga solder joints were found 24.2 and 20.5 MPa on bare Cu and Ni metallized Cu lead-frame respectively which was lower than that of standard Pb-5Sn solder (28.2 MPa) but within the industrial acceptable limit [22, 31].

CONCLUSION

The electronics industry is still searching for a drop-in replacement for high-lead (85%) solders. The existing studies on alternatives to high-lead solders are scattered, and there is a lack comprehensive studies addressing the reliability of these lead-free alternatives under different environmental conditions.

The currently use Zn-Al-based ecological high-temperature solders is for various applications in electronic industry, mainly in the form of wires or ribbons for silicon (Si) die attaching in high-temperature applications, for power modules, in a foil form for die bonding, because of its proper melting range and excellent thermal and electrical properties.

While electronic equipment manufacturers have increasingly gained experience in the application of lead-free solders to commercial products, there still remains a serious difficulty's to achieving full application of lead-free solders to all products.

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THE EFFECTS STUDIES OF SHEAR STRENGTH PARAMETERS MORAINE MATERIALS ON ENVIRONMENTAL PROTECTION

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ABSTRACT

Glacial fluvial sediments or moraine material occupies over 60% of the surface area of the deposit "Zagrad" near Niksic. Material are built of limestone and dolomite sand, gravel and pebbles, rarely large blocks - thickness from 0 to 100 m. In terms of geo-mechanical material is complicated and difficult to test. First phase of designing of the angle of internal friction and cohesion for the moraine material carried out in the laboratory do not provide satisfactory results. Situation on the terrain require additional tests. The results of these investigations of strength parameters change the geometry of mine and a very favorable impact on the exploitation conditions and environmental protection.

Key words: moraine, bauxite, strength parameters, environmental protection.

INTRODUCTION

Modern exploitation of mineral raw materials is facing harder and harder working conditions. In cases of both open – pit and underground mining, shallow deposits, closer to the surface, mostly disappeared, so the exploitation is going deeper and deeper underground. In the case of open - pit mining, deeper location of the mineral raw materials is followed by larger layers of chats. In these cases the costs of excavation, transport and disposal of chats are growing with the increasing of the depth. As a consequence, there is also a growing peril for the environment. A million cubic meters of excavated chats should be transported and put away, which occupies great surfaces of the surrounding terrain.

Numerous factors influence the process of excavation, transport and disposal of chats. Knowing them properly will obtain finding, among other things, the optimal solution for the protection of the environment, from the consequences of mining activities. Some of the most important factors are:

- geological and engineering factors of the deposit
- hydro-geological characteristics of the deposit
- features of the climate in the region

- topography of the terrain, and very important
- geo-mechanical properties of ore and following rocks, etc.

Depending of the above mentioned factors, and particularly of the level of reliability of the data regarding the physical and mechanical properties, working environment, the geometry of mine can be solved, as well as the stability of working benches and final slopes, stability of waste dump slopes, portability of waste dump foundation, possibility of dumping large amounts of chats, land reclamation of the excavated spaces and waste dumps. The extent of the influence of the increased reliability of determining the physical and mechanical properties of the working environment, can be seen, with arguments, on the example of open – pit bauxite mine "Zagrad" near Niksic, in Montenegro.

GEOLOGICAL COMPOSITION OF THE "ZAGRAD" DEPOSITE

The following lithologic units exist in the geologic profile of the "Zagrad" deposite (Niksic district):

1) Light gray limestone karstified Upper Triassic
2) Red Jurassic bauxites (bx)
3) Alluvial-colluvial pre-glacial coating composition mainly bauxite (PH_1)
4) Glacio-fluvial gravels (MINDEL)
5) Dark gray to brown organic-carbonate sandy interglacial humus (PH_2)
6) Coarse grain glacio-fluvial gravels (RIS), formed in three stages (H_1, H_2, H_3)
7) Medium and fine-grained glacio-fluvial gravels (WURM), formed in 8 stages (III_1-III_8)

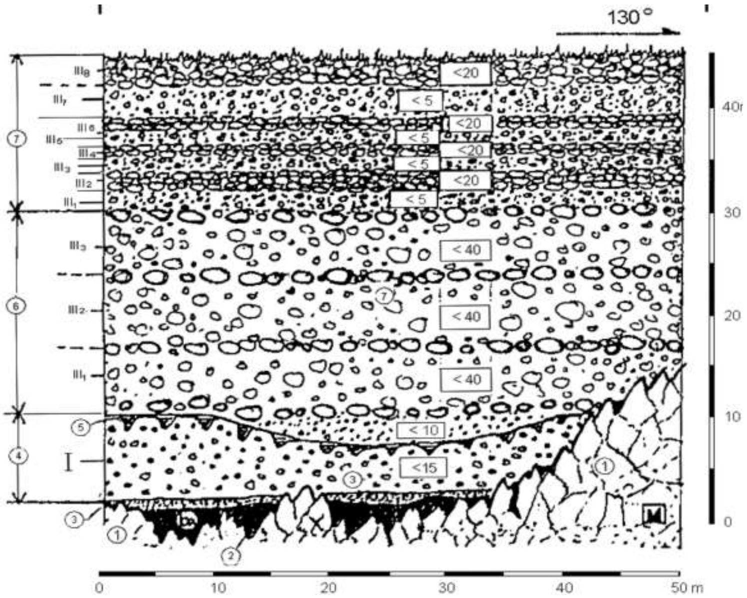

Figure 1. Geologic profile of the "Zagrad II" deposit (Niksic district)[1]

From these lithologic units, the least researched and known one both from practice and literature, is the moraine material. Depending from the position of profile, moraine material occupies from 0 to 100 m depth. Therefore, knowing this material is of a special importance. Moraine material is made of limestone and dolomite sand and pebble, rarely from larger boulders of up to three meters in diameter. So, it is a desultory, heterogenous material with wide boundaries regarding its granulometric content. As such, it is very complicated for determination of its physical and mechanical properties. This fact caused the designing process and mining and technology operations, to be carried out in two phases.

FIRST PHASE OF DESIGNING

In which the making of the Main mining project was carried out on the basis of shear parametars data (the angle of internal friction – φ and cohesion c) of the morraine material, which have been determined in laboratory conditions. These examinations were carried out by the JUS criterions (table 1.).

Table 1. Parameters used in the I and II phase of designing [2-4]

Parameters of shear strength I phase			
Lithologic unit	Angle of internal friction φ (°)	Cohesion c (kN/m^2)	Unit weight γ (kN/m^3)
Moraine material	29.83	5.76	20.36
Roof limestone	39.41	307.13	26.94
Roof dolomite limestone	35.72	266.00	27.21
Bauxite ore	28.52	103.00	26.67
Floor limestone	36.37	126.00	27.02
Floor dolomite limestone	30.37	356.00	27.38
Parameters of shear strength II phase			
Moraine material	30	200.00	23.14

On the basis of the data for the angle of internal friction (φ) and cohesion (c) for the moraine material, the following geometry was adopted for the moraine material (Table 2.).

With the adopted, above mentioned geometry of the mine, the exploitation of the "Zagrad" deposit began, excavating of the moraine material, transport and dumping of waste. However, with the making and development of the working benches in the moraine material, it was notable, on the basis of the way that the slopes stand, that in their geometry, inclination and height exists a significant reserve in their safety. The reason for this lies in the observed fact, that the shear parameters of the moraine material are not properly determined. This material, with very specific granulometric content (Fig. 3.), size of the particles from 0.02 mm to 3000.00 mm can not be examined with standard laboratory procedures, on the standard samples. By using the small samples, the structure of this material is destroyed and the obtained values for the angle of internal friction (φ) and cohesion (c) are no longer valid.

SECOND PHASE OF DESIGNING

Second phase of designing of the working benches in the moraine material was carried out on the basis of the values for the angle of internal friction (φ) and cohesion (c), which were determined on the terrain, "in situ". The shear tests were carried out on the blocks of large dimensions, on the predisposed angles: $\alpha_1 = 60°$; $\alpha_2 = 45°$ and $\alpha_3 = 30°$.

Figure 2. Sample for direct shear test [5].

During the shear of the blocks of large dimensions, along the predisposed planes, the values of tangent (τ) and perpendicular (σ) components, are showed in the system of coordinates τ – σ in Fig. 2.

This figure shows the results of the direct shear test, on the blocks of 40 x 40 x 60 cm (Fig. 3), and the results obtained by the reverse stability analysis of slopes in moraine material. All three methods, that have been mentioned, were carried out with laboratory tests.

Based on these values verified geometry of the final slopes in morraine material is showed in table 2.

Table 2. Maximal heights and angles α of the final slopes for safety factor $F_s = 1.3$

I Phase of designing	α = 23°	H = 100 m
II Phase of designing	α = 50°	H = 100 m

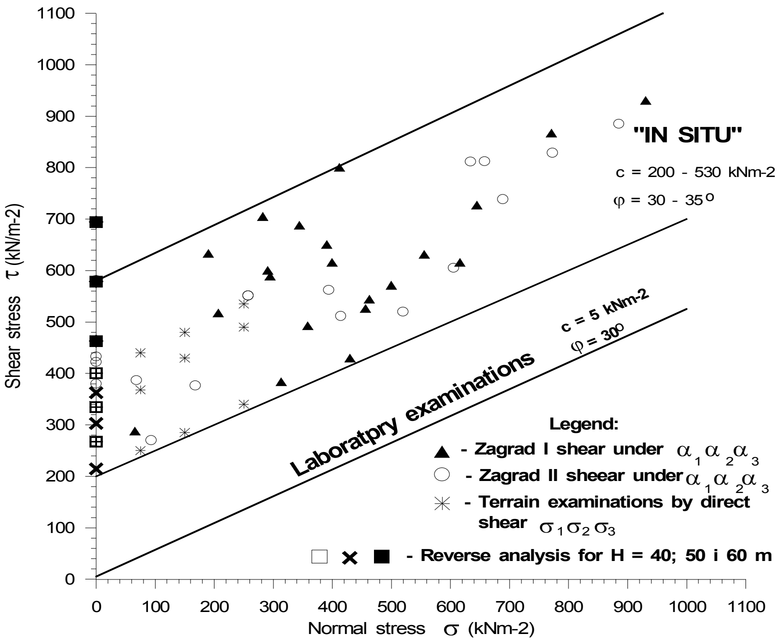

Figure 3. Laboratory results, "in situ" results and reverse analysis [6].

It is obvious that the terrain tests have confirmed that the cohesion of moraine is not 5 kN/m^2. Actual value of moraine cohesion is from 200 – 500 kN/m^2, which is 100 times larger than the values determined in laboratory. Values of angle of internal friction determined in the laboratory and in the "in situ" are almost identical (Table 1).

CONCLUSION

From the experience of the "Zagrad" deposit results the conclusion that it is necessary for the geomechanical examinations to be carried out permanently, from the first investigative works to the end of exploatation.

The newly formed angles of final slopes in moraine, with slopes α = 23° and later α = 50° caused great and significant savings in exploitation costs of the bauxite ore on the "Zagrad" deposit.

The savings consist in the following:

- Savings in the reduced volume of excavated moraine material by forming the final slopes, which are around 3 – 4 €/m^3;
- Savings in the reduced excavating of limestone in the final slope, around 7.15 €/m^3;
- Savings in the reduced duration of exploitation of deposit for 4, 5 years;
- Savings through the increased mining of the bauxite ore (45 000 tones);
- Savings in the space and volume of the waste dump, on which 4 500 000 m^{3}was not disposed.

These savings were achieved by using the data for the properties of moraine material – the angle of internal friction (φ) and cohesion (c), determined on terrain ("in situ") and in all they amount: 32.525.000 €.

On the example designing and exploitation of bauxite deposit "Zagrad" near Niksic, the effects of environmental protection in depenence of reliability implemented geomechanical examination can be seen.

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THERMAL AND ELECTRICAL PROPERTIES OF THE AS-CAST Sn-RICH ALLOYS

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ABSTRACT

Solidification properties of six as-cast Sn–Sb–Zn alloys with 80at.% of Sn and variable contents of Sb and Zn were experimentally investigated using differential thermal analysis (DTA). Experimentally obtained results were compared with predicted phase equilibria according to calculation of phase diagram (CALPHAD) method and with Scheil solidification simulation. An electrical conductivity measurement of investigated alloys was also performed.

Key words: Sn – Sb – Zn system, solidification, differential thermal analysis, electrical conductivity.

INTRODUCTION

Electronic devices are operating faster and becoming smaller, lighter and more functional and for this reasons, advanced packaging technology is required. Many advanced packaging technologies have been developed. The multi-chip module (MCM) is a group of highly functional electronic devices interconnected to the substrate. When integrated circuit chips are packaged in MCM, step soldering is used.

Step soldering refers to a process in which soldering is applied more than once in different stages during the manufacturing. To avoid remelting of the earlier solder joints in the later soldering processes, solders with different melting points are used [1].

The 95Pb–5Sn solder with a melting temperature of 308–312^{o}C is used for high temperature applications in step soldering [2]. Due to environmental concerns the use of Pb is restricted and new Pb-free high temperature solder alloys are required.

Several studies of Pb-free high temperature solder alloys have been performed[3-6]. It was concluded that among various lead-free solders, Sn-Sb based alloys are promising candidates for the replacement of the high-melting-point Sn-95wt%Pb alloy [3-6]. In those studies authors investigated the phase diagram, melting behavior, electrical resistivity, wettability, viscosity and mechanical properties of Sn–Sb alloys.

Since the properties of the binary Pb-free solders cannot fully meet the requirements for applications in electronic packaging, additional alloying elements were added to improve the performance of these alloys [7]. Hence, ternary Sn–Sb–Zn alloys may also be considered as promising lead-free solders. To our best knowledge, small number of studies on the Sn-Sb-Zn ternary alloys has been published. Gancarz and Gasior [8] performed the electromotive force measurement in order to obtain zinc activity in liquid Sn–Sb–Zn alloys. Phase transition temperatures and compositions of coexisting phases after long-term annealing at 200, 250 and 350^{o}C have been determined by Zobac et al. [9]. Stability of one ternary phase with the chemical composition corresponding to the Sb_2SnZn compound in some of investigated samples has been experimentally determined [9].

In this study, phase transition temperatures of the investigated alloys were measured using DTA technique and also compared with the results of thermodynamic prediction. Taking into consideration the possible applications of investigated samples, we broadened our study with measurements of samples' electrical conductivities.

EXPERIMENTAL PROCEDURE

Six ternary alloys, with constant atomic percent of Sn (80 at.%) and variable contents of Zn and Sb were prepared using Sn, Zn, and Sb (Purity 99.99%) as starting materials.

The appropriate weights of the elements were melted in an induction furnace under an argon atmosphere. The alloys were melted several times to improve homogeneity. The molten solders in crucible were chill cast in a graphite mold to form cylindrical ingots of 17mm in diameter. As-cast alloys were obtained by cooling in air.

Differential thermal analysis (DTA) experiments was carry out using a laboratory-made DTA apparatus with the thermocouples inserted directly into the sample and inert reference material under following conditions: flowing argon atmosphere, sample masses about 2 g, and alumina as the reference material. A heating rate of 5 C/min was employed both for calibration and measurement of the prepared samples. The data were collected using the personal computer.

Electrical conductivity measurements were carried out using Foerster SIGMATEST 2.069 eddy current instrument.

Experimental results

Thermal properties

Experimentally determination of phase transition temperatures of the investigated samples was done using differential thermal analysis (DTA).

The phase transition temperatures were taken from peak maximum on heating. In the present DTA measurements the thermocouple was immersed directly in the sample and because of that DTA signal corresponding to peak maximum was used for determination of phase transition temperatures. The accuracy of the given temperatures is ±2°C.

The overall DTA results are given in Table 1.

Table 1. DTA results for the investigated alloys in the Sn–Sb–Zn ternary system.

Alloy	Sample composition (at. %)	Temperature [°C]	
		Other peaks	Liquidus
I	Sn = 80.08 Sb = 3.97 Zn = 15.95	192	291
II	Sn = 80.31 Sb = 7.97 Zn = 11.72	199	308
III	Sn = 80.39 Sb = 10.04 Zn = 9.57	195	312
IV	Sn = 80.37 Sb = 11.70 Zn = 7.93	198, 235	311
V	Sn = 80.38 Sb = 14.13 Zn = 5.49	180, 230, 253	307
VI	Sn = 80.52 Sb = 17.57 Zn = 1.91	249	299

Characteristic DTA heating curve for the sample IV with marked phase transition temperatures is given in Fig. 1.

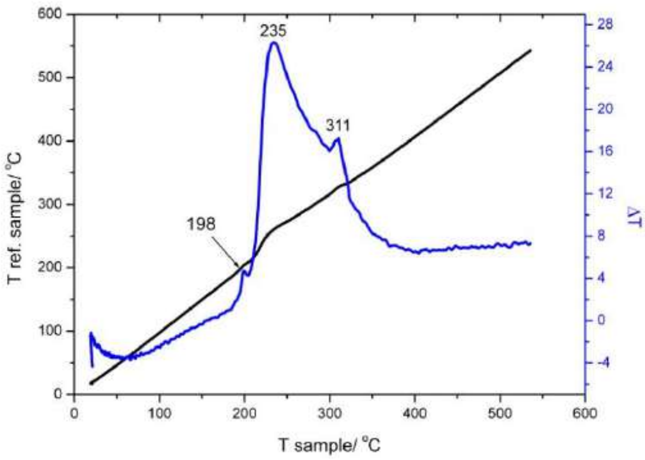

Figure 1. DTA heating curve for the alloy sample IV ($Sb_{11.07}\,Sn_{80.37}\,Zn_{7.93}$ composition in at.%) (conditions: argon atmosphere, sample mass 3g, heating rate 10K/min)

Figure 2 represents DTA curve for the sample V. The registered peaks temperatures on heating are denoted in Fig. 2.

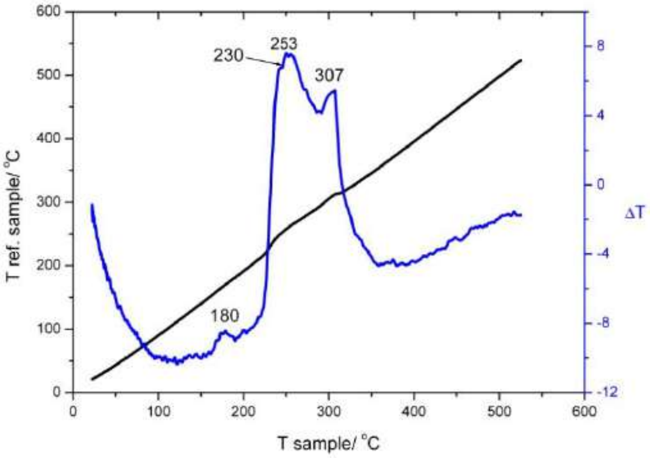

Figure 2. DTA heating curve for the alloy sample V ($Sb_{14.13}Sn_{80.38}Zn_{5.49}$ composition in at.%) (conditions: argon atmosphere, sample mass 3g, heating rate 10K/min)

Electrical conductivity measurements

Electrical conductivity (σ) of the investigated samples of ternary Sn-Sb-Zn system was measured. Referring alloys and their electrical conductivities as well as electrical conductivity of alloy Pb-5Sn, are given in Table 4.

Table 4. Alloys and corresponding electrical conductivities

Alloy	Electrical conductivity, σ ($MS\ m^{-1}$),				
	Ref.	Meas. 1	Meas. 2	Meas. 3	Average value
I	This work	6.05	6.15	6.10	6,10
II	This work	5.88	5.71	5.81	5,80
III	This work	5.24	5.32	5.34	5,30
IV	This work	5.97	5.98	6.05	6,00
V	This work	5.77	5.77	5.86	5,80
VI	This work	5.29	5.32	5.29	5,30
Pb-5Sn	Ref.[2]				5.52-5,95

The results presented in Table 4 show that there are no significant differences between electrical conductivity of investigated alloys of the ternary Sn-Sb-Zn system and high temperature Pb-5Sn soldering alloy.

CONCLUSION

In this work six as-cast alloys with 80at.% of Sn and variable contents of Sb and Zn were experimentally investigated using differential thermal analysis (DTA).

Experimentally obtained results were compared with results of thermodynamic binary-based prediction of phase equilibria according to CALPHAD methodology and Scheil solidification simulations.

The agreement between liquidus temperatures measured using DTA and thermodynamically predicted liquidus temperatures is very good for all investigated samples. Also, experimentally determined solidus temperatures are close to the predicted temperature of ternary eutectic reaction L↔ β+(Sn)+(Zn) at calculated temperature 198°C.

Electroconductivity of investigated alloys is close to electroconductivity of high temperature Pb-5Sn soldering alloy.

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THE EFFECT OF PULP DENSITY AND TIME OF FLOTATION ON THE RESULTS OF FLOTATION CONCENTRATION IN INDUSTRIAL CODITIONS

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ABSTRACT

The density of the pulp in the flotation process of copper ore has an impact on the copper recovery. Density of the pulp determines the physical characteristics of the system. In industry the process of flotation is continuous, if the ore income is constant, the density is determined by adding water. The ratio of the solid and liquid phase is directly proportional to the volume of pulp which further means that with increasing or decreasing the volume of the pulp it has influence to the time of flotation. The change of density of the pulp in industrial process has influence on two factors which are inportant for results of flotation. The first factor is that by changing the density it changes characteristics of the pulp, and the second factor is the time of flotation. With higher density, flotation time increases. In this paper are results of lab simulated flotation process with industrial conditions, changing the time of flotation and the density of the pulp. The results indicate that with increasing density and time of flotation, with all other parameters constant, recovery rises to a certain limit, after which begins to gain a negative impact.

Key words: technology, flotation, flotation time.

INTRODUCTION

In flotation plant Veliki Krivelj processed porphyry copper ore, flotation capacity is 10.6 million tons per year. The process of flotation is organized in three independent lines of flotation cells, each cell per 100m^3, where one line has six flotation cells. Rough concentrate is further enriched in the process of purification. This paper examined the optimal pulp density in order to achieve maximum recovery of copper. Based on hour capacity of ore and pulp density it is calculated the volume of pulp and time of flotation. These results are transferred to the laboratory. Flotation test are performed in which the only variable is density of pulp and time of flotation process.

EXPERIMENTAL PART

For processing capacity of 400t/h it is calculated volumetric flow of the pulp for the following pulp density: 1165kg/m^3, 1200kg/m^3, 1220kg/m^3, 1240kg/m^3.

$$V_p = \frac{Q \cdot V_k}{\rho_p \cdot p} \text{ [m}^3\text{/h]}$$

Q - Hour capacity (t/h), V_k - flotation cell volume (m^3), ρ_p - pulp density (t/m^3), p - the ratio of solid (%).

Based on the results of the flow rate it is calculated time of flotation in a flotation line.

$$t_f = n \cdot V_k \cdot 0{,}85 \cdot \frac{60}{V_p} \text{ [min]}$$

Table 1. Calculation results of flotation time with changing density of the pulp

Hour capacity Q(t/h)	Solid density $\rho_č(t/m^3)$	Pulp density $\rho_p(t/m^3)$	Ratio of solid p(%)	Volumetric flow Vp(m^3/h)	Flotation time t(min)
400	2,7	1,17	22,49	1526,37	20,05
400	2,7	1,20	26,47	1259,26	24,30
400	2,7	1,22	28,64	1144,78	26,73
400	2,7	1,24	30,74	1049,38	29,16

Based on the results, flotation tests were carried out in the laboratory in which was changed pulp density and time of flotation which corresponds to a certain density of pulp which is obtained by calculation.

Table 2. Results of the test of flotation concentration at different densities and times of flotation

Pulp density (kg/m^3)	Flotation time t_f(min)	Mass recovery Im (%)	Copper recovery It (%)
1165	20,05	9,14	79,44
1200	24,30	9,48	80,85
1220	26,70	10,64	84,46
1240	29,20	8,90	74,43

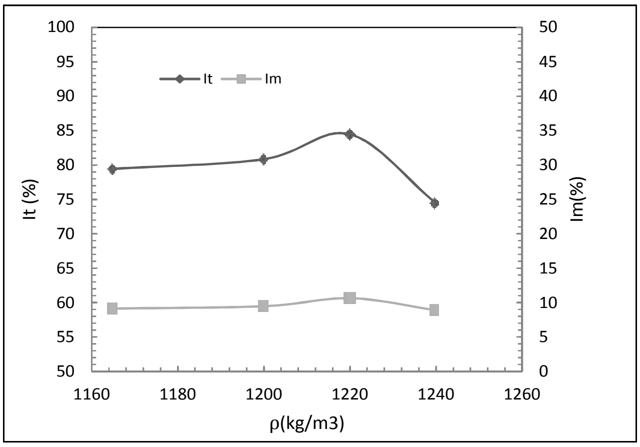

Figure 1. Dependence of copper recovery and mass recovery in function of pulp density.

From the results it is evident that with the increase of density and time of flotation, it is growing mass recovery and copper recovery to a density of 1220kg/m^3. For a density of 1220kg/m^3 and the time of flotation 26,7min obtained the highest value of the copper recovery which is 84,46%. A further increase in density and time of flotation leads to recovery decreases.

CONCLUSION

With the increasing density of the pulp, increases the time of flotation. The optimum density for pulp for analyzed ore is 1220kg/m^3 which correspond to time of flotation 26,7min. Further increase in density of the pulp, despite the increase in the time of flotation, recovery of copper begins to fall.

The results apply to the tested sample, becouse the influence of density is different and depends on many factors (particle size distribution, mineral composition of ore, pulp viscosity, etc.). On the other hand with increasing the time of flotation increases the recovery of minerals. It is necessary to find the optimal ratio of density and time of flotation in order to achieve maximum results.

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ENDANGERMENT EVALUATION OF BUILDINGS SITUATED IN LOCAL COMMUNITY „SEVER“ NEAR OPEN PIT BOR

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ABSTRACT

Mining operations at Open Pit Bor were officially terminated in 1992, but numerous problems related to it are still present. One of the dominant problems is endangerment of buildings in local community Sever, situated near the western boundary of open pit. This paper presents the endangerment evaluation of buildings near open pit as a consequence of slope failure.

Key words: surface mining, slope stability, slope failure, damages on buildings.

INTRODUCTION

Area of Local Community Sever (LC Sever) is the oldest town core of Bor. Urban development of the town started in this area, along with beginning of mining operations. First buildings were located in Northern Settlement, in a typical mining colony style, built for miners and other employees. In this period, between 1903 and WWI, the settlement was developing in the area between today’s Ive Lole Ribara, Kestenova and Vajfertova Streets. Many of these buildings still exist and are in use. Second phase of settlement development, between WWI and WWII, included both private houses and office buildings, where today’s RTB Bor Head Office, Technical Faculty in Bor and Municipal Hospital are situated. After WWII, this area completed its development. By the end of 60’s, urban development of the town of Bor moves to towards south, while this area, due to environmental issues and expansion of open pit, gradually loses attractiveness and real estate values.

Extensive relocation of population from this area, due to negative influence of mining works, lasts for twenty years. Phase relocation of entire local community, with a total of 500 households, was defined through Detailed Urban Sanitation Plan for LC Sever, introduced in 1970. According to this plan, majority of endangered households were relocated by 1980, although there is a certain lack of data from this period, neither in RTB Bor nor Municipal Government databases. So it is estimated that majority of relocated households were settled in other local communities in Bor Municipality area.

According to data gained from RTB Bor data services, there are 133 households relocated or in process of relocation from 1980 to date. [1]

Regulatory Plan of Bor Municipality [2] includes removal of buildings endangered by open pit, along with buildings with no civil engineering, architectonic or urban value. Also, Regulatory Plan includes removal of buildings situated at locations where construction of new buildings is planned. New buildings, according to Plan, include construction of buildings, civil engineering objects and street trees. Finally, Regulatory Plan includes removal of outbuildings, hovels and other power-quality structures.

STABILITY OF WESTERN SLOPE OF OPEN PIT BOR

Mining operations require defining of both geological properties of the deposit and influence of mining works on ground surface. This is especially important in situation when negative influence of mining works affects surrounding area and causes damages on buildings inside the influence zone.

There are several issues related to slope stability of Open Pit Bor:

- slopes are instable due to negative influence of underground mining, still active bellow the pit; but also due to non-controlled atmospheric water and mud inflow from catchment area around open pit;
- underground mining works near slope toe, i.e. its further undercutting, may cause serious problems in stability of southwest slope of Open Pit Bor and consequently cause endangerment of buildings in the area near the slope;
- open pit influence zone included several buildings northwestern from the pit, causing damages, without any safety measures carried out in the area.

Increasing costs related to damages on buildings caused by open pit slope instability, forced the change in way of thinking and acting in mining company. From more or less passive approach to problem, they turned to active problem solving, by applying any technique and method that could provide increase of slope stability. [4]

Preliminary analysis of slope stability included the overview of ore deposit general properties, along with surrounding ground and boundaries of open pit; defining of geological and geo-mechanical properties of rock mass, slope stability calculations and defining of slope failure criterion and finally defining of level of endangerment for buildings situated near southwestern part of open pit.

Preliminary analysis has shown that stress redistribution occurred in rock mass near open pit slopes after the termination of mining works at Open Pit Bor. In practice, stresses usually concentrate around the plane in rock mass near the slope. When the values of shear stress exceed the values of resisting forces in that plane, part of slope slips. Slope failure can occur in a single bench or entire side of a pit. Slope failure of entire side of open pit occurs on specific failure plane and it represents a large-scale failure that affects entire open pit geometry. [5]

Landslides and failures in the area close to open pit were not closely investigated, as well as entire process of slope instability, due to lack or inaccuracy of geotechnical data.

Western slope of Open Pit Bor, where LC Sever is located, consists mainly of solid rock according to available geotechnical and geological data. In order to determine stability and shear strength of the slope, it was suitable to run the analysis using Hoek-Brown failure criterion. This criterion is used to define rock stability through relations between principal stresses and normal and shear stress.

For reliable analysis of slope stability it is necessary to define rock mass strength and plastic behavior properties accurately. First step was to gain all of the available data on properties of each specific material included in rock mass in this area. [3]

Analysis of slope stability was carried out in seven geological cross – sections, whose layout is shown in orthophotograph in Figure 1. With circular failure interface assumed, the analysis included application of several most widely used methods. Using Rockscience's Slide 6.0 software, the analysis included following methods: Bishop's, Janbu's generalized, Spencer and GLE/Morgenstern-Price. [6]

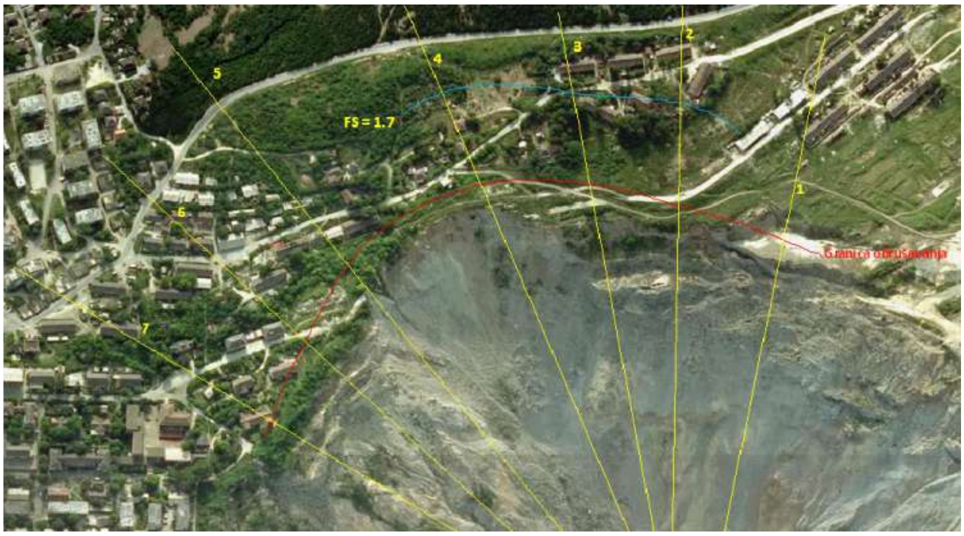

Figure 1. Ortophotograph of open pit slope and LC Sever with cross sections and influence zone boundary

Potential failure planes, with lowest values of Factor of Safety (F_s), lie along entire open pit slope in cross-sections 1, 2, 3, 4, and 7. In cross-section 5, failure plane with minimal F_s ends above 250 m level, and in cross-section 6 above 310 m level.

Overview of minimal values of Factor of Safety, by cross-sections and methods, is given in Table 1. Lowest values occurred in mid cross-section (4), while highest values were recorded in ending cross-sections, 1 and 7. Values presented in Table 1 show that variations of Factor of Safety by methods are not significant, so we can conclude that calculation method is not essential for accurate determination of F_s.

Table 1. Overview of calculations of F_s by cross-sections and methods

Cross section	Calculation method				Mean value
	Bishop	Janbu generalized	Spencer	GLE/ Morgenstern-Price	
1 - 1	2.57	2.51	2.58	2.55	2.55
2 - 2	1.69	1.60	1.76	1.74	1.70
3 - 3	1.65	1.57	1.71	1.73	1.67
4 - 4	1.52	1.46	1.56	1.56	**1.53**
5 - 5	1.81	1.75	1.82	1.80	1.80
6 - 6	1.96	1.90	1.96	1.96	1.95
7 - 7	2.03	1.96	2.07	2.06	2.03

Figure 2 shows mean values of F_s presented in Table 1.

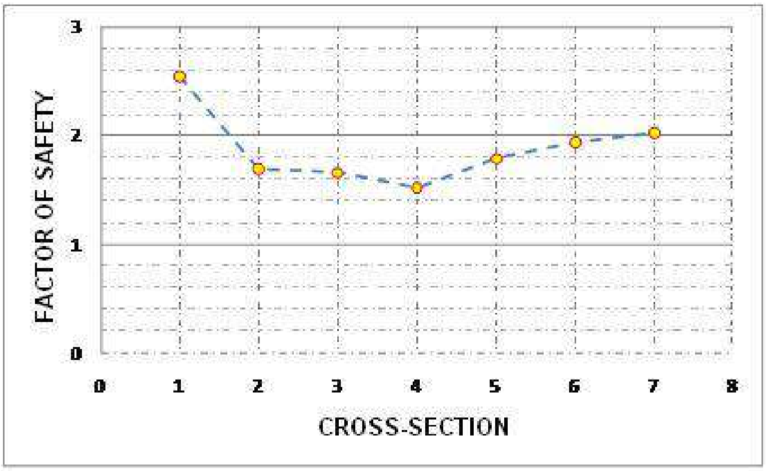

Figure 2. Values of Factor of Safety by cross-sections

LOCATION OF BUILDINGS IN LC SEVER IN RELATION TO INFLUENCE ZONE BOUNDARY

Although mining operations at open pit Bor had been terminated in 1992, some significant changes occurred in last decade, with a strong impact to slope stability:

- Due to waste disposal from Open Pit Veliki Krivelj and partial failure of western slope, bottom of the open pit is currently at +140 m level, which is 30 m above the level recorded in 2008;
- Benches and bench slopes, which were clearly visible before, are now overlaid by fractured rock, and general slope angles at cross-sections of western slope are reduced to 35^o – 37^o, except in cross-section 3 -3. Reduced slope angles are approximately the same as angles of repose for these materials;

- Ground movement process in the slopes of open pit did not affect the terrain near to western boundary of open pit.

Ground movement process on western slope, presented through landslides and slips, is in the terminating phase, phase of settling.

According to current condition and angle of western slope, it is possible to define maximal range of influence zone on each cross-section. Influence zone boundaries define the range of possible endangerment for buildings and other facilities.

It is determined that majority of buildings in LC Sever are out of influence zone and they won-t be affected by slope failure. The only exceptions are two buildings in Vase Drecuna Street, Number 2 and 5, which are located very close to influence zone boundary.

Evaluation of endangerment of buildings in LC Sever

In defining of correlations between ground movement process induced by mining operations and damages occurring at buildings and structures, there are few questions that always need answers, such as: how was the process getting closer to the building; at which specific moment did process begin to affect the building and how did the building respond when affected by ground movement process?

Answers to these questions are gained through systematic geodetic field survey. The aim is to survey the advance of ground movement process in space and time, record the moment when process begins to affect buildings, and then survey the affected building, its behavior and damages.

International experiences in this area are showing the necessity of constant survey of buildings, which includes installation system of benchmarks specific points on building. Installed benchmarks enable constant survey through leveling and measuring of distance. Also, it is suitable to form a database for each building, which includes surveying data, photographs, visual observations and any other relevant data related to damages of building. Surveying program starts with "zero survey" and lasts as long as damages on buildings are recorded. All of that should help to get an insight of every building affected by process and accurately define damages caused by mining operations.

In our country, there are no relevant regulations in this area yet. There is no definition of maximal permitted deformations on buildings caused by mining operations. According to Regulation on Technical Standards for Surface Mining, Factor of Safety for final slopes of surface mines has to be greater than 1.3, or 1.5, depending on rock type. Considering the lack of reliability of geotechnical data for western slope of Open Pit Bor, it was decided that minimal value of Factor of Safety should be $F_s = 1.5$.

According to data shown in Table 1 and Figure 2, it is obvious that Factor of Safety values are higher than 1.5, which means that western slope of Open Pit Bor is stable. In other words, there is no danger of western slope failure and buildings in LC Sever are not endangered by open pit.

However, there are occurrences of landslide and subsidence on this location, but they are caused by underground mining. Jama Bor underground mine is located bellow open pit, and in some ore bodies applied mining methods included roof caving. Roof caving is causing ground movement process at the surface and may also endanger buildings and other structures. As a consequence of underground mining, seven buildings in LC Sever suffered severe damages and collapsed, or had to be abandoned.

As an example of severe damage, we have a house in Dositeja Obradovica 38, located 40 – 50 m away open pit edge, very close to influence zone boundary. There are multiple fractures and overall shape of the house is poor.

Figure 3. Fractures on front wall and side walls of house in Dositeja Obradovica 38

CONCLUSION

Instead of conclusion, we should point out that a job of a researcher is not finished with presentation of study on geotechnical survey and defining of zone of influence. It is necessary to continue the analysis by including geodetic survey and defining of influence zone according to surveying data, too.

Mine surveying methods are more and more included in analyses and studies of slope stability and its influence to ground surface in the area, along with geological and geotechnical methods. Surveing data should be analyzed and used in a program of survey and repairment of buildings affected by mining operations. It is especially important to focus on regulatory segment, in order to define degrees of damages of buildings and degrees of their protection, depending on deformations caused by mining operations.

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SUGAR BEET PULP AND MOLASSES AS A SOLID STATE FERMENTATION MEDIA FOR CELLULASE PRODUCTION BY *Paenibacillus chitinolyticus* CKS1

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ABSTRACT

Sugar beet pulp (SBP) and molasses, by-products from sugar industry were used as a substrate for cellulase production in this study. Solid state fermentation (SSF) was performed by a natural isolate *Paenibacillus chitinolyticus* CKS1. Data showed that cellulose in SBP could be used as a substrate to produce both cellulases, CMCase and Avicelase. An optimum solid: moisture ratio for maximum cellulase production was investigated. Maximum CMCase 3.159 U/g and Avicelase activity 4.840 U/g was obtained at the fourth day of incubation with 10% of inoculum. The cellulase production during SSF on SBP indicates that this process is economically very justified.

Key words: Cellulases, Sugar beet pulp, Molasses, *Paenibacillus chitinolyticus* CKS1.

INTRODUCTION

Sugar beet pulp (SBP) and molasses, the two main by-products of the sugar industry, are produced in large amounts annually which creates disposal problems [1, 2]. SBP is a lignocellulosic by-product with low economic value, mostly used as animal feed [3, 4] is mainly composed of polysaccharides consisting of approximately (dry basis) 22–24 wt.% cellulose, 30 wt.% hemicelluloses and 15–25 wt.% pectin [5]. Molasses from the sugar beet processing contain up to 54% sugars [1]. Sugarcane molasses are used as nutrient medium for the cellulase production [6] while literature data about using sugar beet molasses are very limited. SBP is used as a substrate for microbial protein production [1] and in a recent years for ethanol production [7].

The cellulase production on SBP and molasses by *Paenibacillus* sp. is a new approach. Cellulases are industrially important enzymes with a potential to convert cellulose into fermentable sugars which can then be converted into value-added products or bioenergy [8]. Cellulases are enzymes that hydrolyze cellulose while the mechanism of enzymatic activity differs between the different enzyme classes: endoglucanases (carboxymethyl cellulases; CMCases), exoglucanases (Avicelases) and β-glucosidases [9-11]. Endoglucanases cut the amorphous cellulose polysaccharide chain at random internal sites and generate oligosaccharides of various lengths [12]. Exoglucanases are active on the reducing or non-reducing ends of the cellulose polysaccharide chains and liberate either glucose or cellobiose as major products [12].

Solid state fermentation (SSF) is used for cellulase production because of its several benefits like high enzyme titer, low labor cost, lower capital input, etc.[13].

In this research we used SBP and molasses, for the cellulase production by a novel strain *Paenibacillus chitinolyticus* CKS1. SSF was applied for cellulose production including both CMCase and Avicelase. Due to the application of SBP and molasses as a cheap and abundant substrates for the enzyme production, it may be considered that the economic aspect of this method is very promising.

MATERIALS AND METHODS

Microorganism and inoculum preparation

Paenibacillus chitinolyticus CKS1 was natural isolate from soil sample (sequence accession number KP715850). The inoculum was prepared by growing the microorganism in 300 ml Erlenmeyer flask with 50 ml of ISP1 broth containing 3 g/l yeast extract and 5 g/l casein hydrolisate. The medium was inoculated at 30 °C for 24 hours in a rotary shaker at 150 rpm and was used for the fermentation process.

Fermentation substrates

SBP (Fibrex 620, Nordic Sugar, Denmark) and molasses (ethanol Factory Alpis, Kovin, Serbia) were used as fermentation substrates. SBP was grounded in a mortar and pestle to a particle size of 800µm -2mm. Molasses was diluted in distilled water to a concentration of 2%.

Solid state fermentation - SSF

Solid state fermentation was carried out according to Moftah et al. [14] with some modifications. 5 g of SBP and molasses as a moistening agent was placed into the 300 ml Erlenmayer flask Solid (SBP):moisture ratio was adjusted as follows - 1:1 (4.5 ml molasses), 1:2 (9.5 ml molasses) and 1:3 (14.5 ml molasses). The media in flasks were autoclaved at 121 °C for 20 min. In each flask 10% of inoculum (v/w) was added. Fermentation was carried out at 30 °C for 4 days. To extract the enzyme, a known quantity of the fermented media was mixed with 0.1 M acetate buffer pH 4.80 (1:5, w/v) by shaking on a rotary shaker (190 rpm, 30 min, 25 °C); then, the whole contents were centrifuged at 6.000 rpm for 10 min (4 °C), and the supernatant was used as a crude enzyme extract and was further analysed for cellulase activity.

For solid:moisture ratio 1:1, which shown the maximum cellulase production, the effect of different concentrations of inoculum (5, 10 and 15 % (v/w)) and different time of incubation (2, 3, 4, 5 and 6 days) on cellulase production was studied.

Enzyme assay for cellulase

Cellulase activity was measured by reduction of 3,5-dinitrosalicylic acid in the presence of glucose released by enzymatic hydrolysis of cellulose [15].

CMCase (endogluconase) activity was determined as follows: 500 µl of enzyme solution (crude supernatant) was mixed with 500 µl 1 % CMC in 0.1 M acetate buffer pH 4.80 and incubated at 50°C for15 min in a rotary shaker at 150 rpm. After incubation, 1 ml of DNS reagent was added. The reaction mixture was then boiled for 15 min. After cooling at room temperature 5 ml of distilled water is added to each tube and absorbance was measured at 540 nm against the blank. One unit of CMCase activity was defined as the amount of enzymes that released 1 µmol of glucose per minute. It is expressed as U/g where *g* is the gram of solid substrate (SBP) used.

Avicelase (exoogluconase) activity was determined at 80 °C using the same procedure as for CMCase with the exception that 1% Avicel was used as substrate instead of CMC.

RESULTS AND DISCUSSION

Investigation of cellulase production during growth of *P. chitinolyticus* CKS1 on SBP and molasses showed that microorganism produced cellulases, with different efficiency, at all tested solid:moisture ratio (Figure 1) .

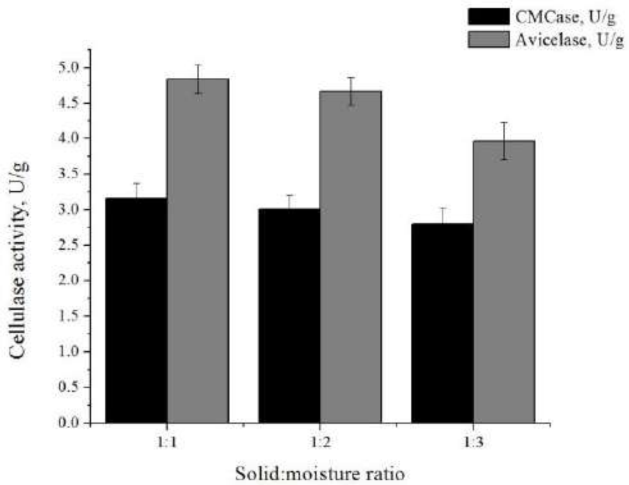

Figure 1. Cellulase production by P. *chitinolyticus* CKS1 on SBP an molasses with different solid:moisture ratio

The literature data shows that the production of cellulases is inducible and affected by the nature of the carbohydrate used during fermentation [16]. SBP contains cellulose that can be an inducer for the cellulase production. SBP is used as a substrate for cellulase production by fungi *Trichoderma* [17, 18] but until now there has been no literature data about cellulase production using SBP by *Paenibacillus* sp. *P.*

chitinolyticus CKS1 produced CMCase and Avicelase after four days of incubation at different solid:moisture ratio. For the strain CKS1, the optimum solid: moisture ratio, during SSF, appeared to be 1:1 for maximum CMCase 3.159 ± 0.213 U/g and Avicelase activity 4.840 ± 0.201 U/g. The moisture content in the substrate can be considered as an important factor in SSF and microbial growth [19]. Low moisture content may lead to poor accessibility of nutrients and a lower degree of substrate swelling, resulting in poor microbial growth and decreased enzyme production. On the other hand, higher moisture contents appeared to cause decreased porosity, loss of particle structure and development of stickiness, which, in turn, prevented oxygen penetration [14]. For *Paenibacillus curdlanolyticus* DSMZ 10248 an optimum solid (palm kernel cake): moisture ratio was 1:1 and for *Paenibacillus polymyxa* ATCC 842 was 1:0.8 [19].

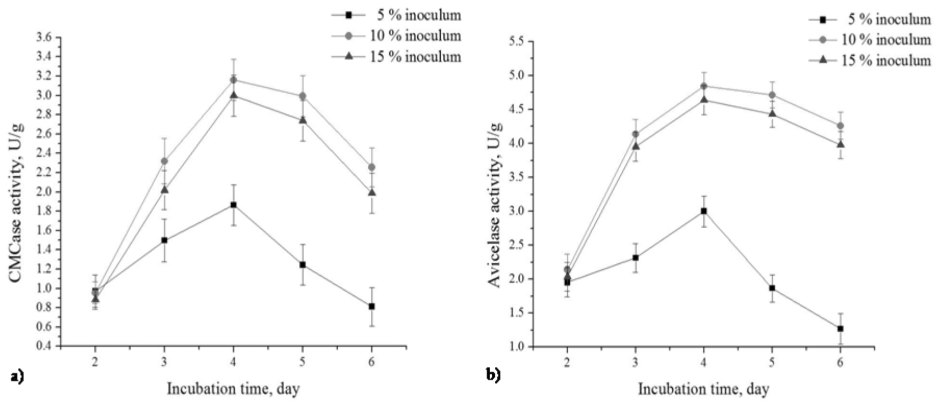

Figure 2. Cellulase production by *P. chitinolyticus* CKS1 using SBP during six days of incubation: a) CMCase activity and b) Avicelase activity.

The pattern of cellulase production, for both CMCase and Avicelase, indicates that the cellulase activity increased during the first four days, reached the maximum on day 4 and then decreased at the end of cultivation (Figure 2 a-b). The decrease of cellulolytic activity could be a consequence of changed conditions in the medium (pH change, production of inhibiting by- products), or due to the depletion of nutrients in the fermentation medium as seen for other bacterial strains [20]. The fourth day of incubation during SSF was found to be optimal for maximum CMCase production for other *Paenibacillus* sp. [19]. The importance of inoculum size with regard to microbial fermentation processes is generally accepted. There is a significant increase in cellulase production with an increase in inoculum concentration from 5 to 10 % and found to be maximum at 10% (Figure 2 a-b). Maximum CMCase activity 3.159 ± 0.213 U/g and Avicelase activity 4.840 ± 0.201 U/g was reached after four days of incubation with 10% of inoculum. Higher inoculum size 15 % resulted in a decrease in enzyme production. This demonstrates that inoculum density does not exert an unlimited effect on fermentation processes. High inoculum density can reduce enzyme production due to competition for available nutrients while low density can result in a reduce of enzyme secretion, owing to a drop in cell numbers [21].

CONLCUSIONS

SBP and molasses, as by-products from sugar industry could be a good substrate for cellulase production by P. *chitinolyticus* CKS1. During SSF, the optimum solid: moisture ratio appeared to be 1:1 for maximum cellulase activity. The maximum CMCase and Avicelase activity was reached at the fourth day of incubation with 10 % of inoculum. In addition, the use of SBP and molasses for the enzyme production is economically very suitable. The conversion of cellulose in SBS into fermentable sugars, could make these substrates suitable for the application in bioethanol production.

Acknowledgements

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APPLICATION OF ELECTROCHEMICALLY SYNTHESIZED FERRATE(VI) FOR THE REMOVAL OF Pb(II) IONS FROM WATER SAMPLES FOLLOWED BY KINETIC MEASUREMENTS

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ABSTRACT

The objective of this study was demonstration of applicability of electrochemically synthesized ferrate(VI) in order to remove Pb(II) ions from water samples, on the basis of its coagulation and oxidation effect. Pb(II) concentration was measured following newly developed kinetic-spectrophotometric procedure, based on its inhibitory effect on applied redoxsystem: (tri−sodium−5−Hydroxy−1−(4−sulfophenyl) −4−[(4−sulfophenyl)azo]pyrazole−3−carboxylate) (Tartrazine®), with H2O2 in alkaline media of borate buffer, at λmax of 428 nm of indicator substance. Obtained results confirmed successfully application application of ferrate(VI) and decreasing Pb(II) concentration after treatment of analyzed water samples.

Key words: lead(II), kinetic determination , ferrates(VI).

INTRODUCTION

Environmental pollution of heavy metals and metalloids has received considerable attention. Lead as a dominant poisonous metal is a one of the most hazardous element to human health, even in low concentration. Due to the still widespread use and production of fossil fuels, can be distributed in water, soil and air, especially in certain geo-morphological areas as well as some industrial areas. Lead is widely distributed in global environment and can accumulate in both, in humans and a wide range of biota through air, water and food. In recently reported literature, Pb(II) was determined by thermospray-flame-furnace atomic absorption spectrometry (TS-FF-AAS), inductively coupled plasma optical emission spectrometry (ICP-OES) and inductively coupled plasma mass spectrometry (ICP-MS) anodic stripping voltammetry

[1-9]. Among them, the kinetic-catalytic methods give high sensitivity and accuracy, without expensive and special equipment using different masking reagents or liquid/solid extraction to improve their selectivity and its application. Kinetic-spectrophotometric methods for Pb(II) trace determination published in last decades used various types of indicator reactions. Many of the developed kinetic methods have good analytical performance such as sensitivity (ppm, ppb or sub-ppb levels), accuracy, precision, rapidity, simplicity and reproducibility. From the other side, ferrates(VI) as a new generation of green chemistry, relatively stable and easy to synthetize electrochemically, based on principle of dissolution of iron anode having a strongly alkaline media, in an electrolysis cell, and having electric current to oxidize the dissolved iron to Fe(VI) ion [10]. Ferrates(VI) act as coagulant, disinfectant and oxidant. It is shown that the usage of common disinfectants, i.e. chlorine compounds and ozone, for water treatment may lead to strew 500 products harmful to human health [10]. Challenges have existed for the implementation of ferrate(VI) technology in practice due to instability of ferrate(VI) solution or high cost of ferrate(VI) products. In addition, ferrate(VI) effectively used to remove metals such as Cr, As, Fe, Mn from drinking and groundwater. Many of the research studies indicate that ferrate(VI) are more effective coagulants then other inorganic coagulants (aluminum, ferric, ferrous salts, etc.). Ferrate(VI) has advantages as coagulating agents in relation to the iron salts and aluminum due to the combination of its coagulating effect and a strong oxidizing wherein the degradable organic compounds which bind heavy metals and make it difficult to coagulate. New approaches have been explored to obtain ferrates(VI) focusing on high yield and stability, not only low-cost, which is substantially achieved by the method applied in this study. The efficiency of the process of water treatment using the ferrate (VI) is explained by the high oxidation-reduction potential in acidic and neutral media, the formation of iron(III)-hydroxide, product reduction ferrate(VI), extremely good coagulation resources, and oxygen generated by oxidation of water.

In this work, the coagulation efficiency of Na_2FeO_4 solution, electrochemically generated by trans-passive anodic oxidation of electrical steel in 10 M NaOH solution, is confirmed in the process of removal of Pb(II) ions which was spiked in natural waters samples. The efficiency of the removal of traces of lead was evaluated by comparing the values of Pb(II) concentration, obtained before and after treatment water samples with ferrates(VI) solution. On the basis of this study it is successfully confirmed previously observed purification effect of ferrates(VI) in many environmental water samples. Concentrations of Pb(II) were measured applying proposed simply kinetic-spectrophotometric procedure.

EXPERIMENTAL

Apparatus. Spectrophotometric measurements were performed on Perkin-Elmer Lambda 15 UV-Vis spectrophotometer. pH measurements were carried out using a Hanna Instruments pH-meter. A potentiostat-galvanostat PAR EGG connected to a computer with a built-in data recording system ED 2000 Electronic design with the use of LABVIEW program for recording the results of measurements were used. For heating and mixing the electrolyte solution was used laboratory magnetic stirrer with heating.

Angular velocity of mixing the electrolyte was in all measurements of $\omega \approx 2\ s^{-1}$. The anodic dissolution of electrical steel M120 in 10 M NaOH at a constant current density of A 0,046 cm^{-2} for a period of 3 h. *Materials.* Analytical grade chemicals and deionized water (MicroMed high purity water system, TKA Wasseraufbereitungssysteme GmbH) were used for the preparation of all solutions. A 1.000 g/l Pb(II) (Merck©) was used as stock solution. A solution of Tartrazine (TZ) (Fluka©) of $1\cdot10^{-3}$ mol/L was prepared by dissolution an appropriate amount in a calibrated volumetric flask. A 2 mol/l solution of H_2O_2 was prepared by suitable dilution of 10.2 ml of 30 % H_2O_2 solution (Merck©) with deionized water up to 50 ml. A 100 ml of borate buffer was prepared by mixing of 47.2 ml of 0.1 mol/l NaOH with 52.8 ml of 0.05 mol/l of $Na_2B_4O_7\cdot10H_2O$ and checked using a pH-meter . All working solutions were kept in a thermostatic water-bath at 25.0 ± 0.1ºC before the beginning of the reaction. All the glassware used were washed with aqueous solution of HCl (1:1) and then thoroughly rinsed with running, distilled water, and then, finally with deionised water.

Kinetic measurements. In a standard flask (Bouderin) with four separated compartment, a suitable aliquot of working Pb(II) solution and apropppriate volume of deionised water, a solution of Cu(II) ions were placed in one compartment, 0.2 ml of $1\cdot10^{-3}$ mol/l solution of TZ in the second, 2 ml of borate buffer pH of 10.5 in the third, and 1 ml of 2 mol/l H_2O_2 (total volume of 5 ml) in the fourth compartment. The flask was kept at 25.0 ± 0.1ºC in the thermostated bath, and then was vigorously shaken and reaction was initiated by mixing of reagents. Synchronously with start of reaction (mixing of reagents) a chronometer was turned on for monitoring duration time of reaction. The spectrophotometric cell was rinsed well and filled with the reaction mixture. The absorbance at 428.4 nm was measured every 30 s over a period of 6 min after mixing, against the reagent blank.

RESULTS AND DISCUSSION

Oxidation of TZ by hydrogen peroxide in borate buffer in the presence of traces of Cu(II) was measured spectrophotometrically at an absorption maximum of 428.4 nm, and significantly decreases in the presence of Pb(II) ions. For all experimental parameters investigated in this study, the rates of non-inhibited and inhibited reaction were simultaneously measured. The optimum conditions of the reaction system, regarding reagents concentration were established, regarding on the sensitivity and reproducibility of proposed kinetic method. Also, analytical and statistical data, LOD and LOQ were determined (Table 1). The tangent method was used for processing obtained kinetic data. Under established optimum reaction conditions at the temperature of 25.0 ± 0.1°C, good linear relationship was obtained over range from 0.829-8.29 (μg cm^{-3}) of Pb(II). This method was applied for determination of micro-amounts of Pb(II) in analyzed spiked water samples before and after ferrate(VI) treatments. The efficiency of the process of water treatment using the ferrate (VI) is explained by the high oxidation-reduction potential in acidic and neutral media, equation (1), the formation of iron(III)-hydroxide, product reduction ferrate(VI), extremely good coagulation resources, and oxygen generated by oxidation of water. Reduction reaction ferrate (VI) in acidic medium is shown to equation (10):

$$FeO_4^{2-} + 8H^+ + 3e^- \rightarrow Fe^{3+} + 4H_2O \quad E_0 = +2{,}20V \tag{1}$$

The ferrate salts when dissolved in water, oxygen is evolved and ferric hydroxide is precipitated, equation (2), [10]:

$$4K_2FeO_4 + 10H_2O \rightarrow 4Fe(OH)_3 + 8KOH + 3O_2 \tag{2}$$

In this study Na_2FeO_4 electrochemically generated by trans-passive anodic oxidation of electrical steel in 10 M NaOH solution was applied to remove of thorium(IV) from spiked water samples [29]. The stability of ferrate(VI) of its aqueous solutions depends on several factors such as ferrate(VI) concentration, temperature of the solution, presence of other ions, pH. The spontaneous decomposition of ferrate(VI) in aqueous solutions was reported to be increased significantly with decreasing the solution of pH. Ferrates(VI) because of their characteristics, as well as a strong oxidizing compounds, quite unstable in aqueous solutions, due to the oxidation of water, so it is necessary that the qualitative and quantitative analysis is performed immediately after the completion of the synthesis process to obtain reliable data. Therefore, the chromite analytical method [29] adapted for relatively simple and reliable determination of the yield of the process synthesis of ferrate(VI). The aqueous solution of ferrate(VI) prepared in alkaline media (10 M NaOH) are stable with red-purple color.

Table1. Analytical and statistical data of the calibration graph for the determination of Pb(II). Experimental conditions: $C_{TZ}= 4\cdot10^{-5}$ mol/l; CH_2O_2=0.4 mol/l; pH=10.5; t = 25.0 ± 0.1°C.

Analytical and statistical data	Dynamic range, n=5 0.829-8.29 (μg cm^{-3})
Limit of detection (μg cm^{-3})	0.1
Limit of quantification(μg cm^{-3})	0.33
Slope ± SD x 10^2	-5.986
Intercept ± SD x 10^2	1.13
Correlation Coefficient	0.9977
Standard deviation of the Fit	1.15

Table 2. Accuracy and precission of proposed kinetic method

Added (μg cm^{-3})	Found[a] (μg cm^{-3})	RSD[b](%)	(x-μ)/μ·100[c]
0.829	0.79±0.03	3.79	-4.7
4.14	4.27±0.12	2.81	+3.1
8.29	8.11±0.20	2.46	-2.2

a. mean value±standard deviation (μg cm^{-3}) (n=5).
b. relativne standardn deviation
c. accuracy of the method

Table 2. Pb(II) determination before (B) and after (A) treatment water samples by ferrate(VI)

Sample	Pb(II) added µg/mL	Pb(II) found µg /mL[a]	
		B	A
Spring water	5.0	5.14±0.42	0.46± 0.06
Lake water	5.0	5.17±0.58	0.50± 0.04
Ground water	5.0	5.20±0.54	0.55± 0.07

[a] Average of five measurements± standard deviation

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THE POSSIBILITY OF PROCESSING BIODEGRADABLE WASTE IN THE AEROBIC FERMENTER

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ABSTRACT

This paper presents the results obtained in the process of processing of biodegradable waste (obtained during agricultural production, as well as municipal waste) by applying aerobic fermenter EWA. Testing was carried out within the Institute of Forage Crops in Globoder - Kruševac. This fermenter is also possible to process waste obtained from forestry production, sewage sludge and animal products. During the one-month test, aerobic fermenter was charging with biologically degradable materials (with different ratios of the components). The fermenter EWA is certified device that is used to stabilize biodegradable waste and make it friendly for the environment. This device is in accordance with European Union regulations.

Key words: aerobic fermenter, biodegradable waste, stabilization, environment.

INTRODUCTION

Increasing economic growth and development in the world, the introduction of new processes and products, as well as the constant growth of the population, produces large quantities of waste materials from households and industry. This waste is necessary to remove and dispose. It is important to find the most suitable method for the disposal and further processing of waste, to stop the pollution of the environment with waste material. Recycling is the best way for the release of waste and its further exploitation in another form.

It is estimated that about 2.5 million tons of waste are collected in Serbia. The bad side is that half of them remain in the yards, roadsides or river beds. It is also estimated that one man produces approximately 0.8 kg of waste per day [1].

In the process of joining to the European Union, adequate development of the waste management system is very important, such as the development of the whole society and economy. The waste management system in Serbia is currently in a very similar position as highly developed European countries such as Holland, Germany and Austria were in the 1970's [2]. In short, waste recycling is in developing in our country, and it is one of the problems that have to be solved in the near future. Also, it is a chance from the economic aspect, to form a special branch that would provide new working places [1].

The chemical composition of the waste is complex, and may results with damage to the environment and health of people and animals. Need for finding a suitable way of processing biodegradable waste, is growing with every next day. Good point for biodegradable waste is that it is suitable for anaerobic or aerobic decomposition [3], [4].

Waste structure analysis in bigger cities in Serbia showed that the greatest part of it is organic waste (biodegradable waste - 31.0%, garden waste - 11.9%, cardboard - 7.5% and paper - 7.3%), which makes total of 54.7% of the waste that can be decompose. The rest consists of other types of waste such as glass (5.26%), cardboard with wax (0.98%), cardboard with aluminum (0.9%), metal packaging and other (1.45%), metal-aluminum cans (0.36%), plastic packaging paper (4%), plastic bags (6.7%), hard plastics (4.4%), textiles (5%), skin (0.6%), diapers (4%), fine elements (8.7%) [5].

Applying of different kinds of living microorganisms, bacteria, fungi, algae and protozoa, which under aerobic or anaerobic conditions may remove, transform or convert organic compounds into inorganic is a good way to solve this problem [6].

Composting is processing of certain types of organic waste in the presence of oxygen, in order to obtain material like humus. This, also, reduce the volume of organic waste. After this proces, organic material could be returned to nature. After completion of the composting process in EWA, the processed material is suitable for fertilization with reduced volume (20% to 60% from initial material). Moisture content is below 40%, and the mass is reduced by 50%.

For this purpose is suitable mainly backyard waste in the form of cut grass, leaves, parts bushes and trees, food waste, paper, cardboard, organic fractions, agricultural wastes (plant residues, animal manure). Also it could be using organic components of communal waste, partially treated and mixed communal waste and the organic fraction of communal waste with sludge from wastewater [7]. The composition of the compost should not be consist impurities such as visible particles of metals, plastics and glass and coliform bacteria such as *Salmonella ssp., E. coli, Enterococcus*, etc. [8].

The aim of the study was the practical application of aerobic digester EWA and testing the quality of the product obtained from biodegradable materials.

MATERIAL AND METHOD

Aerobic fermenter EWA (Ecological Waste Apparatus) was used for processing of biodegradable waste at the Institute for forage crops in period from 23.10.2013. to 19.11.2013. Czech Republic (a member of the EU), in its law has regulations for dealing with biodegradable waste [9]. Aerobic fermenter EWA (Fig. 1) is certified device for processing biodegradable waste (BDW), including sewage sludge and animal products in accordance with decree EU [10]. The device consists of a thermally insulated space where the air intensively blows of the injector system. System for filling mass consists of a segment of the floor conveyor which is located inside the fermenter, and an integrated device for charging and discharging. Segmented floor used hydraulic cylinders which receive power from the hydraulic pump. Work fermenter is automatic whereby throughout the process temperature is measured at 16 points. Control of the work process, and determining the mode is done in the industrial touch screen display computer that is built into the fermenter. Blowing air into the digester is done fan [11]. The principle of work of the fermenter is composed of chopped and mixed inserting a biodegradable material to the fermenter. The optimum moisture of the material is 50-60%, wherein the inserting the air activate work of aerobic bacteria. Also, the mixing of the mass is done during the metabolic activity of which leads to an increase in temperature and an increase of bacteria. This speeds up the composting process, whereby complex organic materials decompose and transform into another.

At temperatures above 70°C is gradually denature the proteins. High temperature for a certain period of work caused by the inactivation of the bacteria present and pathogenic organisms (viruses, bacteria, yeasts, fungi, protozoa and worms). Due to the high temperature reduce the number of microorganisms and weed seeds lose their germination ability.

Important for biological degradation is a sufficient supply of oxygen, which allows hydrocarbons as the source of carbon and energy for bacterial growth. This results in the conversion of pollutants to carbon dioxide, water and biomass [12].

Mulch-compost is obtained by controlled aerobic fermentation (thermophile fermentation). It is a mixture of agricultural and forest biomass with biodegradable waste. Its structure is fibrous, crumbly with noticeable ungraded pieces of biomass (bark, wood chips, straw). The color is brown, brown-gray and smells like mushrooms or wet wood. Table 1 shows the basic technical characteristics of aerobic digester EWA.

Table 1. Technical parameters of aerobic fermenter EWA (Agro-eko)

Length (mm)	12192
Width (mm)	2438
Height (mm)	2896
Empty fermenter weight (kg)	14800
Maximum weight of the full fermenter (kg)	32000
Working zone volume (m^3)	36
Load weight (t)	10-17
Electric supply (kW)	15

The operation cycle of the fermenter EWA is controlled on the basis of operation reading of conditions and values which characterize the aerobic fermentation. One operation cycle consist of three or four time separated phases. The first phase is the phase of the charging and takes 4 hours. The second phase is the fermentation phase and takes 48 hours. The third stage is the final drying phase and it takes 42 hours. The fourth phase is the discharge (2 hours). The total time of the whole process is 96 hours. The most important phase is the fermentation itself. The intelligent control is based on measuring of these values: fill temperature in the whole section and oxygen content in the exhaust gas. Current values are recorded and assessed by an industrial computer.

RESULTS AND DISCUSSION

The composition of the fermenter feeding EWA during examination is presented in Table 2. Charging is carried out from biodegradable material that is obtained from agricultural production from livestock around of Kruševac (cow manure, chicken voiding). The digestate was obtained from the manure from the farm cows and whey from milk from dairy "Lazar" in Blace. Part of the biomass was obtained from economy of the Institute for forage crops. Plant mass was previously chopped in chopper-blower and then mixed with "Bobcat" loader in certain proportions and transporters inserted into the fermenter. Depending on the composition of the components inside the fermenter, and the total weight of the fermentation process is differently ranged, and lasted for five days with the charging of 081310036. The longest process (6 days) was in charge of 081311031 and 081311034.

Table 2. The composition of the fermenter EWA charging

Series	Composition of charging	Charging (%)			Total (t)
		1	2	3	(1+2+3)
Digestate and manure	Number of charging	081310031	081311034	081311036	
	Date	23.10. - 28.10.	07.11. - 12.11.	15.11. - 19.11	
	Digestate - Blace	100.00	25.70	81.45	
	Alfalfa + grass	0.00	19.80	3.62	
	Cow manure	0.00	21.00	0.00	
	Straw	0.00	0.00	2.26	
	Chicken voiding	0.00	21.00	12.67	
	Wood chips	0.00	12.50	0.00	
	Σ	100.00	100.00	100.00	
	Mass (t)	13.00	25.70	22.10	60.8

The lowest mass charging was 13 t. The maximum charging weight was 25.7 t. During the examination of three charging of biomass in the fermenter EWA, 60.8 t of biodegradable materials was processed. During operation, all the relevant parameters of work were monitored.

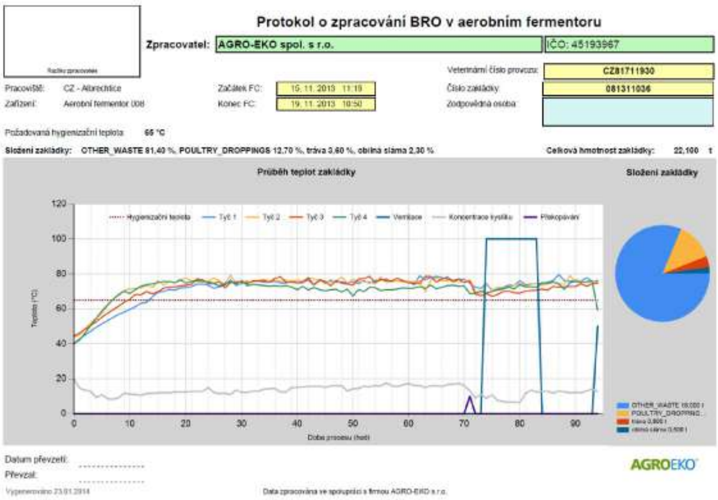

Figure 1. Display of temperature, time of fermentation and the charging ratio of the components (sample No. 081310036)

The movement of the charging temperature during the fermentation process, and the total operation time was presented in Figure 1. The graph (Fig. 1) was obtained from the computer that controls the whole process of work, and can be seen charging ratio of the components (digestate 81.45%, chicken voiding 12.67%, straw 2.26%, alfalfa and grass 3.62%). The temperature of fermentation is measured and conducted at sixteen locations within the fermenter at four different heights (four lines of different colors on the chart). The maximum temperature during the fermentation was more than 70°C, which caused protein denaturation and inactivation of bacteria and pathogenic organisms. Also at this temperature loses the ability to germination for seed of weeds. For each charge all the relevant parameters such as the number of charging was showing on the graphs. Digester work with integrated Wi-Fi device allows monitoring all parameters remotely.

In the authorized chemical and microbiological laboratory in Albrechtice (Czech Republic) was done the chemical (Table 3) and microbiological (Table 4) analysis of obtained material. The particular methodology is compliant with the Regulation of the European Parliament [13].

Table 3. The chemical composition of the digestion number 081310036

Chemical analysis	Number of samples 081310036		
Composition	Result	Measure unit	Method
Arsenic	3.10	mg/kg in dry matter	SOP 02C (ČSN EN ISO 15586) A
Cadmium	0.31	mg/kg in dry matter	SOP 02 C (ČSN EN ISO 5961) A
Chrome	16.0	mg/kg in dry matter	SOP 23 C (ČSN EN 1233) A
Copperr	33.7	mg/kg in dry matter	SOP 23 C (ČSN ISO 8288) A
Mercury	0.018	mg/kg in dry matter	SOP 03 (ČSN 465735, ČSN 721227) A
Nickel	19.5	mg/kg in dry matter	SOP 23 C (ČSN ISO 8288) A
Plumb	9.66	mg/kg in dry matter	SOP 23 C (ČSN ISO 8288) A
Zinc	100	mg/kg in dry matter	SOP 23 C (ČSN ISO 8288) A
Calcium	24.0	g/kg in dry matter	SOP 23 C (ČSN ISO 8288) A
Magnesium	4.36	g/kg in dry matter	SOP 23 C (ČSN ISO 7980) A
Potassium	19.8	g/kg in dry matter	SOP 28 B (JPP - UKZUZ, Brno) A
Phosphorus	5.53	g/kg in dry matter	SOP 62 A (JPP - UKZUZ, Brno) A
Total dry matter	33.71	%	SOP 32 (ČSN EN 12879) A
pH (H_2O)	8.66		SOP 44 (JPP - UKZUZ, Brno) A
Flammable substances	77.3	% in dry matter	SOP 32 (ČSN EN 12879) A
Ratio C:N	17.0		SOP 85 (JPP - UKZUZ, Brno) N
Total nitrogen	2.26	% in dry matter	SOP 61 A (JPP - UKZUZ, Brno) A

The microbiological composition of the sample 081310036 showed in table 4., which is also done in an approved chemical and microbiological laboratory in Albrechtice.

Table 4. Microbiological composition of the digestion number 081310036

Microbiological analysis of samples number 081310036			
Composition	Result	Measure unit	Method
Enterococcus	$6.7x10^3$	KTJ/g dry matter	SOP 103 A (ČSN EN ISO 7899-2) A
Thermotolerant coliform bacteria	$<5x10^1$	KTJ/g dry matter	SOP 102 A (ČSN 757837) A
Salmonella	Negative	-----	SOP 117 A (ČSN EN ISO 6579) A
Test for Salmonella	Negative	-----	SOP 117 A (ČSN EN ISO 6579) A

During operation, test tubes are inserted into the fermenter with seeds of corn, alfalfa and grass to determine the seed germination after the fermentation process. After the fermentation process there was not seed germination.

CONCLUSION

In agricultural production, part of the amounts of organic matter from the soil is removed from the land in the form of food. The second part after cutting and pruning incinerated or landfilled. Such a mode of food production is irretrievably lost organic matter, nutrients and land. It also pollutes the environment. This way degrades fertile land especially in intensive agricultural production. Part of the organic matter can be compensated for processing biodegradable organic material, which makes up more than 50% of municipal waste in Serbia.

One of the ways for solving the problem of the organic biomass processing is the application aerobic digester EWA which showed very good results during the one-month tests. Aerobic fementator EWA is a device that allows, with control of the whole technological process, processing of biodegradable waste from agriculture, forest biomass and municipal waste.

Acknowledgment

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ENVIRONMENTAL CONCERNS OF SHALE GAS PRODUCTION IN POLAND

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ABSTRACT

The discovery of unconventional gas resources in Poland initiated actions that are focusing on the exploration and production of these resources. In order to extract unconventional gas it is necessary to apply either hydraulic or “non-aqueous” fracturing method. Gas production stages involve a different type and range of potential environmental impacts for which different assessment procedures and mitigation measures are applied. The paper gives a brief outlook on the current situation of shale gas exploration in Poland and potential risks to the environment that may be caused by gas production.

Key words: shale gas, hydraulic fracturing, environmental risk.

INTRODUCTION

The demand for energy has been steadily growing along with the development of economy. Rising energy prices and security of supply concerns have spurred interest in unconventional energy resources. The necessity of importing gas from a monopolist provider makes it possible for that monopoly to dictate deposit prices, which are in Poland among the highest in Europe, even after the renegotiation agreement. The prospect of increased natural gas production creates new hope for rationalization of the Polish energy policy, which is currently based mainly on coal. The domestic production of shale gas could made Poland independent of gas imports from Russian Federation and decrease energy dependency of the country - even the most pessimistic estimate indicating sufficient reserves to make Poland self-sufficient for 65 years.

Natural gas has become a preferred fossil fuel not only for political reasons but also environmental. It may be a potential transition fuel that will allow for the shift from coal to cleaner energy resource that helps to reduce the emissions of CO_2.

SHALE GAS IN POLAND

The unconventional gas resources in Poland were initial estimated by US Energy Information Administrtation (EIA) to be roughly $5{,}3 \cdot 10^{12}$ m^3 (U.S. Energy…,

2011) According to a report published by the Polish Geological Institute - National Research Institute in March 2012, estimated recoverable shale gas resources are probably in the range of 346 to 768346,1-767,9·10^9 m^3. (Assessment…, 2012). Nevertheless, these reserves place Poland third in Europe in terms of recoverable shale gas resources.

The most prospective shales gas resource in Poland are located along a belt stretching through the Central and Eastern Poland, in three main sedimentary basins: Baltic, Podlasie and Lublin (Fig.1). The most promising in terms of potential unconventional gas reserves within this belt are the Upper Ordovician and lower Silurian shales formed 485 – 420 million years ago (Poprawa, 2010). They seem to have adequate geological characteristics to be classified as an unconventional hydrocarbon reservoirs. The depth to the potential gas-bearing shales is variable and ranges from about 500–1,000 m in the east to more than 4,500 m in the west (www.pgi.gov.pl)

Until 4st of May 2015, according to the Polish Ministry of Environment, 70 exploratory shale gas shafts were drilled in Poland. There are now 48 licenses for prospecting and exploration of unconventional hydrocarbon resources, including shale gas deposits. These concessions have been awarded to 12 Polish and foreign capital groups - the world's largest private sector oil companies, including Chevron Corporation, Marathon Oil Company and Lane Energy, as well as state-controlled energy holdings such as Orlen Upstream Sp. z o.o. or LOTOS Petrobaltic Sp. z o.o. (www.lupki.mos.gov.pl)

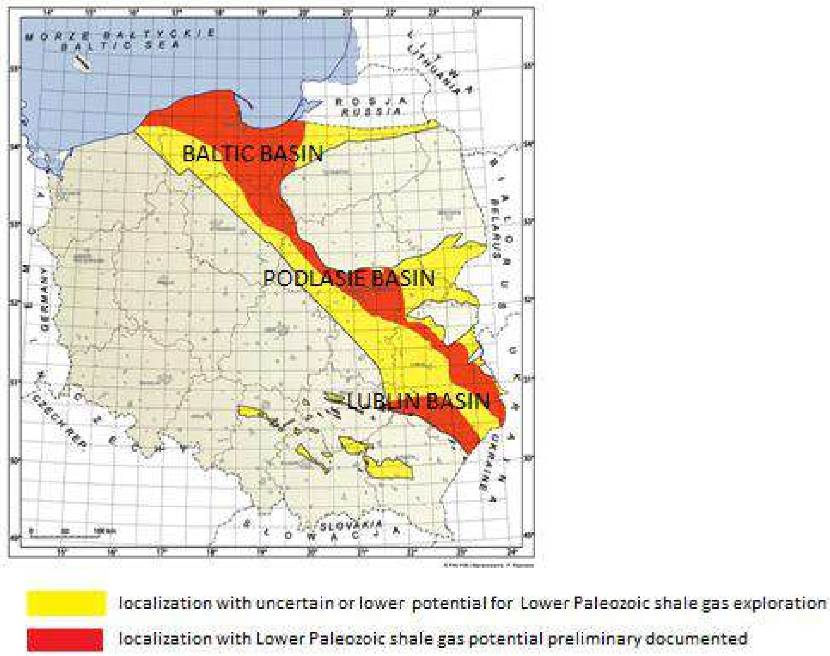

Figure1. Location the sediments with potential for development of shale gas accumulations

SHALE GAS PRODUCTION TECHNOLOGY

Shale formations are represented by clastic rocks which exhibit extremely low permeability (well below 1mD) that limit the recovery of the gas and require additional techniques to achieve economical flow rates. It is necessary to carry out intensifying operations which leading to an increase of permeability in the well section and to inflow of gas to the well bore. The hydraulic fracturing is currently the basic and most popular stimulation treatment used for shale gas production. This process is performed by injecting water with chemical additives and proppant under high pressure which makes rock mass fractured and interconnects pores creating flow paths for the gas.

An alternative to the hydraulic fracturing process, allowing to reduce the impact on the environment, could be other technology of unconventional gas extraction such as "dry" or "non-aqueous" fracturing with CO_2, N_2 or foams (Rogala et al., 2013; Lutyński, Lutyńska, 2013).

Initial hydraulic fracturing in Poland was carried out in August 2011 by Lane Energy from the 3Legs Resources group at the Łebień LE 2H well in Pomerania. Results of flow tests performed in October 2012 didn't appear promising as the recorded flow of 20,000 m^3 per day corresponded to lower values obtained from American shale gas wells (Environmental…, 2012).

ENVIRONMENTAL ISSUES

All mining operations, including prospecting, exploration and exploitation of shale gas deposits are to some extent an interference to the environment. The process of shale gas production is broken down into the following stages:

- preparatory work;
- well drilling;
- reservoir stimulation process (hydraulic fracturing);
- production preliminaries;
- production (extraction of the gas from wells);
- well liquidation and area reclamation.

Each of these stages involves a different type and range of potential environmental impacts for which different assessment procedures and mitigation measures are applied.

Potentially endangered elements of the environment are: water (both underground and surface) soil and atmosphere.

For surface and groundwater water numerous hazards of quantitative and qualitative changes occur in the phases of recognizing and documenting shale gas resources and intensify repeatedly during their exploitation. Depending on the reservoir, the amount of water needed for fracturing operation varies between 8 to 17 thousands m^3 of water (Tab.2). Often for the purpose of gas exploitation from one shale reservoir dozens of wells are drilled.

Table 1. Average quantities of water using in the hydraulic fracturing technologies

Investigated area	Water quantity per one well using in a complete fracturing process [m^3]
Barnett (USA)*	8 700
Marcellus (USA)*	14 300
Fayetteville (USA)*	10 900
Haynesville (USA)*	10 200
Łebień (Poland)**	17 300

Source:
**(Council and Consulting, 2009) - average values from drillings*
***(Environmental Aspects of Hydraulic Fracturing Treatment Performed on the Lebien LE 2H Well - Final Report, 2012) - actual value from one well*

The necessity to provide such large amounts of water may adversely affect the state of surface and groundwater resources in the vicinity of the wells, especially in the case when significant water consumption in a small area in a relatively short time (so-called cumulative uptake) occurs. Water supply can be a major problem because Poland is distinguished by relatively low water resources in comparison with other European countries (according to hydrological data, it is on the 22nd place in the European Union in terms of water quantity). National water resources per capita represent only about 36% of the European average (Diagnoza…, 2010).

Besides using of significant amounts of water, fracturing processes also require the use of different chemical products in the fracturing fluid. Most hydraulic fluids are a mixture of water and chemical additives – they typically contain acids (eg. citric, hydrochloric), gum guar, isopropanol, borate salts and petroleum derivatives. Part of the fluid used in the fracturing process and the solids that are flushed from the rock massif is pumped back to the surface and forms flowback water, which is treated as wastewater. The chemical composition of flowback water is characterized by high concentration of total dissolved solids (TDS), organic hydrocarbons, inorganic and organic additives, and naturally occurring radioactive material (NORM). These pollutants can be toxic to humans and aquatic life, radioactive or corrosive. Particularly dangerous is the possibility of migration of fracturing fluid and flowback water to the Major Groundwater Basin (MGB) (Woźnicka, Konieczyńska, 2011). The potential water contamination pathways could be e.g.: failure in a well casing that may cause a leak of fluids to the surrounding groundwater, migration of hydraulic fracturing fluid through fractures into overlying aquifers, water contamination from drilling site spills due to improper handling or leaks from storage tanks and retention ponds, leaky pipelines etc (Fig. 2).

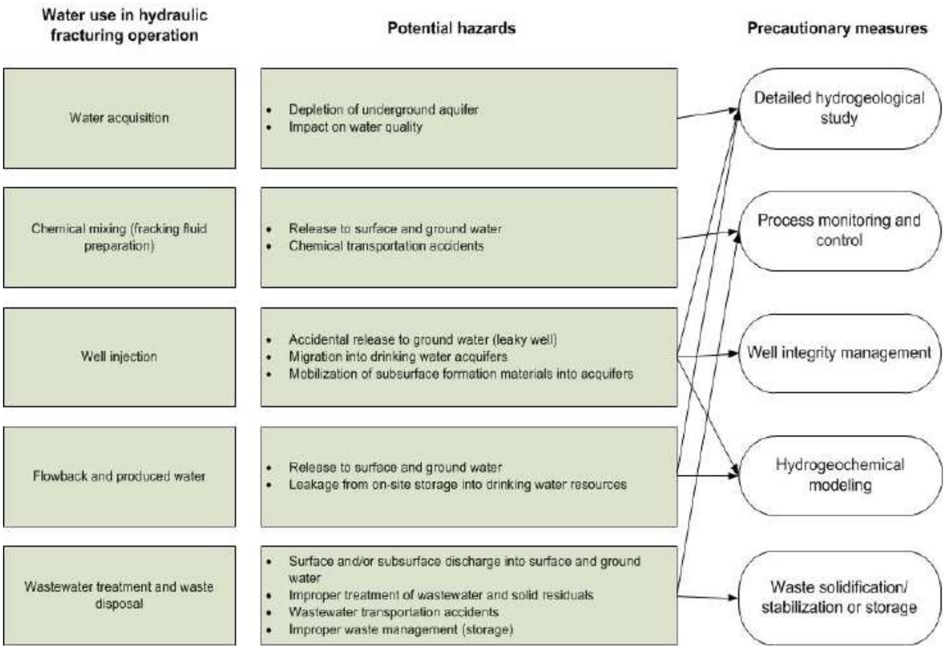

Figure 2. Hydraulic fracturing watercycle with associated hazards and precautionary measures.

Gas shales present in Poland have a small level of radioactivity, which is safe for people and the environment. The fracturing treatments cause no vibrations or shocks on the ground which could create hazards for buildings or the infrastructure. Because Poland is an aseismic region, there is no risk of inducing seismic vibrations by shale gas production. The other issue related to shale gas exploration and extraction is the air pollution which is caused either by gas flaring or gas escapes from the well. The other source of air pollution is the use of diesel engines for drilling or electricity generation in the vicinity of the well. Nevertheless, taking into account the volumes of pollutants released into atmosphere this problem can be regarded as irrelevant for the environment.

Drilling exploitation openings is accompanied by noise emitted by power generating units, drive engines for the drilling device and washer pumps, washer pumps and vibration sieves. In Polish conditions the noise emitted by high-power diesel engines during hydraulic fracturing does not exceed the acceptable levels. Drilling works conducted in areas with a high degree of urbanization or in areas requiring specific protection, require monitoring of the noise level and using devices with well-muffled subassemblies and installed acoustic barriers. (www.polishshalegas.pl)

Adequate surface protection and reclamation of the drilling site allows full restoration of its original character and the way of land use. According to Polish legal regulation, the entity managing areas with contamination of soil or unfavorable transformation of natural land, after the end of investment, exploration-reconnaissance or operational works, is obliged.

CONCLUSIONS

The current process of shale gas exploration and production works technology in Poland guarantees minimizing hazards to the environment related to the possibility of contamination of the ground surface and underground waters within the drilling rig, noise emission and contamination into the atmospheric air. All stages of the works take place according to detailed and verified standards and practices ensuring the leveling of negative effects of these activities for the environment and the community. However, emergency situations cannot be excluded. Taking into the consideration the potential risk for the environment, it is necessary to monitor the entire exploration process.

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REDUCTION OF ENERGY CONSUMPTION AND CO_2 EMISSIONS THROUGH INCREASE OF COMBUSTION EFFICIENCY

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ABSTRACT

This paper identifies cost-effective energy savings in the metallurgical industry that can be achieved through performance improvement of combustion process. The specific energy efficiency technologies and measures to reduce energy use and carbon dioxide emissions potential for the existing furnaces were described, giving the focus on retrofit measures using commercially available technologies such as combustion air temperature preheating, control air-to-fuel ratio and use advanced commercially available combustion technologies.

Key words: metallurgical industry, energy efficiency, CO_2 emissions.

INTRODUCTION

Steel and iron making industries have been driven by the requirements of maintaining or improving product quality and minimization of production costs [1-6]. Within this requirement the overall energy management and energy efficiency play important roles. To meet the higher requirements it is necessary to improve existing furnace by optimising the efficiency and by reducing the pollutant production of burners and combustion chambers. Likewise, the choice of combustion technology for furnaces in steelworks is one of the key factors in minimization of energy consumption per unit of product. In general, the cost-effective energy savings at a furnace in the metallurgical industry can be achieved through performance improvement of combustion process and heat transfer. Possible energy savings achievable on the existing furnaces are given in Table 1.

Table 1. Furnace energy savings through performance improvement of combustion process and heat transfer [7]

	Performance Improvement Description	Savings
Heat Generation Opportunities	Control air-to fuel ratio	5 to 25%
	Preheat combustion air	15 to 30%
	Use oxygen enriched combustion air	5 to 25%
Heat Transfer Opportunities	Improve Heat Transfer with Advanced Burners and Controls	5 to 10%
	Improving Heat Transfer within a Furnace	5 to 10%

FURNACE PRODUCTION RATE

A furnace fuel economy depends on many factors which are often neglected in practice. For example, the fuel consumption significantly depends upon the furnace production rate (output, throughput). Total energy consumption per unit mass of production to the required specification will follow the curve in Fig. 1, which shows the lowest value at 100% of furnace capacity and progressively higher values as the farther throughputs deviate from 100%. Furnace efficiency varies inversely with the total energy consumption. The lesson here is that furnace operating schedules and load sizes should be selected to keep the furnace operating as near to 100% capacity as possible. Idle and partially loaded furnaces are less efficient.

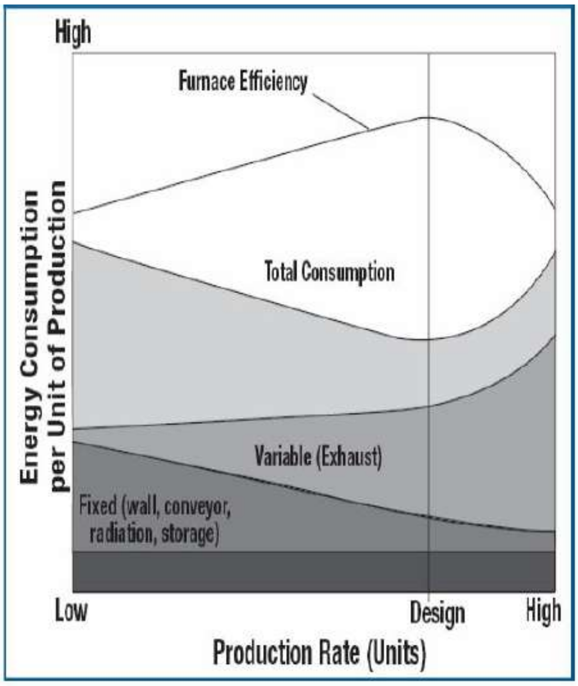

Figure1. Specific fuel consumption as a function of the production rate [7]

AIR-TO FUEL RATIO

The loss due to incomplete combustion of the fuel can be avoided by improving by fuel/air mixing and, oftener, by operating with some excess combustion air. However, care should be taken not to add more air than is necessary to complete the combustion process in practice since the addition of excess air can markedly reduce the combustion efficiency, which is determined of all by the exhaust gas temperature after the recuperator and by the volume of exhaust gas (Fig. 2).

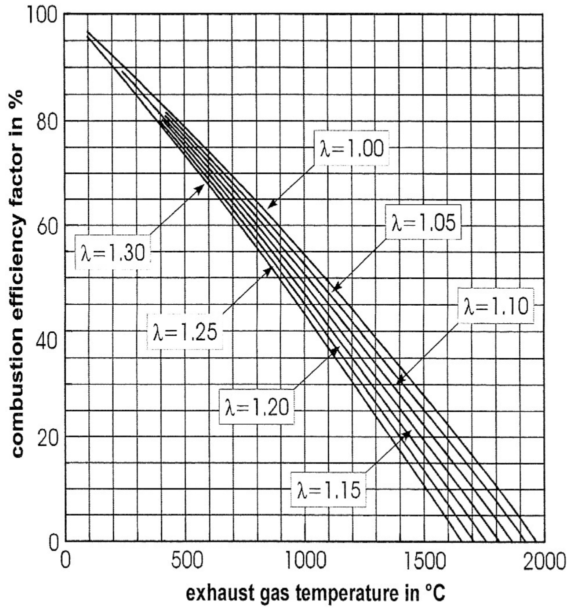

Figure 2. Combustion efficiency for natural gas L without combustion air preheating [8]

The theoretical available heat is used to show the thermal efficiency trends as functions of exhaust gas temperature, oxidizer and fuel consumption, mixture ratio, and air and fuel preheat temperatures. Its physical meaning is identical to the combustion efficiency, i.e. to the percentage of the gross energy input which is available to heat the load and energy oriented to the furnace superstructure, defined as:

$$\eta_{\mathrm{f}} = \frac{h_{\mathrm{fuel(LHV)}} + h_{\mathrm{air}} + h_{\mathrm{flue\ gas\ (inlet)}}}{h_{\mathrm{fuel(LHV)}}} \tag{1}$$

Where $h_{\mathrm{fuel(LHV)}}$ is lower heating value of the fuel, h_{air} is the enthalpy of the preheated combustion air, and $h_{\mathrm{flue\ gas\ (inet)}}$ is the enthalpy of the gas at the inlet of the recuperator.

PREHEAT COMBUSTION AIR

The *relative air preheat rate* is expressed as:

$$\varepsilon = \frac{T_{\text{air (outlet)}} - T_{\text{air (inlet)}}}{T_{\text{flue gas (inlet)}} - T_{\text{air (inlet)}}} \tag{2}$$

Fig. 3 shows the relationship between the combustion efficiency and the relative air preheating rate for various gas inlet temperatures. Preheating of the combustion air is an efficient method to reduce fuel consumption in high temperature processes. If a heating process may be performed both with and without preheating of the air, then the chosen operating method influences only the combustion efficiency. The furnace heat flux must remain the same for both methods as the same heating process is to be accomplished in the furnace. Therefore, an increase in the combustion efficiency necessarily permits a reduced delivered energy and thus the lower fuel mass flow.

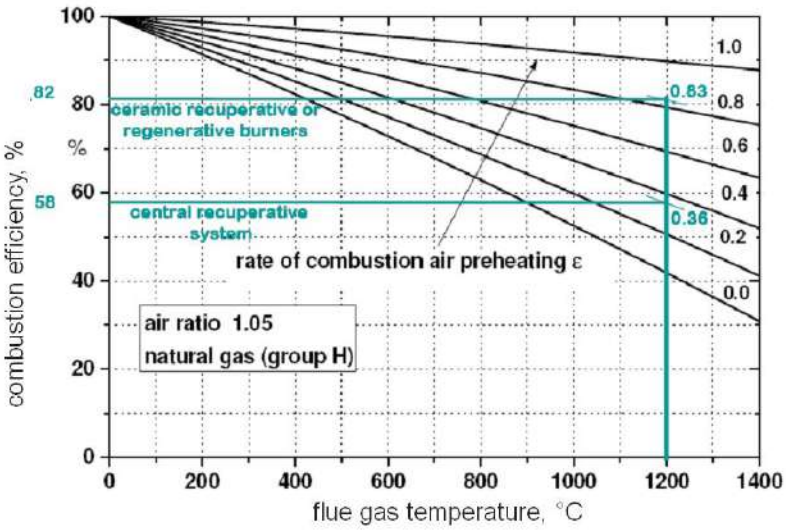

Figure 3. Combustion efficiency by combustion air preheating [9]

This fact enables a "*fuel saving factor*" or more simply a "*fuel saving*" to be defined as follows:

$$\eta_b = \frac{q_{m,0} - q_{m,P}}{q_{m,0}} = 1 - \frac{q_{m,P}}{q_{m,0}} \quad \Rightarrow \quad \eta_b = 1 - \frac{\eta_{f,0}}{\eta_{f,P}} \tag{3}$$

Whereby $q_{m,o}$ is the delivered flue mass flow without air preheating, $q_{m,p}$ is the delivered flue mass flow with air preheating. Fig. 4 shows the relationship between the fuel (energy) saving factor and the temperature of combustion air preheating for various flue gas inlet (before the recuperator) temperatures.

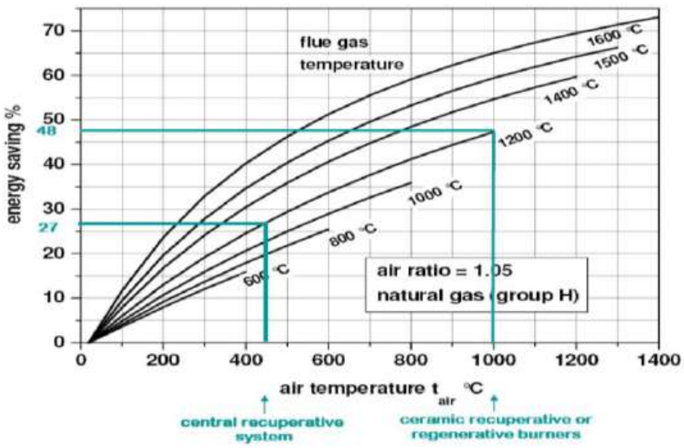

Figure 4. Fuel saving by combustion air preheating [9]

Cold air burners are not suitable for preheated air. *Hot air burners* can be supplied with air of approx. 400°C preheated in an external (central) preheater: regenerator or recuperator. That is, so-called, *central air preheating technology*. On the other hand, there are the so-called "advanced" commercially available *decentralized air preheating technologies* such as High Temperature Air Combustion (HiTAC) [8-13], which have many advantages. In recuperative burners the air preheater (recuperator) is integrated in a single unit within the burner. Heat loss and hot air piping are eliminated and therefore preheat temperature are higher, usually 500-700°C or more in the case of ceramic recuperative burners. In regenerative burners, the burner and the heat regenerator are designed as a unit. Thanks to the high heat transfer area that allows for a very compact design, air preheat temperature of 800-1000°C or more are attained.

COMBUSTION USING OXYGEN ENRICHED AIR

Oxyfuel technology has been used in metal heating and melting, glass melting and waster incineration. It is known that rising oxygen concentration in the oxidiser leads to: (a) higher process efficiency, thus reduction in fuel consumption and therefore in CO_2 emission, (b) higher flame temperature (c) heat transfer enhancement, thus higher productivity at the highest possible level of product quality, (d) achieving low NO_X. In order to achieve very low emission of nitrogen oxides, the Flameless Oxy-Fuel Combustion has been developed [14-16]. This new combustion technology is characterised by a lower temperature flame, more uniform temperature distribution and low concentrations of oxygen as well as nitrogen inside the combustion chamber. However, the economy of oxyfuel combustion is dependent on the cost of oxygen so that the availability of low cost oxygen is critical to the application economy.

COMPARISON OF THE COMBUSTION EFFICIENCY OF ADVANCED COMBUSTION TECHNNOLOGIES

Flameless Oxy-Fuel burner (REBOX –W, Linde AG), HiTAC burner (REGEMAT 350 FLOX burner regenerative type that heats combustion air to 950°C) with oxygen enrichment (HiTAC-OE) and Cold Air burner without oxygen enrichment (rearranged HiTAC burner), were evaluated and compared [17]. Available heat as a function of exhaust gas temperature for propane combustion at 2% O_2 in exhaust gases is presented in Fig. 5.

From Fig. 5 it can be seen, that the available heat for the oxy-fuel technology is higher than that for air-fuel technology for the same temperature of exhaust. The difference in available heat increases as the exhaust temperature increases. The available heat for oxygen enhanced combustion is in the middle of these two technologies. The available heat is equal or almost greater at the regenerative burners in relation to the oxy-fuel burners because of the lower temperature of exhaust gases (practically ≈ 200°C at the regenerative burners and ≈ 1000°C at the oxy-fuel burners) and the effect achieved by the high temperature air preheating. Consequently, there is no justification to apply oxy-fuel combustion, because the oxygen is additional cost.

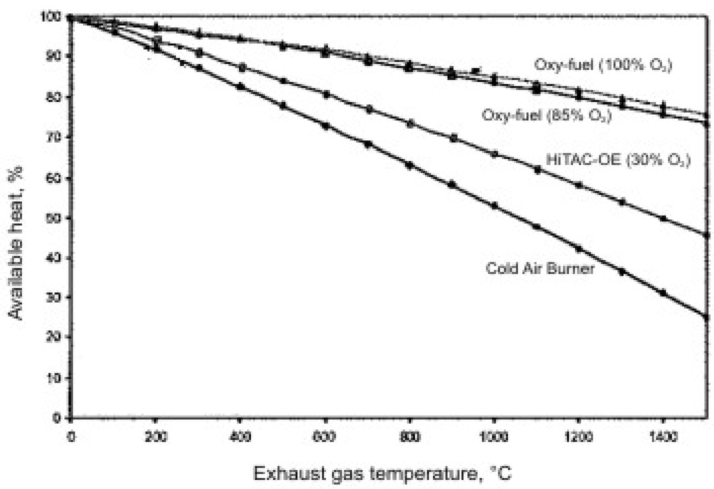

Figure 5. Available heat vs. exhaust gas temperature for propane combustion at 2% O_2 in exhaust gases [17]

The others limits of oxy-combustion are: maintenance of combustion system is delicate (must be executed by specialized technicians) and with very short steps, due to really high flame temperature reached, refractory life is shorten than at combustion air combustion, temperature uniformity on reheating load is not improved, production can be increased to increase set-point temperatures but it is not necessary in the case of the furnace under consideration.

Also, there is no need for oxygen enriched air at the regenerative burners. As it can be seen from Fig.3, the available heat for HiTAC burner without oxygen enrichment is about 91%, and with oxygen enrichment to 30% (vol) is 94% at the same exhaust gas temperature of 200°C and 80% extracted flue gases through the burner regenerator. It is evident that the slight difference in the available heats cannot justify the cost of oxygen. Application of oxygen would be justified only if it would be necessary to implement a reduction in CO_2 emission.

CONCLUSION

One of the main reasons for this poorer energy utilization is inadequate organized combustion process. With regard to this fact, the furnaces in the industry work mainly with low energy efficiency. This paper points to the ways of improving the energy utilization in open-flame furnaces considering how various operating factors and combustion technologies can affect the thermal performance of industrial furnaces.

The oxy-fuel combustion is less efficient than the air-fuel combustion considering the available heats and non economic costs of oxygen producing. Accordingly, in the absence of any need to reduce CO_2 emissions the oxy-combustion is not competitive.

However, oxy-fuel is a viable alternative to removing CO_2 from the flue gas in a conventional air-fired fossil fuel plant. Namely, the big advantage of oxy-combustion is reduction of the mass and volume of the flue gases for approximately 75%.

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PRODUCTION OF BIOETHANOL AS A BIOFUEL FROM COTTON FABRICS BY SIMULTANEOUS ENZYMATIC SACCHARIFICATION AND FERMENTATION

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ABSTRACT

Bioethanol, as one of the dominating biofuels today, can be produced from different renewable biomass resources. It can also be produced from cotton-based materials by enzymatic hydrolysis and ethanol fermentation. The cellulosic part of cotton-based textile can be used for the production of bioethanol, and there is no lignin or hemicelluloses to negatively affect the hydrolysis process.

Desized and bleached cotton fabric (168 g/m^2) was used as a substrate in this study. Celluclast® 1.5L, a cellulase from *Trichoderma reesei* was used for enzymatic hydrolysis of cotton fabrics and yeast *Saccharomyces cerevisiae* var. *ellipsoideus* was used for the ethanol fermentation. We investigated the effect of substrate concentrations on the enzymatic hydrolysis and optimal initial substrate concentration of 32 g/L and duration of enzymatic hydrolysis of 5 days were determined. Also, the kinetics of fermentation process was assessed with different inoculum cocnetrations (2, 5 and 7% v/v). An optimal ethanol concentration of 0.29% (w/w), utilized glucose of 94.83%, ethanol yield of 0.48 g/g, a percentage of theoretical ethanol yield of 94.77% were achieved after 18h of fermentation with inoculum concentration of 5% (v/v).

Key words: bioethanol, cotton, saccharification, fermentation, yeast.

INTRODUCTION

Non-renewable energy sources, such as fossil fuels, are limited and have a considerable negative environment impact. Therefore, bioenergy resources must substitute fossil fuels in near future, which is an obligation of today society according to the sustainable development strategy. Bioethanol, as an alternative bioenergy resource, is renewable and environmentally clean biofuel. Bioethanol produced from renewable biomass is one of the dominating biofuels today [1-4].

Bioethanol can be produced from sugar, starch or lignocellulosic materials [5]. It can also be produced from cotton-based materials by enzymatic hydrolysis followed by ethanol fermentation. In cotton, there is no lignin or hemicelluloses, therefore, the cellulosic part of cotton-based textile can be used for the production of bioethanol. This also represents the opportunity to utilize waste cotton fabrics left after sewing and cutting in the textile industry.

The typical process of enzymatic hydrolysis of cellulosic material utilizes cellulase as a biocatalyst for conversion of cellulose to glucose. Common cellulases to perform this process include fungi such as: *Fusarium solani, Clostridium thermocellum, Trichoderma reesei*, and *T. viride* [6]. *Saccharomyces* strains are well-known ethanol-producing microorganisms. In this study yeast *S. cerevisiae* var. *ellipsoideus* was used. Typically, yeast *S. cerevisiae* is used for bioethanol production, but *S. cerevisiae* var. *ellipsoideus* was found to be the best for the fermentation among tested yeasts (*S. cerevisiae, S. carlsbergensis and Schizosaccharomyces pombe)* as presented in our previous study [7]. The current world bioethanol research is driven by the need to reduce the costs of production. Improvement in feedstock pretreatment, shortening of fermentation time, lowering the enzyme dosages, improving the overall cellulose hydrolysis could be the basis of cutting down the production costs.

The aim of this study was to investigate the enzymatic hydrolysis of cotton fabric and ethanol fermentation of the obtained hydrolyzates by *S. cerevisiae* var. *ellipsoideus* yeast in a batch system. The effect of initial substrate on the enzymatic hydrolysis was studied. The kinetics of ethanol fermentation and the parameters such as ethanol concentration, ethanol yield, percentage of the theoretical yield of ethanol and volumetric productivity were assessed.

MATERIALS AND METHODS

Raw material

Desized and bleached cotton fabric (168 g/m^2) was used as a substrate in this study. In order to eliminate the surface impurities before hydrolysis, cotton fabric was cleaned in a manner described before [8]. The content of cellulose as a main substrate was 96% (w/w).

Enzymes and microorganism

Celluclast® 1.5L, a cellulase from *Trichoderma reesei* was used for enzymatic hydrolysis of cotton fabrics. The enzyme activity was 700 EGU/g (endoglucanase unit EGU is defined as the amount of enzyme which releases 1.0 μmol of glucose units per min at 50 °C and pH 4.8). The enzyme was a gift from Novozymes, Denmark.

Saccharomyces cerevisiae var. *ellipsoideus* was used for the fermentation of hydrolyzed materials. The culture originated from the collection of Department of Biochemical Engineering and Biotechnology, Faculty of Technology and Metallurgy, Belgrade (BIB-TMFB), and was maintained on a malt agar slant. The agar slant consisted of malt extract (3 g/l), yeast extract (3 g/l), peptone (5 g/l), agar (20 g/l) and distilled water (up to 1 l). Before use as an inoculum for the fermentation, the culture was aerobically propagated in 500 ml flasks in a shaking bath at 30 ºC for 48 h and then separated by centrifugation. The liquid media consisted of yeast extract (3 g/l), peptone (3.5 g/l), KH_2PO_4 (2.0 g/l), $MgSO_4 \cdot 7H_2O$ (1.0 g/l), $(NH_4)_2SO_4$ (1.0 g/l), glucose (10 g/l) and distilled water.

Enzymatic hydrolysis and ethanol fermentation

Different amounts of cotton fabric (3, 5 and 10 g), cut in sizes of around 0.5 x 0.5 cm^2, was mixed with 150 mL of acetate buffer (pH=5.0) containing constant concentration of Celluclast® 1.5L in order to investigate the effect of substrate concentration. Thus, three different cellulose concentrations: 19.2, 32 and 64 g/l were tested. The concentration of the cellulase solution was 6 ml of enzyme per liter of solution, which correspond to cellulase concentration of 18% (v/w of cotton fabric). The enzymatic hydrolysis was carried out at 50 ºC for 8 days in flasks in thermostated water bath with shaking (100 rpm). The glucose yield of enzymatic hydrolysis is defined as (grams of glucose released)/(grams of initial cellulose). The percentage of theoretical glucose yield is defined as (grams of glucose released)/(grams of initial cellulose×1.111) and presented as hydrolysis efficiency. The dehydration factor (1.111) was used to convert the cellulose chains to glucose monomers, thus grams of cellulose×1.111 represents theoretical glucose concentration.

Hydrolyzates obtained by hydrolysis of the cotton fabrics were filtered and subjected to ethanol fermentation by yeast *Saccharomyces cerevisiae* var. *ellipsoideus* under anaerobic conditions (pH 5.0; 30 ºC; mixing rate 100 rpm) for 30 h. In order to investigate the effect of inoculum concentration, three different concentrations: 2, 5 and 7% (v/v) were tested, which corresponds to initial viable cell number of $\sim 0.6\times10^6$,$\sim 1.5\times10^6$ and 2.5×10^6 CFU/ml, respectively. The salts required for the yeast growth were added to the mashes: KH_2PO_4 (4.0 g/l), $MgSO_4\cdot 7H_2O$ (0.4 g/l) and $(NH_4)_2SO_4$ (2.0 g/l). The fermentation was performed in flasks in a thermostated water bath with shaking. It was considered that the pasteurization of the substrate achieved during the enzymatic hydrolysis was sufficient thermal treatment, and thus no additional sterilization prior to fermentation was performed. During the fermentation, the consumption of the substrate glucose, the formation of ethanol and the number of viable yeast cells were followed. The ethanol yield is defined as (grams of produced ethanol/grams of glucose), the percentage of theoretical ethanol yield as (grams of produced ethanol/grams of glucose produced after hydrolysis×0.511) and volumetric productivity as (grams of produced ethanol in 1l/ time of fermentation). The theoretical ethanol production is 51.1 g of ethanol generated per 100 g of glucose in the biochemical conversion of the sugar. Utilized glucose (%) was calculated as the ratio of the consumed mass of glucose to initial mass of glucose.

Analytical methods

The cellulose content was determined by using the method as described by Updegraff [9]. During the ethanol fermentation, the content of reducing sugars, calculated as glucose, was determined by 3.5-dinitrosalicylic acid [10]. A standard curve was drawn by measuring the absorbance of known concentrations of glucose solutions at 505 nm. The ethanol concentration was determined based on the density of alcohol distillate at 20 ºC and expressed in weight % (w/w) [11]. Indirect counting method i.e. pour plate technique was used to determine the number of viable yeast cells. Serial dilutions of the samples were performed, and after the incubation time at 30 ºC, colonies grown in Petri dishes were used to count the number of viable cells. The experiments were done in triplicates. The results are expressed as means ± standard deviations.

RESULTS AND DISCUSSION

One of the important factors that affect the degree of enzymatic hydrolysis of cellulose from the cotton fabric is the substrate concentration. The first set of experiments was conducted in order to determine the optimal concentration of cellulose. We tested three different initial substrate concentrations: 19.2, 32 and 64 g/l L while the enzyme concentration was constant at 6 ml/l. The results of the obtained glucose concentrations and other significant hydrolysis parameters are presented in Table 1.

As shown in Table 1, a maximum glucose concentration of 6.00 g/l, glucose yield of 0.19 g/g and hydrolysis efficiency of 16.85% were achieved during hydrolysis with substrate concentration of 32 g/L at 5th day of hydrolysis. In this case, a product inhibition was noticed after 5 days of hydrolysis due to enzyme inhibition by glucose accumulation, since the final glucose concentration of 5.73 g/L was lower than the maximum one.

Muratov and Kim [12] used similar substrate concentration of 20 g/l, cellulase from *T. reesei* with concentration of 6 g/l and the same process conditions, but obtained higher glucose concentrations (around 11 g/l) after 48 h of hydrolysis, probably due to different type of substrate called „Omad" cotton fibers. Also, Jeihanipour et al. [13] reported that enzymatic hydrolysis of the untreated cotton fibers resulted in rather low theoretical glucose yield of 11% after 24 h. The results concerning the substrate inhibition in the work of Shen and Agblevor [14] were in good agreement with ours, since the glucose and ethanol yields were much lower at substrate concentration of 60 g/l than those at substrate concentration of 40 g/l (with cellulase concentration of 4 g/l).

Table 1. Values of the significant parameters obtained during enzymatic hydrolysis of cotton fabrics. Enzyme Celluclast® 1.5L concentration was 6 ml/l.

Parameter	Initial cellulose concentration, g/l					
	19.2		32		64	
Hydrolysis time, days	5	8	5	8	5	8
Glucose concentration, g/l	4.35±0.09	5.12±0.69	6.00±0.92	5.73±0.61	5.35±0.82	5.41±0.39
Glucose yield, g/g	0.22±0.004	0.27±0.036	0.19±0.29	0.18±0.19	0.083±0.013	0.084±0.006
Hydrolysis efficiency, %	20.38±0.42	24.00±0.32	16.85±1.59	16.12±1.71	7.52±1.15	7.61±0.59

Further experiments were conducted in order to investigate the bioethanol production from hydrolyzed cotton fabrics. Fig. 1 presents the time course of ethanol production and glucose consumption in the fermentation process with three different inoculum concentrations: 2, 5 and 7% (v/v).

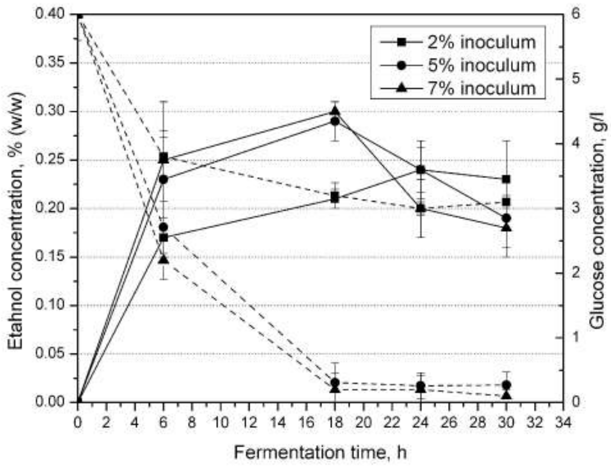

Figure 1. Time course of glucose consumption and ethanol production in the fermentation of hydrolyzed cotton fabric by S. cerevisiae var. ellipsoideus with various inoculum concentrations

As shown in Fig. 1, maximum ethanol concentration of 0.30% (w/w) was achieved after 18 h of fermentation with inoculum concentration of 7% (v/v). At the same time, rather similar ethanol concentration of 0.29% (w/w) was obtained with inoculum concentration of 5% (v/v). Therefore, by increasing the inoculum concentration from 5 to 7% (v/v) no significant increase in ethanol concentrations was realized. For this reason and from the economic viewpoint, the inoculum concentration of 5% (v/v) was chosen as optimal.

After 18 h of the fermentation, a decline of the ethanol concentration could be noticed because of the exhaustion of the released glucose and the transition of the yeast metabolism towards utilization of ethanol as a carbon source. The glucose consumption was in accordance with the results of ethanol concentration since the glucose was consumed as a carbon source by the yeast. The glucose utilization was almost completed within 18 h of fermentation time, since the value of utilized glucose was 94.77% at this point of fermentation with inoculum concentration of 5% (v/v) (Table 2).

Jeihanipour et al. [13] obtained percentage of theoretical ethanol yield of 17.84% (based on the initial cellulose) from untreated cotton fibers after 24 h of fermentation by *S. cerevisiae*, which is similar to our result of the percentage of theoretical ethanol yield of 16.84%. (based on the initial cellulose). Also, Baig and Dharmadhikari [15] obtained maximal ethanol concentration of 0.956% (w/v), ethanol yield 0.191 g/g and utilized sugar of 97.81% after 48h of fermentation of cotton stalks using co-culture of *S. cerevisiae* and *Pachysolen tannophilus*.

Table 2. summarises the significant parameters of ethanol fermentation of cotton fabrics by *S. cerevisiae* var. *ellipsoideus* obtained at optimal conditions.

Table 2. The values of significant parameters of the fermentation of cotton fabric by S. cerevisiae var. ellipsoideus obtained under optimised conditions.

Optimal conditions	Ethanol concentration, % (w/w)	Ethanol yield, g ethanol/g glucose	Percentage of the theoretical ethanol yield, %	Volumetric productivity, g/l·h	Utilized glucose, %	Number of viable cells, CFU/ml
Inoculum concentration 5% (v/v), 18 h of fermentation	0.29	0.48	94.77	2.21	94.83	$1.41 \cdot 10^7$

CONCLUSIONS

The kinetics and effect of different process parameters (initial cellulose concentration and inoculum concentration) on hydrolysis and fermentation of cotton fabrics by *S. cerevisiae* var. *ellipsoideus* was studied in this paper. An initial cellulose concentration of 32 g/l, hydrolysis time of 5 days, inoculum concentration of 5% (v/v) and fermentatiom time of 18 h were selected as optimal parameters for ethanol production from cotton fabrics.

The results obtained in this study qualify the cotton fabric as a good substrate for ethanol production. Additional benefits of the utilization of this raw material can be accomplished in a simultaneous saccharification and fermentation process mode (SSF) and with adequate pretreatments of cotton fabrics.

Acknowledgments

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THERMAL IMAGING OF PUBLIC BUILDINGS

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ABSTRACT

Based on the struggle for saving energy and improve the sustainability and the economy of the cross-border region, Vršac in Serbia and Deta in Romania, the efficiency of street lighting were highlighted as one of the most prosperous options. The ambitious goals resulted in a plan for replacement of old bulbs containing mercury with new high performance street lights. Within the IPA project named “Green Lights for Safety and Sustainability of Roads” a thermal imaging camera for the energy saving control of public buildings was purchased, also. The result obtained using this camera on two schools in Vršac is presented in this paper.

Key words: Saving energy, Thermal imaging camera.

INTRODUCTION

The increased pressure for sustainable development, green and eco cities and reducing maintenance budgets are now pushing cities to find solutions to reduce their spending on energy for public buildings. For reducing energy consumption, maintaining costs and improving human comfort, the object of study was an energy audit of 28 public buildings in Municipality of Vršac. This is one of the activities within the project “Green Lights for Safety and Sustainability of Roads” which is implemented within the Cross-Border Programme between Romania and Serbia for the period 2007-2013. It lays the foundations for using EU funds under the cross-border component of the IPA Regulation, to support cross-border cooperation on the Romanian-Serbian border[1].

MATERIAL AND METHODS

A thermal imaging camera records the intensity of radiation in the infrared part of the electromagnetic spectrum and converts it to a visible image. Infrared radiation lies between the visible and microwave portions of the electromagnetic spectrum. The primary source of infrared radiation is heat or thermal radiation. Any object that has a temperature above absolute zero (-273.15 degrees Celsius or 0 Kelvin) emits radiation in the infrared region. In this survey we use FLIR B335 infrared camera and FLIR Tools software suite designed to create inspection reports.

RESULTS AND DISCUSSION

Similarly to conventional digital cameras, infrared or thermal cameras utilize this radiation and produce thermal images or thermographs. Thus, according to the black body radiation law, the environment can be observed even without visible light, in the process known as "thermovision". Recording of this type of emitted light is performed via thermal imaging equipment, which enables efficient surveillance at night, during reduced daylight visibility, as well as during unfavourable weather conditions[2]. Infrared energy coming from an object is focused by the optics onto an infrared detector. The detector sends the information to sensor electronic for image processing. The electronics translate the data coming from the detector into an image that can be viewed in the view finder on a LCD screen. Infrared thermography is the art of transforming an infrared image into a radiometric one, which allows temperature values to be read from the image. So every pixel in the radiometric image is in fact a temperature measurement[3].

A building diagnostics inspection with a thermal imaging camera can help to: visualize energy losses, detect missing or defective insulation, source air leaks, find moisture in insulation, in roofs and walls, both in the internal and the external structure, detect mould and badly insulated areas, locate water infiltration in flat roofs, detect breaches in hot-water pipes, detect construction failures, find faults in supply lines and district heating and detect electrical faults.

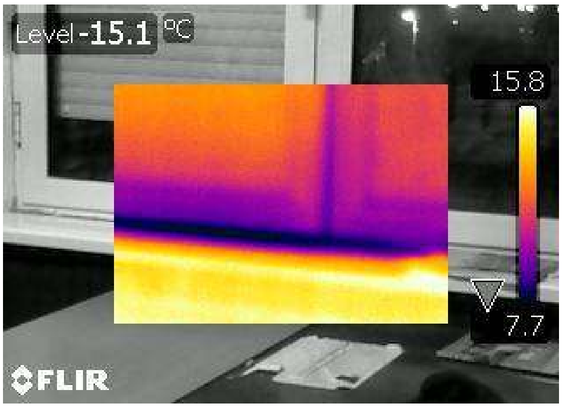

Figure 1. Thermal image inside the school building (FLIR Tools ©)

Before imaging it's necessary to set minimum and maximum of the temperature, emissivity and relative humidity. For precise measuring it's needed to measure the temperature and humidity inside and outside the building and emissivity of construction materials. Measurements should be performed in winter period with outside temperature less than 5°C. Because of heating by sun, better results can be achieved if images be taken by night with large temperature difference inside and outside the building.

After equipment is supplied by Contracting Authority we were provide general inspection services of thermal efficiency of 28 public objects: schools, kindergartens, hospital, town hall, museum, health centre, town library, theatre…

Each image has the basic information that can be seen on the screen: the scale of the upper and lower temperature presented in the colours defined in the left corner or the upper and lower temperature. On image it's also possible to define measuring spot with cross or with rectangle area. Camera detects the highest and the lowest temperature and values of walls humidity.

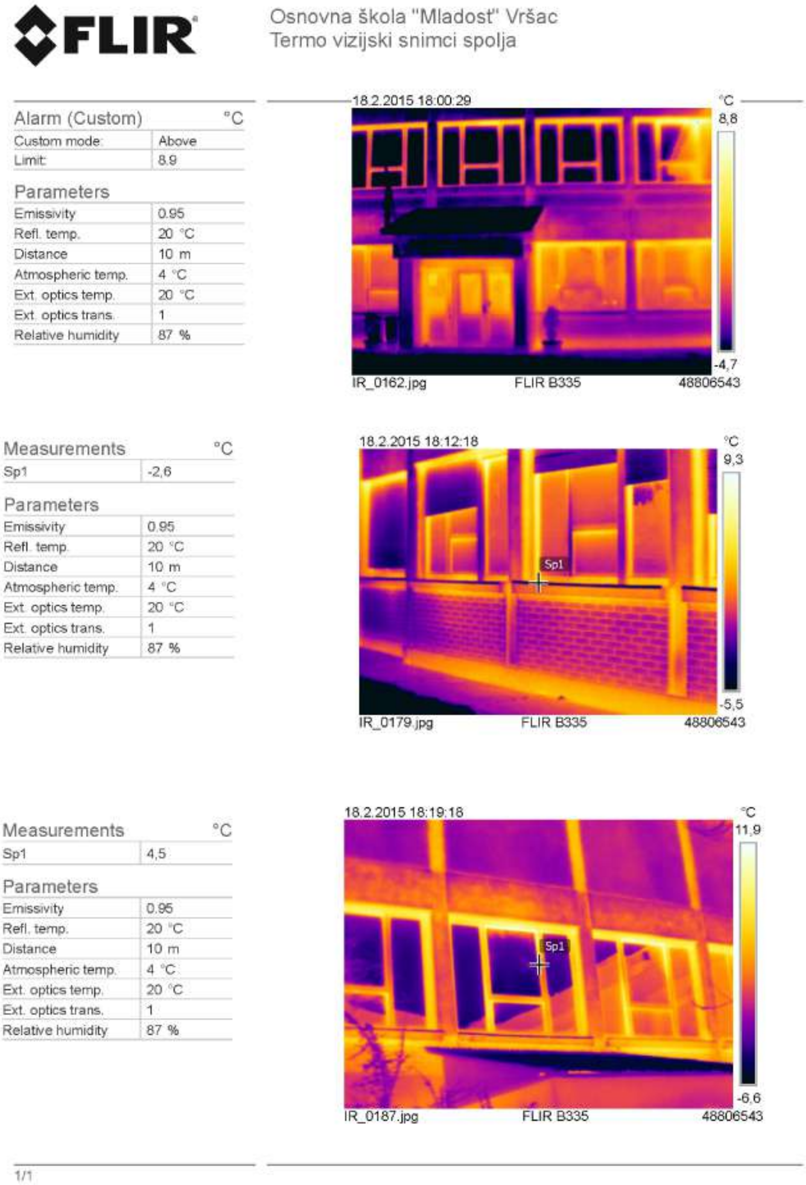

Figure 2. Outside inspection report of school building (FLIR Tools ©)

After field work images were processing by FLIR Tools software, additional information such as electricity, water and gas consumption was gathered for the further analysis. With thermal imaging we identified and locate poor insulation, air and heat leakage, water damages due to leaks or condensation or mould problem for all 28 public buildings in Vršac.

CONCLUSION

Thermal imagers measure radiated thermal energy from which a temperature is derived based on the amount of energy detected. This is an initial step towards analysing the energy efficiency of a building. Thermal images provide a means to capture visible proof before and after repairs have been made. Having concrete evidence reduces uncertainty during reconstructions of buildings and decreases energy loss. This study of the building diagnostics inspection with a thermal imaging camera will be used to improve energy efficiency of public buildings in Vršac through applications of best available techniques of insulation.

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POSSIBILITIES FOR THE IMPROVEMENT OF THERMAL PLANTS EFFICIENCY

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ABSTRACT

This paper presents the review of the heating plant's status in Serbia. Also, heating system development is given in the example of heating plant in Bor. The basic principles and sustainable use of natural resources are described. Measures for increasing energy efficiency in thermal plants are listed, having in mind distribution systems, heat substations, buildings and households.

Key words: thermal plant, efficiency, heating system.

INTRODUCTION

Energy efficiency represents the sum of planned and implemented measures in order to use less energy (i.e. energy resources) to perform the same operation or function (heating or, lighting, production of various products, etc.) [1]. Energy efficiency should not be treated as energy saving because saving always involves some sort of waiver, while efficient energy use never distorts the conditions of work and life. It is important to emphasize that the improved efficiency of energy use aims to reduce the consumption of the same amount of product (service), which results in a proportional cash savings [2, 3].

In practice, there are a number of plants with low energy efficiency. This implies that energy consumption is unnecessarily high which causes the high product price and, therefore, production is becoming untenable. A reliable and effective operation of city heating systems is very important for the stability of the energy systems. The mismatch of production and consumption of energy in the winter is large, especially when outside temperatures are low, and any disruption in the work of city heating systems refers citizens to heat up the apartments with expensive electricity. Coal reserves, which are the basis of over 50% of electricity generation, are quite limited, so it is essential that electricity consumption is a rational and responsible, both by individuals and by society as a whole [4, 5].

Basic principles and sustainable use of natural resources

In the context of natural resources, it is understood that the use of natural resources in a sustainable way means to ensure their availability in the future and reduce the impact of their use on the environment. Sustainable use and management of natural resources, renewable and non-renewable, requires the use following key principles:

- the use of renewable resources should not exceed the rate of their renewal (regeneration);
- application non-renewable resources should not exceed the rate at which substitutes for these resources are developed;
- the application should be limited to the extent to which the physical or functional equivalent can be replaced by renewable resources or where consumption can be compensated by increasing the productivity of renewable or non-renewable resources;
- the quantity of substances released into the environment must not exceed the capacity of transformation of pollutants harmless or less harmful to the living organisms [6].

HEATING SYSTEMS DEVELOPMENT - EXAMPLE OF HEAT PLANT IN BOR

Until the passage of the transmission line from Djerdap 1 (1971), the main activity of thermal power plant was the production of electricity with seven steam boilers and four steam turbines for the needs of RTB Bor facilities and a small number of apartments in the region. After commissioning of Djerdap hydroelectric power plant, transmission lines from "Kostolac" became a reserve, which made supplying industry with electricity safer and cheaper. Then the idea came upon that the production capacity of thermal plants can be used for the production of thermal energy for technological processes in RTB Bor production units and heating business premises. Instead in the turbine, the steam was directed to the newly built thermal station and hot water pipelines.

The construction of a new hot water pipeline (2 x 150 mm), towards the newly built Cultural Centre in 1973, toplification of Bor began. From 1.575 apartments that were warmed from local boiler, on newly built hot water pipeline 174 apartments were connected with total area of 9.246 m^2 and 7.398 m^2 of office space which was 16,27 % of the total area of which was heated from local boiler stations. During this period, the available thermal power from power plant boilers and the smelter was 80 + 25 MW. The next step was the development of a project to increase the number of users of such low-cost ways of heating, taking into account the fact that the smelter steam in the summer can still be used to produce electricity. The construction of new thermal stations TP-2 and the main line "A" (400 mm) from the plant to 4th Local Community[1] in 1977, began the first phase of district heating. After connecting buildings from the "B" group in the 5th Local Community in 1980, already 58 MW of power has been connected to the city

[1] Local communities refer to groups of streets in certain areas of Bor, which are further devided into kilometres.

heating system and 48 MW on heating system of RTB. As a first result, 29 local boiler stations which worked on fuel oil and coal were turned off, which gave a significant contribution to the improvement of air quality in an environmentally polluted environment.

In order to monitor the planned development of Bor, in 1981 a study was conducted which envisaged the construction of new thermal plant with two hot water boilers (58 MW), with accompanying thermal station and hot water pipelines (600 mm, 450 mm, 350/300 mm, etc.) as well as links to the existing hot water pipelines. The new thermal plant had been constructed from 1982 to 1987 and in that time, district heating was burdened with 86 MW of power. Upon completion and commissioning of the new plant, the conditions were created to stop working steam boiler 2, 3 and 4, which date from 1932, in which fine coal dust was incinerated, with no flue gas purification system and with low chimneys. These were also the largest emitters of ash in Bor. During 1987 and 1988 to the district heating system were connected Local Communities "Centar" and "Sever," the individual settlement GHI, sports hall, medical center and newly built facilities in the New City Centre (NGC), so connected consumption reached about 120 MW. During 1989 following attached objects were attached to new heating system: "Metalurg" Industrial Zone at 7th km, part of local community "Staro Selište", Sports Centre with indoor swimming pool and new buildings in the area New City Centre (NGC), with achieved 155 MW.

Very rapid expansion of the city district heating with more and more problems in the work of old boilers, impose the need to expand the plant, mostly in production capacity, which would create real conditions for a complete heating city. "The study energy development until 2010" done in 1991, was the basis for a contract to build another water boiler of 58 MW, which will use heavy oil as fuel and natural gas in future perspective perspective, which would completely overcome the existing problems and create conditions for reliable and efficient operation of heating plants in all conditions. Despite the problems with the new boiler, by the end of 1999, substations TP-5 ("Staro seliste"), TP-6 ("Novo seliste") and three substations in local community "Sloga" were put into operation.

Public utility company "Toplana" Bor, founded in 2002, seceding from the RTB Bor. The company is exclusively engaged in the production and distribution of heat and hot water production, as well as providing services to third parties in the maintenance of thermal installations. Bor is town with, in percentage terms, the largest number of households connected to the district heating system. Of the 14.200 households heating has 11.600 households. The total heating area of housing units is 682.178 m^2, making a total of 95 % of the territory of the city and other business units and institutions with an area 125.140 m^2. Boiler power capacity is 174 MW. Age of coal-fired boilers is 24, and heavy fuel boilers - gas 17 years. The entire distribution network is about 200 km long. Distribution network consists of a hot water pipeline length of 74 km and 150 km length hot water pipeline, so the length of the entire distribution network is about 224 km (Figure 1).[7]

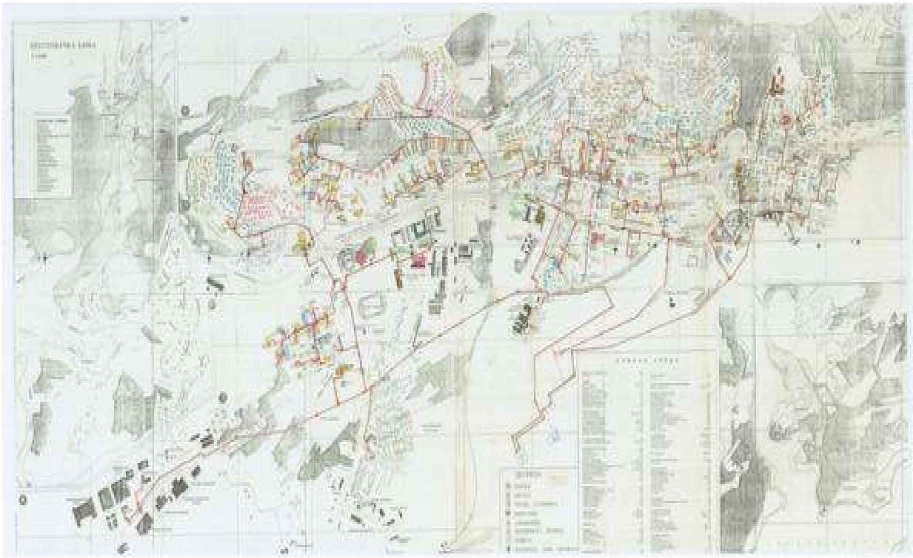

Figure 1. Map of the heating system in Bor

„Toplana" Bor consists of production part, distribution part and the boiler room in Banjsko Polje. The heating plant in 2012 produced 202.646 MWh of thermal energy. The delivered energy was 161.237 MWh. For generated electricity from power plants 42.865 tons of coal was spent. In Banjsko Polje was spent 870.500 t of coal. For combustion in boilers were used high-quality brown coal and dried lignite from Kolubara.

MEASURES TO INCREASE ENERGY EFFICIENCY IN THERMAL PLANTS

National level data indicate that average boiler efficiency is 0,85. In the present circumstances, it is necessary to reduce costs in some extent, while maintaining production. Thermal plant Bor has been part of the project KfW4 from 2012, that will enable multiple improvements in terms of the plant production and therefore contribute to a better energy efficiency. The program included several sub-projects, which consisted of [8]:

- complete repair of hot water boiler,
- construction of new plant for the chemical preparation of water (in order to improve the quality of decarbonized water, which prevents the build-up of deposits on pipes and oxygen corrosion occurrence),
- replacing the pipes into five areas in the city (total length of the route is about one kilometer with frequent breakthroughs during heating season),
- reconstruction of 80 heating substations with built-in automation, installation of SCADA monitoring systems in more than 20 heat substations.

As for the situation in other Serbian heating plants and the possibilities for improving energy efficiency, following technological procedures are also possible:

- installation of devices for use of combustion gases, waste heat, the boiler efficiency can significantly be increased up to 20%
- regular control of the burners by the specialized service,
- preparation of fuels in terms of water content, purity and temperature of combustion in boilers using heavy fuel oil,
- daily inspection of softened water which is fed into boilers and distribution system
- replacing motors with higher energy efficiency class EF-1 and EF-2,
- repair of boiler insulation if heat losses are obvious.

Distribution network

Water losses in the distribution network represent a serious problem, often causing heating disruptions. Losses are tolerated to a maximum of 10 %, while the losses of hot water can be up to 3 – 4 % of the total exchange volume of water in the system for one heating season. Damage caused by heating interruption and costs for water creates additional costs. Production and distribution have to be balanced, coordinated and controlled on a daily basis in terms of standards, consumption of prescribed water flow and temperature. High-quality and long-lasting thermal insulation is an essential prerequisite for reducing heat losses in the heating system.

The average age of hot water pipelines in Serbia is about 20 years, and some sections are older than 30 years, only 49 % are so-called pre-insulated hot water pipes, with heat losses average about 17 % . In thermal plant in Bor, average age of pipelines is between 25 to 35 years, with notable thermal and hot water losses in the network. Building new hot water pipelines, will lead to reducing the damage and losses due to timely prevent damage on hot water pipeline without any major investment, but with much more commitment and responsibility. All the activities should include:

- upon termination the heating season, it is necessary to carry out the pressure test of contentious system routes and, in accordance with the situation, make the necessary repairs. This will provide substantial savings, because there will be fewer interruptions in the supply of thermal energy in the next heating season,
- partial reparation the insulation, especially in places where the problems were observed during the heating,
- the network control executed with respect to a prescribed flow rate and water temperature,
- daily monitoring the water losses through the network and intervene as soon as possible in order to have them removed,
- obtaining detection devices for accidents in hot water pipeline for faster elimination of hot water losses on a daily basis,
- repairing the sectional valves on worn sections of the existing hot water pipeline or install a new one,
- it is necessary to exert strict adherence to the prescribed flow in heating system and prescribed temperature diagram, in the event where is no automatic regulation,

Savings in maintenance, energy consumption and reducing heat losses due to imbalances networks can be achieved by installing circulation pumps with the changed number of revolutions (automatic speed control).

Heat substations, buildings and households

Submission of heat, with hot water and hot water systems, is controlled via the internal heating substations to home thermal installations. The average age of the heating substations is 13,6 years; many of heating plants in Serbia carried out the substation reconstruction. Although some reconstructions were partially worked out, the most difficult situation is in Zrenjanin, Pirot, Negotin and Bor. About 11% of the substations are older than 20 years.

When talking about the degree of automation of the substations, about 63 % are with remote control, 12 % with local management via control units, with partial control about 15 % and about 10 % with manual control. Considering these parameters, it can be said that the heat substations are in much better condition than the other elements of district heating systems, which is good because in this way the basic prerequisites for quality control, distribution and heat metering are created. On the other hand, home heat installations in old buildings are in very poor condition. Significant problems make the regulating valves on rising lines which have become obsolete and unreliable for regulating or closing during interventions in the flats. It is desirable to replace them, but for these works means of the tenants are necessary. Almost the same situation is with radiator valves in the flats.

Reducing unjustified thermal energy consumption is one of the most important activities in order to reduce unnecessary costs of energy, which can be achieved through implementation of a number of daily and long-term activities:

- reconstruction of obsolete substations or good regulation of existing,
- repair and regulation of home installations and devices,
- reduction of heat loss in buildings, and
- measuring individual consumption of heating energy.

The prescribed temperature in rooms that are heated should be 20 °C +/- 1 ° C, with the exception of hospitals and special institutions. If the room temperature is lower than required, it creates dissatisfaction among users. If, on the contrary, is higher than required, it increases the consumption of energy and creates unnecessary costs. Reducing unjustified heat consumption in buildings is one of the basic conditions for the reduction of total specific energy, and therefore to increase the overall energy efficiency.

Although the station is in the best condition of all heat production units, there are still a lot of work and investment, because about 38 % of the substations should be reconstructed and introduce remote control and automatic control and incorporate the counters for consumption. For the facilities that had been built long ago, home heat installation are quite in poor condition, with parts of non-insulated pipelines, and many faulty valves in horizontal distribution and risers, faulty radiator valves and dirty radiators.

CONCLUSION

In practice, there are a number of plants with low energy efficiency. This implies that energy consumption is unnecessarily high which causes the high product price and therefore production is becoming untenable. A reliable and effective operation of city heating systems is very important for the stability of the energy systems. The mismatch of production and consumption of energy in the winter is large, especially when outside temperatures are low, and any disruption in the work of city heating systems refers citizens to heat up the apartments with expensive electricity.

The permanent task of the whole society should be directed to rational and efficient application of energy and use of existing renewable energy sources in order to reduce import dependence and the implementation of international commitments in terms of environmental protection and global warming. It is important to reduce the cost of energy per unit of GDP, which are now significantly higher than those in developed European countries. The state should play a leading role in the implementation of measures for increasing the energy efficiency, in terms of increasing energy efficiency in buildings, renewable energy sources, education and training of managers for rational energy management, and others. On the other hand, the heating should be organizationally, technically and financially stabilized, to have good cooperation with the local government, educate their staff and users of heating, and to be carriers of the necessary programs and projects to increase the energy efficiency of remote systems in the cities.

Acknowledgement

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RENEWABLE ENERGY SOURCES AND SUSTAINABLE DEVELOPMENT IN TRANSITION COUNTRIES

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ABSTRACT

Current trends on global energy market point out the necessity of energy security and sustainable development. Transition economies are especially vulnerable due to unfavourable situation on energy market, since they already face numerous macroeconomic imbalances. The root of these imbalances is often related to sector of energy. In order to solve this problem, these economies are turning to energy from renewable sources, thus increasing the stability of domestic energy market. This paper shows analysis of trends in this area in transition economies, during entire transition period.

Key words: renewable energy sources, transition economies, sustainable development, regulations.

INTRODUCTION

Renewable energy sources may have a key role in achieving sustainable development, especially in transition countries. Economies in these countries are usually struggling with high energy consumption and high dependence on imported energy, which is a significant limitation for economic development of these countries. Energy gained from renewable sources provides following benefits:

1. Lower dependence on imported energy, which enables improvement in balance of payments and price stability (due to imported inflation);
2. Diversification of energy suppliers and increased competitiveness in this sector, which provides disestablishment of monopoly and lower energy prices;
3. Improved energy availability to rural areas, thus providing decrease of poverty and increase of standard;
4. Lower negative influence of energy production to the environment.

Despite of awareness on significance and advantages of energy from renewable sources, most of transition economies were unable to achieve respectful advance in this sector. There are several reasons for this situation, such as slow development of technology (due to lack of investments needed for research, development and construction of capacities for production of energy from renewable sources), inconsistent and incoherent strategy of sustainable development and its inefficient application. Some authors highlight the importance of defining of “transition sustainability policy” [1], which provides sustainable development through sustainable consumption, production and distribution of energy. Such policy enables uniting of previously opposed policies, such as energy usage, efficiency of utilization of resources, waste management, transport systems, technological innovations, social entrepreneurship and regulations in environment protection. Defining of such policy requires multidisciplinary approach, in order to overcome problems and limitations in its implementation and enable its wide social acceptance. We often have a situation where certain institutions included in policy implementation, from different levels of authority, have opposed interests. It is very difficult to create a policy that enables wide social consensus on necessity of such policy and providing public interest [2]. Beside certain institutions, there are other subjects in the process, such as foreign investors, energy producers and consumers, NGOs, professional associations etc, whose interests and roles in policy creation should also be taken in consideration.

Having that in mind, it is necessary to establish close cooperation and continuous information flow with stakeholders during creation and implementation of sustainability policy, in order to find optimal solutions. Transition from consumer society to sustainable society requires complete change of behavior, premises and values. Aside from interests of producers and consumers, there are other participants in the process whose perceptions and roles should also be taken in consideration. Through interactive communication with all of them, policy creators should be able to identify interest groups that are expected to resist, but also ones that should endorse the changes. After identification of these groups, policy creators should adjust measures and instruments of policy in early stages of its creation according to those acknowledgements.

ENERGY PRODUCTION AND CONSUMPTION IN TRANSITION COUNTRIES

Most of ex command economies found it difficult to refuse inheritance of planned economy. High energy consumption is one of the typical examples. Figure 1 shows energy consumption per capita of soma countries during transition period.

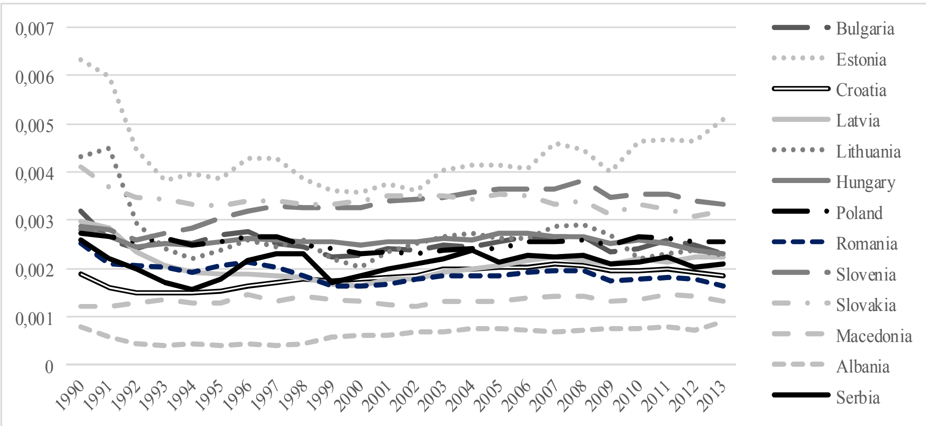

Figure 1. Energy consumption per capita in transition countries in a period between 1990 and 2013(**Source:** Eurostat)

Significant decrease of consumption is recorded in Estonia and Lithuania, two economies that were heavily influenced by Russia in the past, especially in energy supply. Those countries had the highest energy consumption at the beginning of observed period. Decrease of consumption was much milder in other countries (except Romania, with mild increase in this period). After starting years of transition period, Slovenia increased the consumption, while other countries had a relatively flat line. Albania had lowest consumption through entire observed period. Till 2000, energy consumption in Serbia varied significantly, but after 2000 it was relatively stable.
Variations are much more visible in energy production, as we can see in Figure 2.

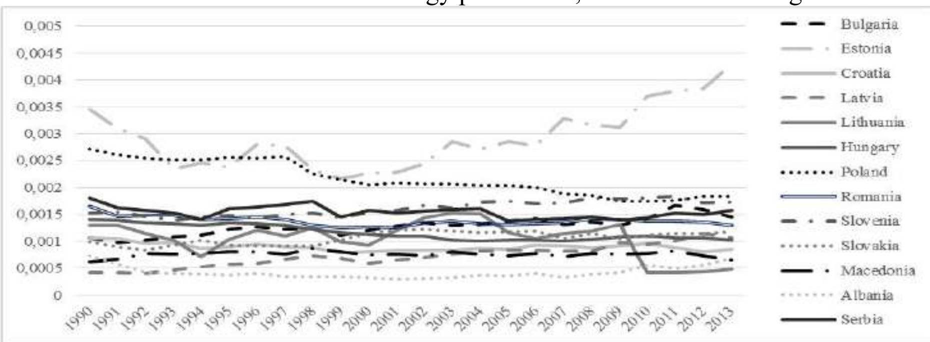

Figure 2. Primary energy production per capita flow in a period between 1990 and 2013 (**Source:** Eurostat)

After few ups and downs, after 2000 Estonia records strong increase of primary energy production, mostly due to actions focused to increase of production from renewable sources. Opposed to Estonia, Poland records constant decrease of primary energy production during entire observed period. Lithuanian production varies, while there are no significant variations recorded in other transition countries.

In order to take an insight of economy's ability to produce enough energy to match the demands of industry and population, we need to define relation between total energy consumption and primary energy production. Figure 3 shows the share of primary production in total consumption.

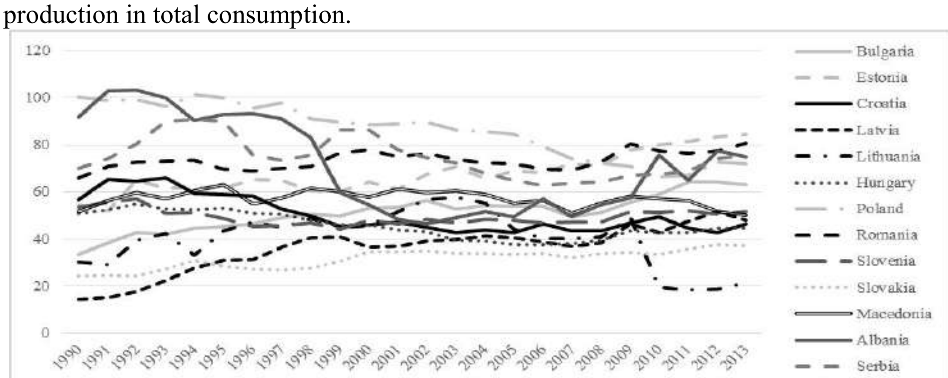

Figure 3. Share of primary energy production in gross energy consumption in a period between 1990 and 2013 (**Source:** Eurostat)

It is obvious from Figure 3 that differences between observed countries have been reduced during the observed period. Also, share of primary energy production records decrease in most of observed countries.

PRODUCTION AND CONSUMPTION OF ENERGY FROM RENEWABLE SOURCES IN TRANSITION COUNTRIES

Utilization of renewable energy sources in transition countries is unequal and insufficient [3]. Reasons are numerous, and most important are lack of investments needed for infrastructure and equipment, complicated regulations and lack of political will and understanding of authorities and society on importance of reorientation to renewable energy sources [4]. That is why, regardless on respectable development potential, share of energy production from renewable sources in total primary production is still low in most of transition countries, as it is shown in Figure 4.

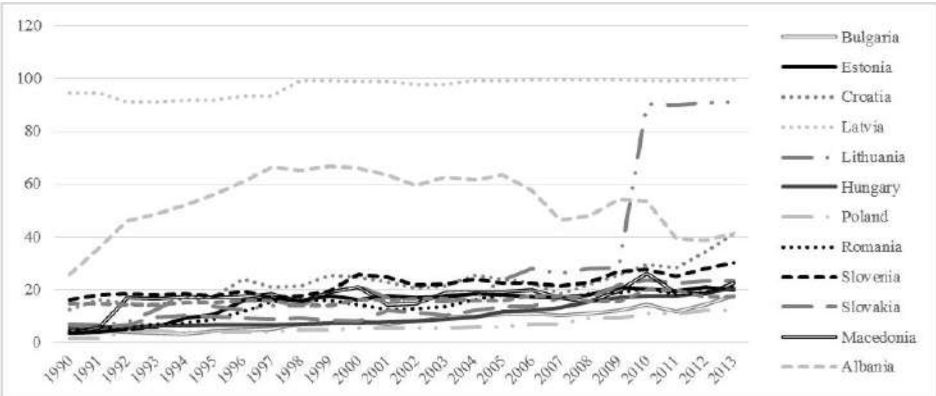

Figure 4. Share of energy production from renewable sources in primary energy production in transition countries in a period between 1990 and 2013 (**Source:** Eurostat)

Latvia recorded very high share of energy production from renewable resource in total primary energy production through entire observed period, and after 1998 it almost reached 100%. Albania also recorded high share of production from renewable sources, with a slight decrease after 2005. From 2009, Lithuania records serious increase of renewable energy, reaching 90% of share after 2010. Poland is again at the bottom of the list, without being able to exceed 12% of share through entire observed period.

In order to take an insight of relative significance of specific renewable resources in gross primary energy production, we can observe shares of most important renewable energy sources in gross energy production from renewable sources in Figure 5.

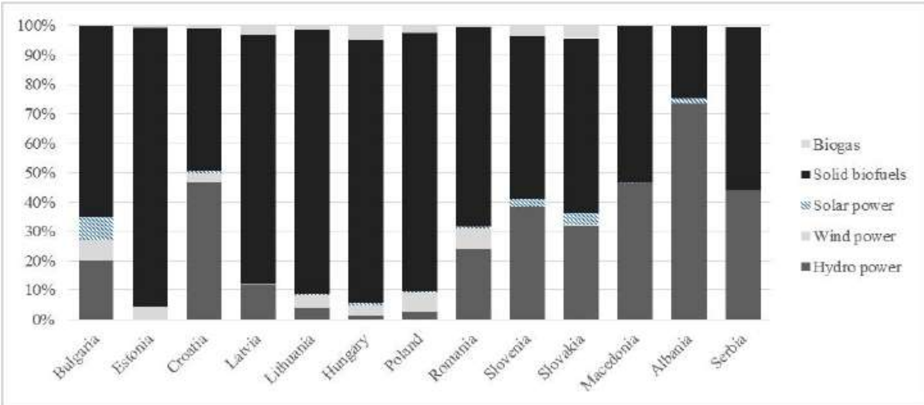

Figure 5. Structure of primary energy production from renewable sources in transition countries in 2013 (**Source:** Eurostat)

Solid biofuels are the dominant renewable energy source in most of transition countries (especially in Estonia, Lithuania, Hungary and Poland). On the other hand, 70% of renewable energy in Albania is hydro energy, while in Croatia, Macedonia and Serbia we have nearly equal share of solid biofuels and hydro energy. Generally, lowest shares in the structure of energy produced from renewable sources belong to solar energy, biogas and wind energy.

If we analyze the share of energy consumption from renewable sources in gross energy consumption, we can conclude that this share is generally still low. Figure 6 shows these shares by countries.

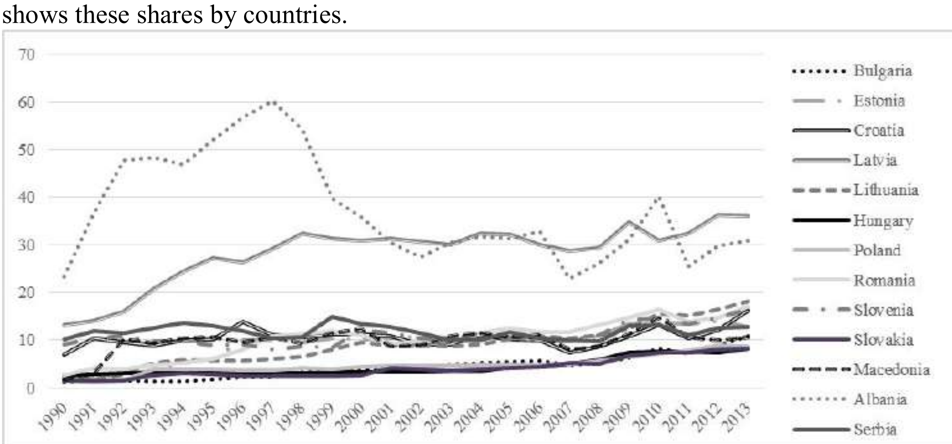

Figure 6. Share of consumption of energy from renewable sources in gross energy consumption in transition countries in a period between 1990 and 2013 (**Source:** Eurostat)

Before 2000, Albania was the leading country in the share of renewable energy consumption, and after 2000 Latvia and Albania alternately held leading position. At the end of observed period, it was Latvia that prevailed on top position. On the contrary, countries with lowest shares of renewable energy consumption were Bulgaria, Slovakia, Hungary and Poland.

PERSPECTIVES FOR DEVELOPMENT OF ENERGY PRODUCTION FROM RENEWABLE SOURCES

Tendencies at global energy market are forcing the economies to provide energy security. Energy security is the ability of a nation to deliver the energy resources needed to ensure its welfare and implies secure supply and stable prices [2]. With understanding of energy security and reduced dependence on imported energy importance, European Union intensively implements measures aiming to diversify energy supply options, but also to control the consumption. One of the main measures related to diversification of supply options is increase of energy production from renewable sources and its share in gross energy production. In that sense, each of EU countries, but also potential members, defined the targets for energy production from renewable sources share in gross energy production till 2020, according to Directive 2009/28/EC (Table 1).

Table 1. National targets of energy production from renewable resources share in gross final energy consumption by 2020 [3]

Transition economy	**Target by 2020**
Bulgaria	16%
Estonia	25%
Latvia	42%
Lithuania	23%
Hungary	13%
Poland	15%
Romania	24%
Slovenia	25%
Slovakia	14%
Albania	38%
Croatia	20%
Macedonia	28%
Serbia	27%

Source: Renewables 2014 Global Status Report

Latvia is the country with highest targeted value, which is understandable since it records constant growth of share of energy consumption from the renewables, and its share is currently highest among transition countries. On the opposite, Hungary has the lowest target, which is also understandable since its share in previous period never exceeded 10%.

In order to accomplish the targets and encourage energy production from renewable sources, transition countries carry out numerous measures, as it is shown in Table 2.

Table 2. Renewable energy support policies

Country	Renewable energy targets	REGULATORY POLICIES							FISCAL INCENTIVES AND PUBLIC FINANCING				
		Feed-in tariff/premium payment	Electric utility quota obligation/RPS	Net metering	Tradable REC	Tendering	Heat obligation/ mandate	Biofuels obligation/ mandate	Capital subsidy or rabate	Investment or production tax credit	Reduction in sales, energy, CO_2, VAT, or other taxes	Energy production payment	Public investment, loans or grants
Albania	O	O	O	O	O	O	*			O	*	O	O
Bulgaria	O	O						O					O
Croatia	O	O						O					
Estonia	O	O						O				O	O
Hungary	O	O						O	O		O		O
Lithuania	O	R	O					O					O
Latvia	O	O		*		O		O			O		
Poland	O		O		O	R		O			O		O
Romania	O		O					O					O
Serbia	O	O							O				
Macedonia	O	O											
Slovenia	O	O			O	O			O	O	O		O
Slovakia	O	R	O					O					O

Source: Renewables 2014 Global Status Report; O - existing national; R - revised; * - new.

According to this table, Albania implements most of renewable energy support measures (11 out of 13). This country implements almost each of regulatory and fiscal measures in order to increase renewable energy share. Only 2 measures are left for implementation. Macedonia is on the other end of line, with only 2 measures in implementation, while Croatia and Serbia are not far away, with only 3 of them. These countries should seriously reconsider their regulatory in this sector, taking an example from countries like Albania and Slovenia.

CONCLUSION

Majority of transition economies face numerous macroeconomic and structural disturbances, inherited from period of planned economy. One of the key imbalances comes from energetic sector. Namely, system of production in command economies was based on cheap energy and enormous energy consumption. Consequently, after disunion of USSR and SEV, new countries and their economies faced numerous macroeconomic problems at the beginning of transition process, such as slow economic growth, imported inflation, payment imbalance etc.

Efficient energy production from renewable sources enables acceleration of economic development for transition countries, but also reduces negative impacts to the environment caused by energy production from traditional sources. Achieving these goals requires active participation of governments in support of renewable energy sector, which leads to creation of favorable ambience for investments, followed by technological development in this sector and stabilization of energy market.

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ENERGY STAR - ENERGY SECURITY MODEL OF TECHNOLOGICAL SYSTEMS

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ABSTRACT

Energy security is an integral part of a dynamic business environment of the company and it involves adequate energy safety based on the balance between costs and benefits, which can be realized by maintaining and improving energy management systems. This enables companies to constantly improve energy characteristics, increase energy efficiency and energy conservation. This paper presents an Energy Star model as an example of maintaining energy security within systems and reducing environmental risk.

Key words: energy security, Energy Star model.

INTRODUCTION

Nowadays, special attention of the scientific community has been given to energy efficiency and energy management, due to a growing demand for energy and a real risk that fossil fuels will be exhausted. Bearing these in mind, it is necessary to make an effort to ensure continuous supply of energy at affordable prices and to take care about environmental protection and conservation.

The term energy security defines the relationship between national security and availability of natural resources for energy consumption. The possibility of access to cheap energy has become crucial for the functioning of modern economy. However, the uneven distribution of energy among supplier countries has led to significant vulnerabilities.

Energy security is a complex area of scientific research based on modeling of energy processes, loss analysis, network reliability, resistant to disturbances, statistical expertise and the risk of injury in technological systems, risk analysis, problems relating to energy supply, as well as technical and other consequences, *J. Augutis, P. Krikstolaitis, L. Martisauskas, C. Peciulyte* [1].

Energy security is a term that covers many issues concerning energy, economic growth and political power. It is rather difficult to come up with a precise definition of energy security, since it has a different meaning for different people depending on the time they work and live in.

Some of the definitions of energy security are as follow:

- Energy security is defined as the uninterrupted supply of energy in terms of quantities required to satisfy the demand at reasonable prices, Europe's Vulnerability to Energy Crises, *World Energy Council* [2];
- Energy security can also be described as the uninterrupted availability of energy sources at an affordable price, which takes into account the environmental aspects, Energy Security, *International Energy Agency* [3];
- The standard definition of energy security is the flow of energy supply to meet demand in a manner and at a price level that does not disrupt the course of the economy based on sustainable development, *The Institute of Energy Economics* [4].

Based on the above definitions it can be concluded that: ***„Energy security in terms of sustainable development is a continuous availability of energy at reasonable prices, from readily available and accessible sources, resistant to disturbances, based on modeling of energy processes, loss analyses, system reliability, statistical expertise and the risk of injury in technological systems"***.

Continuous improvement of energy characteristics of technological systems requires effective practices and processes of energy management based on experiential programmes (models). Each company, regardless of its type, size or sector affiliation, can develop an effective programme for energy efficiency.

The models often used in practice are: The 4 A's model, Model of Short-term Energy Security (MOSES), Index of U.S. Energy Security Risk, Security Iceberg Model, Krugman-type of Iceberg model, Model for energy security level assessment, Energy Star model and others.

This paper is focused on the basics of the Energy Star model, as one of the most widely used models that contribute to the improvement of energy performance, which directly influences the increase of business efficiency and reduces environmental impact.

COMPONENTS OF ENERGY STAR MODELS

Energy Star, developed by the U.S. Environmental Protection Agency, is a model that provides a proven energy management strategy, and is based on the continuous improvement in energy efficiency by reducing environmental impact and making savings through increased competitiveness. The model was developed on the basis of good practices and it helps companies create and implement their own programmes and strategies of energy management.

Figure 1 illustrates the Energy Star model with defined guidelines for energy-efficient systems.

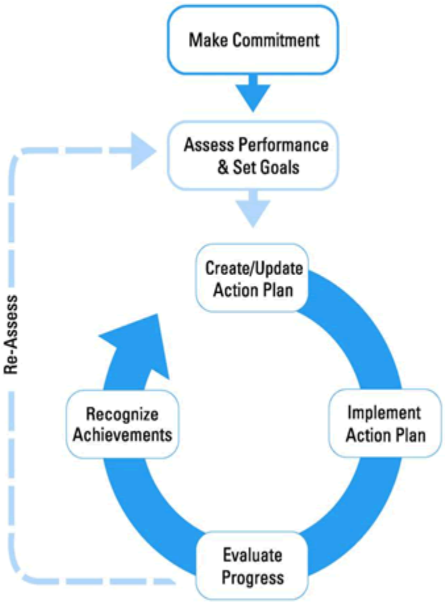

Figure 1. Energy Star model, Energy Star [5]

Seven steps of the Energy Star model are outlined below:

Step 1: Make Commitment

Regardless of the size or the type of an organization, the common element of successful energy management is commitment. The company is obliged to allocate staff and funding to achieve continuous improvement, and to establish their energy programme by forming a team for energy efficiency who will institute an energy policy.

Step 2: Assess Performance

Assessing energy performance is a periodic process of evaluating energy consumption for all major systems and functions in the organization and establishing a baseline for evaluating future results of energy efficiency.

Understanding the factors of energy consumption opens up the possibilities for the company to improve the characteristics of the energy system and gain financial benefits, with the aim to increase competitiveness in the market.

Step 3: Set Goals

Setting clear and measurable goals is crucial for understanding expected results of energy management, as well as for further development of energy system, developing effective strategies and achieving financial gain. Well-defined objectives influence proper short-term and long-term decision-making, and they serve as a starting point for successful monitoring and analysis of energy development. The strategy defined in this way and open communication about the most important issues motivate employees to support the energy policy of the company and actively engage in the process of rational and responsible energy management.

Step 4: Create an Action Plan

Precise definition of future plans and activities develop a roadmap for systematic and successful implementation of the model for the application of measures to improve energy performance and energy efficiency. Unlike the defined „institute“ of organization's energy policy, action plans are constantly monitored and updated. They present the most important and the most recent data concerning the changes of the energy system, recent achievements in the development and shifting priorities.

The company usually internally defines the scope and extent of future activities in accordance with energy policy, and on the basis of opportunities for the development and improvement of the energy performance.

Step 5: Implement an Action Plan

An important factor for the successful implementation of planned activities for improvement of organization's energy performance often depends on the level of awareness about the impact of energy systems, commitment, professional competence, and the continuous development and knowledge-sharing about energy management, primarily among the engineers who will implement plans and projects, but also among other employees at different levels of decision-making.

Step 6: Evaluate Progress

Evaluating planned activities to improve energy efficiency and characteristics of the energy system requires comprehensive approach and analysis of data about energy exploitation and objective assessment of the impact of implemented plans, as well as a comparison of the accomplishments.

The results of this analysis and the information gathered can be used by other companies in the process of creating their own action plans for energy performance and achieving maximum benefit from the process of efficient energy management. They are helpful in terms of creating their own energy policy based on empirical knowledge and defining a strategy for further development, in accordance with the defined goals, using the examples of best practice.

Step 7: Recognize Achievements

Recognizing the efforts and achievements of individuals and teams involved in solving current problems of efficient energy management in the company is a reward and a proven step for further initiatives. The continuous support of the top management to the employees who are making efforts is the basis for successful business. At the same time, this increases employees' motivation and job satisfaction. Providing recognition to the individuals and teams, and recognizing achievements boosts morale and improves the performance enhancement in carrying out current and planned tasks of energy management in the system.

ENERGY STAR ASSESSMENT MATRICES

The assessment matrices have been designed to help companies and energy managers compare their energy management practices to those outlined in the guidelines for an Energy Star energy management model. In this way, the user is provided with detailed checklists that allow each facility, equipment or their part to be assessed and evaluated within the following categories:

- commitment to continuous improvement;
- assessment of performance and opportunities;
- setting performance goals;
- creation of an action plan;
- implementation of an action plan;
- evaluating progress;
- recognizing achievements.

The matrix is designed in a way to emphasize the key actions identified by the Energy Star model and three basic situations in the process of their implementation:

- When there is no record on implementation of energy management;
- When only certain parts of the programme are conducted;
- When an energy management programme is fully implemented.

To apply this useful tool in the organization, the following steps need to be followed:

- Compare the existing energy management programme to the recommendations by the Energy Star model, and identify the degree of implementation that most closely matches the organization's programme.
- Recognize and highlight a cell in the table of Energy Star model that best characterizes the level of programme implementation in the organization. In this way, we could obtain a visual comparison of the organization's programme to the elements of the Energy Star guidelines for energy management.
- Identify all necessary steps and actions to fully implement the elements of energy management process and record them in the „Next Steps" - the last column of the Energy Star assessment matrix.

Table 1 - Energy Management Assessment Matrix enables the implementation of activities and identical programmes of energy management at a number of facilities. It provides users with instructions, guidelines and recommends future steps towards establishing and implementing an effective energy management system in the company, *Energy Star* [6].

Table 2 - Facility Energy Management Assessment Matrix is a useful tool designed to assess the degree of implemented energy management programme in industrial environments. This matrix is in synergy with the previous one - Energy Management Assessment Matrix- and it examines the degree and the manner of implementation of the programme on a single facility. This tool can be used in all correspondence between the programme director of energy management and energy managers engaged in the field, in order to assess the effectiveness of implemented programme, *Energy Star* [7].

ENERGY STAR Energy Management Assessment Matrix				
	Little or no evidence	**Some elements**	**Fully implemented**	**Next Steps**
Make Commitment to Continuous Improvement				
Energy Director	No central or organizational resource Decentralized management.	Central or organizational resource not empowered.	Empowered central or organizational leader with senior management support.	
Energy Team	No company energy network.	Informal organization.	Active cross-functional team guiding energy program.	
Energy Policy	No formal policy.	Referenced in environmental or other policies.	Formal stand-alone EE policy endorsed by senior management.	
Assess Performance and Opportunities				
Gather and Track Data	Little metering/ no tracking.	Local or partial metering/tracking/ reporting.	All facilities report for central consolidation/ analysis.	
Normalize	Not addressed.	Some unit measures or weather adjustments.	All meaningful adjustments for organizational analysis.	
Establish baselines	No baselines.	Various facility-established.	Standardized organizational base year and metric established.	
Benchmark	Not addressed or only same site historical comparisons.	Some internal comparisons among company sites.	Regular internal and external comparisons and analyses.	
Analyze	Not addressed.	Some attempt to identify and correct spikes.	Profiles identifying trends, peaks, valleys and causes.	
Technical assessments and audits	Not conducted.	Internal facility reviews.	Reviews by multi-functional team of professionals.	
Set Performance Goals				
Determine scope	No quantifiable goals.	Short term facility goals or nominal corporate goals.	Short and long term facility and corporate goals.	
Estimate potential for improvement	No process in place.	Specific projects based on limited vendor projections.	Facility and organization defined based on experience.	
Establish goals	Not addressed.	Loosely defined or sporadically applied.	Specific and quantifiable at various organizational levels.	
Create Action Plan				
Define technical steps and targets	Not addressed.	Facility-level consideration as opportunities occur.	Detailed multi-level targets with timelines to close gaps.	
Determine roles and resources	Not addressed or done on ad hoc basis.	Informal interested person competes for funding.	Internal/external roles defined and funding identified.	
Implement Action Plan				
Create a communication plan	Not addressed.	Tools targeted for some groups used occasionally.	All stakeholders are addressed on regular basis.	
Raise awareness	No promotion of energy efficiency.	Periodic references to energy initiatives.	All levels of organization support energy goals.	
Build capacity	Indirect training only.	Some training for key individuals.	Broad training/certification in technology and best practices.	
Motivate	No or occasional contact with energy users and staff.	Threats for non-performance or periodic reminders.	Recognition, financial and performance incentives.	

Track and monitor	No system for monitoring progress.	Annual reviews by facilities.	Regular reviews and updates of centralized system.	
Evaluate Progress				
Measure results	No reviews.	Historical comparisons.	Compare usage and costs vs. goals, plans, competitors.	
Review action plan	No reviews.	Informal check on progress.	Revise plan based on results, feedback and business factors.	
Recognize Achievements				
Provide internal recognition	Not addressed.	Identify successful projects.	Acknowledge contributions of individuals, teams, facilities.	
Get external recognition	Not sought.	Incidental or vendor acknowledgement.	Government/third party highlighting achievements.	

ENERGY STAR Facility Energy Management Assessment Matrix				
Company Name:			Assessment Date:	
	Little or no evidence	**Some elements/ degree**	**Fully implemented**	**Next Steps**
Commit to Continuous Improvement				
Site Energy Leader	None assigned.	Assigned responsibilities but not empowered. 20-40 % of time is devoted to energy.	Recognized and empowered leader having site manager and senior energy manager support.	
Site Energy Champion	None identified.	Senior manager implicitly supports the energy program.	Senior manager actively supports the energy program and promotes energy efficiency in all aspects of site operations.	
Site Energy Team	No site energy team.	Informal organization with sporadic activity.	Active cross-functional team guiding site energy program.	
Energy Policy	No energy policy or awareness of organizational policy.	Organizational policy in place. Little awareness by site energy team and limited application of policy.	Organizational policy supported at site level. All employees aware of goals and responsibilities.	
Site Energy Plan	No written plan.	Informal plan not widely known.	Written formal plan endorsed, distributed, and verified.	
Accountability	No energy budgeting and accountability.	Estimates used for allocating energy budgets.	Key users are metered separately. Each entity has total accountability for their energy use.	
Participation Levels	No reporting of energy performance data internally or involvement in external organizations.	Some participation, sharing, mentoring, and professional memberships. Annual reporting of performance.	Participates in energy network/organizations. Shares best practices/mentors other sites. Reports usage quarterly.	
Assess Performance and Opportunities				
Track and Analyze Data	Limited metering or tracking. No demand analysis or billing evaluation.	Some metering, tracking, analyzing, and reporting. Energy bills verified for accuracy.	Key loads metered, tracked, analyzed, and reported. Facility peak demand analyzed. Adjusts for real-time demand.	

Documentation	No manuals, plans, designs, drawings, specs, etc. for building and equipment available.	Some documentation and records available. Some review of equipment commissioning specs conducted.	Critical building and equipment documentation available and used for load surveys/ recommissioning/ efficiency goals.	
Benchmarking	Energy performance of systems and facilities not benchmarked	Limited comparisons of specific functions, or only same-site historical comparisons.	Key systems/sites benchmarked using comparison tools like Portfolio Manager/Energy Performance Indicators.	
Technical Assessments	No formal or external reviews.	Limited review by vendors, location, or organizational and corporate energy managers.	Extensive regular reviews by multi- functional team of internal and external professionals. Full assessment every 5 years.	
Best Practices	None identified.	Ad hoc or infrequent monitoring of trade journals, internal databases, and other facilities' best practices.	Regular monitoring of trade journals, internal databases, and other facilities. Best practices shared and implemented.	
Set Performance Goals				
Goals/ Potential	Energy reduce goals not established.	Loosely defined. Little awareness of energy goals by others outside of site energy team.	Potential defined by experience or assessments. Goals roll up to unit/site/ organization and status posted prominently.	
Career Development	No career development. No opportunities available.	Exposure to other energy programs. Some temporary or project assignments available elsewhere.	Energy professionals have established career paths that are reviewed annually. Opportunities for growth encouraged.	
Energy Team Incentives	No ties between energy efficiency improvement and compensation.	Spot awards or luncheons for employees on a project.	Accountability tied to performance reviews, compensation, and personal and plant bonuses.	
Create Action Plan				
Improvement Planning	No upgrade plan.	Upgrades implemented sporadically. Some compliance with organizational goals and standards.	Upgrade plans established; reflect assessments. Full compliance with organizational EE design guidelines and goals.	
Roles and Resources	Not addressed, or addressed on ad hoc basis only.	Informal interested person competes for funding. Little support from organizational program.	Internal/external roles defined and funding identified. Organizational or corporate program support secured.	
Site Planning Integration	Impact on energy from changes not considered.	Decisions impacting energy considered on first-cost basis only.	Projects/contracts include energy analysis. Energy projects evaluated with other investments. Lifecycle costing applied.	
Implement Action Plan				
Communication Plan	Site plan not developed.	Periodic communications for projects. Some reporting of energy use information.	All stakeholders are addressed on regular basis.	

Energy Awareness	None conducted.	Occasional energy efficiency awareness campaigns. Some communication of energy costs.	Planned outreach and communications. Support organizational initiatives. Employees aware of site energy costs.	
Building Staff Capacity	No training offered.	Some vendor training for key individuals and perators.	Broad training/certification in technology and best practices. Networking opportunities actively pursued.	
Contract Management	Contracts are renewed automatically without review.	Occasional review of supplier contracts.	Energy-efficient procurement policy in place. Vendors for replacements on standby. Regular review of suppliers.	
Incentives and Rebates	Not researched or pursued.	Occasional communication with utility representatives. Limited knowledge of incentive programs.	Researches rebates and incentives offered regionally and nationally. Communicates often with utility representatives.	
Evaluate Progress				
Measuring Results	No reviews.	Historical comparisons. Some reporting of results.	Compare usage & costs vs. goals, plans, other sites. Results reported to site and organizational or corporate management.	
Review Action Plan	No reviews.	Informal check on progress.	Revise plan based on results, feedback and business factors. Best practices shared with other sites / organization or corporate program.	
Recognize Achievements				
Site Recognition	Not addressed.	Occasional recognition of projects and people.	Recognition system in place. Awards for projects pursued by operators.	
Organizational Recognition	Not sought.	Occasionally when prompted by senior management.	Senior management acknowledges site successes.	
External Recognition	Not sought.	Occasional trade magazine and vendor recognition.	Government and third-party recognition highlighting achievements sought. ENERGY STAR awarded annually.	

CONCLUSION

Based on a partnership between a large number of companies, organizations and consumers, the Energy Star model is a programme developed on the foundations of empirical knowledge and the methods proven at specific cases. The free flow of information provides a flexible set of objective and high-quality solutions to its members, as well as functional tools to improve energy efficiency. Coordinated activities enable market transformations towards efficient and sustainable products and services, by creating jobs and stimulating the overall economy.

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MINERALOGICAL CHARACTERIZATION OF THE ZEOLITIC TUFFS AND ASPECTS OF ITS APPLICATION IN AGRICULTURE

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ABSTRACT

The paper is based on determining the mineralogical character of zeolitic tuff from the territory of South Serbia. Based on the results obtained using the methods of optical microscopy, scanning electron microscopy, energy dispersive spectroscopy, differential thermal analysis and X-ray Diffraction, the mineralogical character of zeolitic tuff has been determined. Zeolite of South Serbian deposits is characterized by the presence of the mineral Clinoptilolite. Content of Clinoptilolite in zeolitic tuffs in the area of South Serbia is extremely high (ranging up to 90%), which is a great advantage in terms of its applicability. Bearing in mind the significant characteristics of the mineral Clinoptilolite for application in various industry branches, zeolitic deposits of the mentioned areas are underutilized. For this reason, the ultimate goal of this paper is to encourage the application of zeolitic tuff in various branches of agriculture.

Key words: zeolitic tuff, clinoptilolite, agriculture.

INTRODUCTION

Zeolites are a group of minerals that are usually composed of aluminosilicates Ca, Na and K, and rarely some other cations [1-3]. This group of minerals is characterized by a specific crystalline structure because they possess characteristic physical-chemical properties. One of the fundamental properties of zeolite has the ability to replace cations and water molecules, various organic and inorganic molecules and other cations through dehydration, and adsorption or by ion exchange. They have the ability to receive and release water at ordinary temperatures, and it does not thereby surpassing to a distortion of the crystal lattice [2].

One of the most important minerals from the group of zeolite is Clinoptilolite of the formula $(Na, K, Ca)_{2\text{-}3}\ Al_3\ (Al, Si)_2\ Si_{13}\ O_{36}\ 12H_2O$. This mineral is widely used in different industries.

The world is already widely used in construction, agriculture, horticulture and in a process of environmental protection through the purification of water and air.

The use of zeolites in agriculture is multiple and significant. They are used as meliorant to improve the physical properties of heavy soils, bind toxic elements in the soil and prevent rapid leaching of fertilizers from the soil. Zeolites thanks to the affinity cations K and NH adsorb these important elements in plant nutrition, and later released them. In this way prolong the effect of artificial (recharge) feeding and effective utilization of plant roots [4].

They adsorb and release the water, exchange cations, without destroying the crystal lattice. Cation exchange capacity is the major characteristic of mineral absorbent. Value of Cation exchange capacity "CEC" determines the usage. This feature allows them to be used for removal of mycotoxins as absorbents and to have function of immunostimulator. Mycotoxins are harmful to the health of livestock and poultry. Immunostimulator minerals reinforce the development of cells of the immune system in poultry and livestock. Immune system cells destroy bacteria and viruses [5].

Zeolite is used for canning and drying of agricultural products, as well as a feed supplement for livestock and poultry [6][7]. As a food supplement for livestock and poultry is particularly distinctive mineral Clinoptilolite, which makes up 90% of the zeolitic tuff. Mineral deposits of zeolite tuffs with such a high content of Clinoptilolite are present both in the world and in our country. Zeolite from the deposit Igroš at Brusa contains up to 95% Clinoptilolite [8], and from the deposit Zlatokop near Vranje to 90% Clinoptilolite [9].

Natural zeolite is in Serbia was added in portions to the calves and cows, and is followed by its effect [10]. It is also used by us and a product that is based on clinoptilolite which is added to animal feed in order to examine the effect on production, performance and health status in dairy cows [11]. Modified Clinoptilolite is already used in Serbia as an additive in poultry feed. It was used in order to investigate its influence on the concentration of vitamin E in the meat and the value of the selected parameters of quality chicken meat [12].

Premix is an integral part in the food production for poultry and livestock [13][14]. It is mixture of organic and inorganic components [15]. Besides the organic part of premix, inorganic part plays also an important role in premix composition. Qualitative and quantitative content of both parts of premix affect the quality of the food. Domestic and foreign premix, depending on the composition have different effects in feeding hogs [16] [17].

The paper presents the results of mineralogical characterization of zeolitic tuff from the territory of southern Serbia. They are the composition and quality very similar to zeolitic tuffs widespread in the world.

EXPERIMENTAL

Experimental part of the work included testing more samples zeolitic tuff. The paper presents the results of two samples. Tests were carried out by different methods. Optical microscopy was done on polarizing microscope for transmitted light type Leica DMLSP. For DTA analysis was used elctronic furnace type Adamel (thermocouple Platinum/Platinum-Rhodium). The X-ray examination of the zeolitic tuff were obtained on Rendgen diffractometer type Philips PW 1710, anticathode copper, wave length of $CuK\alpha$ = 1.54178Å. Obtained data of diffraction peak positions (°2θ), interplanar spacings d (Å) and intensities are compared with literature data and JCPDS.

The samples are tested with electronic microscopy (SEM–EDS analysis) type JOEL JSM-6610 LV with INCA Energy 350.

RESULTS AND DISCUSSION

Figure 1 shows the zeolitic tuff Z1 and Z2. Chemical analysis of zeolitic tuffs is shown in Table 1.

Figure 1. Macro wiev Zeolitic tuff Z1 and Z2

Table 1. The chemical composition of zeolitic tuff 1 and 2(wt-%)

Zeolitic tuff Z1				Zeolitic tuff Z2			
SiO_2	65.71	MgO	0.54	SiO_2	62.70	MgO	0.88
Al_2O_3	10.05	Na_2O	0.50	Al_2O_3	11.35	Na_2O	0.72
Fe_2O_3	2.90	K_2O	1.48	Fe_2O_3	3.85	K_2O	3.95
TiO_2	0.28	SO_3	0.08	TiO_2	0.38	SO_3	0.04
P_2O_5	0.07	LOI	14.95	P_2O_5	0.37	LOI	10.70
CaO	3.41	Suma	99.97	CaO	4.90	Suma	99.84

A differential thermal analysis of the sample to 1000°C Z1 and Z2 are shown in Figure 2.

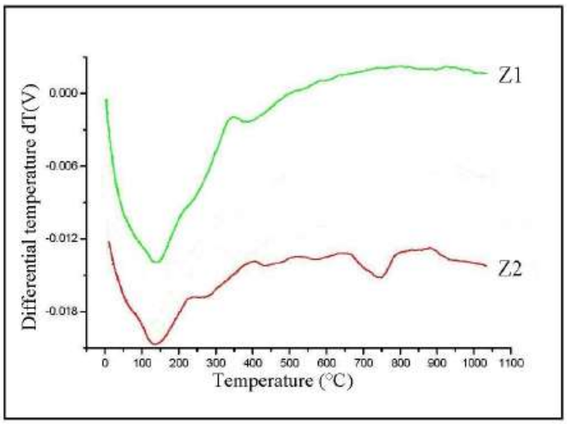

Figure 2. Differential thermal curve of Zeolitic tuff Z1 and Z2

In the samples highlighted the endothermic reaction in the interval 100° to 150°C which is due to evaporation of moisture and loosely bonded surface-adsorbed water. Between 200°C and 300°C can be seen endothermic reaction as a broad depression on the wrong without a clearly defined minimum, or peak temperature reactions as a result of drying of zeolites or zeolitic water evaporation. Between 300° and 400°C or just over 400°C (Z2) only incurred are also poorly defined endothermic peaks, among which the most clearly visible in Z1.

It can be Dehydroxylation hydrokside iron. Weak endothermic reaction by at Z2 between 500°C and 600°C are probably result dehydroxilation small amounts of phyllosilicates. Between 700°C and 800°C occurs in Z2 well defined endothermic reaction that can only be interpreted degradation of dolomitic carbonate. A very weak reaction was between 900°C and 950°C for the same sample can be from the dissociation of calcite.

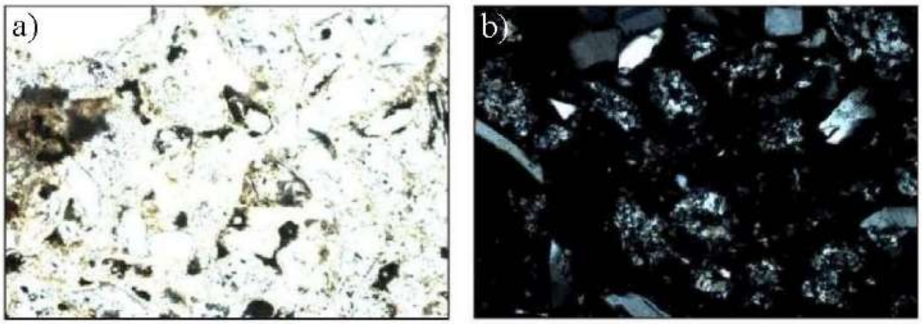

Figure 3. Micrograph of the zeolitic tuff Z1, polarizing microscope, transmitted light a) parallel Nicol prisms, b) crossed Nicol prisms

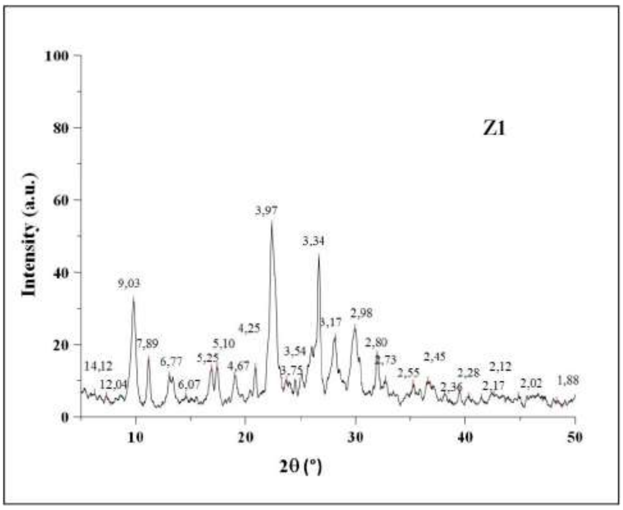

Figure 4. X-Ray diffractogram of the zeolitic tuff Z1

Powder X-ray diffraction analysis of zeolitic tuff Z1 has shown the predominance of Clinoptilolite , with most intensely pronounced peak 3,97Å and smaller ones on 3.17, 2.98, 2.80 and 2.55 Å. Minor amounts of Quartz (small peaks on 4.25, 3.34, 2.45, 2.28 and 2.12 Å) and Muscovite (small peaks on 3.75, 3.54 and 2.73 Å).

Figure 5 shows the SEM micrograph of the zeolitic tuff Z1.

From Fig.5 one can see plate-like and leaf–like forms, as well as stratified structure characteristic for the mineral Clinoptilolite.

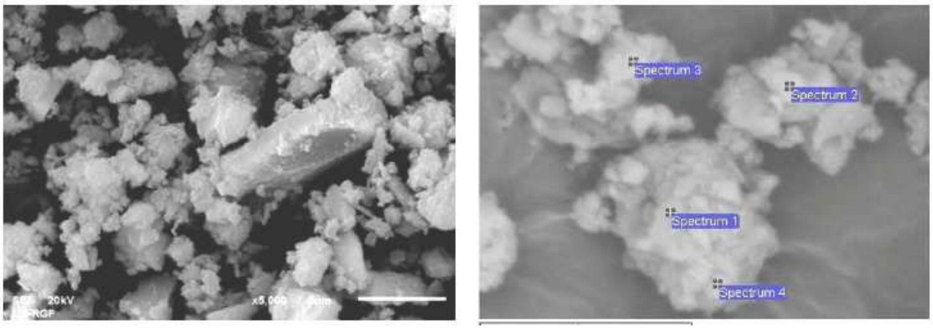

Figure 5 SEM image of the zeolitic tuff Z1

The chemical composition of the selected points is shown in Table 2, and the EDX spectrums in Fig. 6.

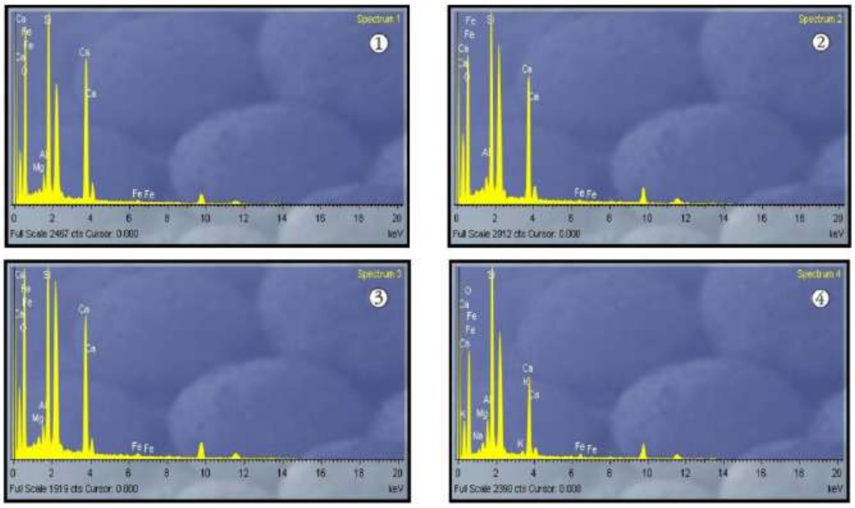

Figure 6. EDX spectrums of zeolitic tuff Z1

The data in Table 2 and in Fig.6 show that the forms, by chemical composition, belong to Clinoptilolite.

Table 2. Chemical composition of zeolitic tuff Z1(wt-%) - selected points

	Na	**Mg**	**Al**	**Si**	**K**	**Ca**	**Fe**	**Total**
Spectrum 1	-	1.30	4.21	48.75	-	44.42	1.32	100.00
Spectrum 2	-	-	4.18	52.11	-	42.16	1.55	100.00
Spectrum 3	-	2.27	5.24	48.10	-	42.29	2.10	100.00
Spectrum 4	1.16	2,60	7.99	57.60	0.94	26.82	2.90	100.00

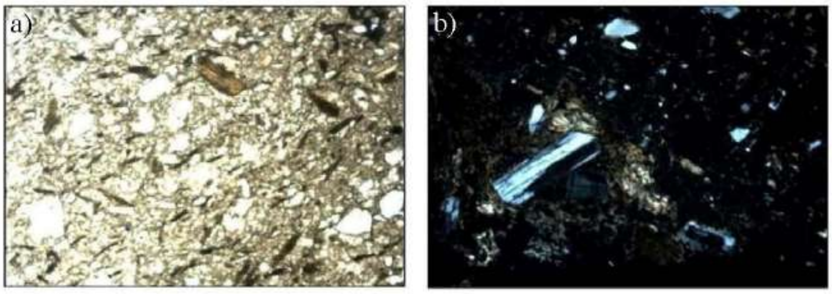

Figure 7. Micrograph of the zeolitic tuff Z2, Polarizing microscope, transmitted light a) parallel Nicol prisms, b) crossed Nicol prisms

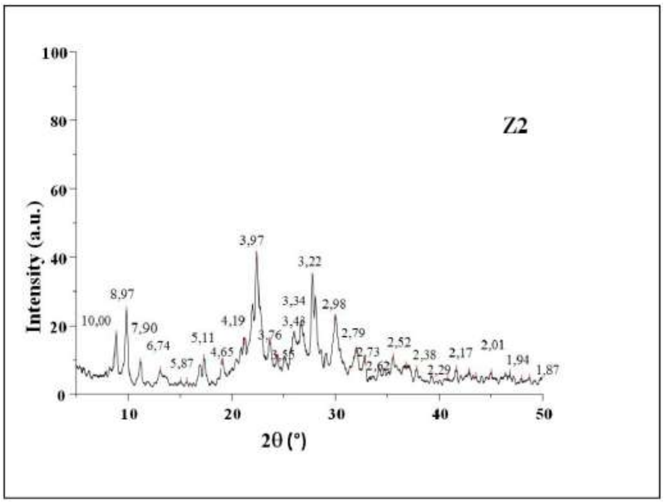

Figure 8. X-Ray diffractogram of the zeolitic tuff Z2

Powder X-ray diffraction analysis of zeolitic tuff Z2 has shown the predominance of Clinoptilolite, with most intensely pronounced peak 8.97Å, 7.90, 6.74, 5.11, 4.65, 4.19, 3.97 and smaller ones on 2.98, 2.80, 2.55 and 2.36Å. Minor amounts of Quartz (small peaks on 3.34, 2.45, 2.28 and 2.12 Å), Muscovite (small peaks on 3.75, 3.54, 2.73 and 2.52 Å), Biotite with peaks 2.62 and 2.17Å and Feldspar with peak 3.22Å. The results of the electronic microanalysis of the zeolitic tuff Z2 are shown in Fig.9 and Fig.10. From Fig.9 one can see plate-like and leaf – like forms, bat also a layered structure of mineral Clinoptilolite. The chemical composition of the selected points is shown in Table 3, and the spectrums in Fig 10.

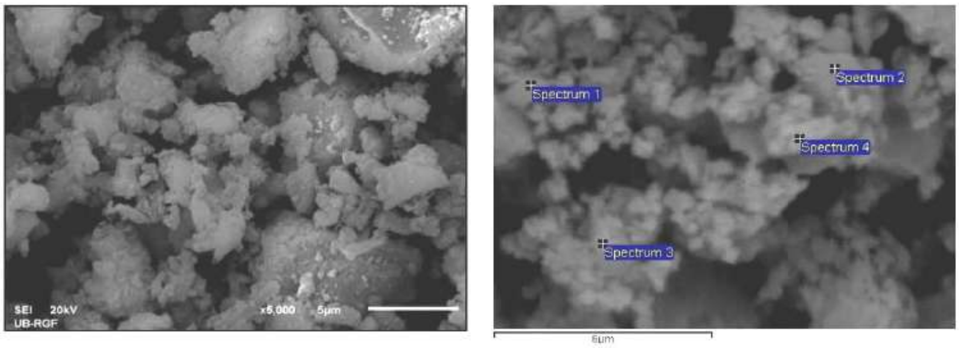

Figure 9. SEM image of the zeolitic tuff Z2

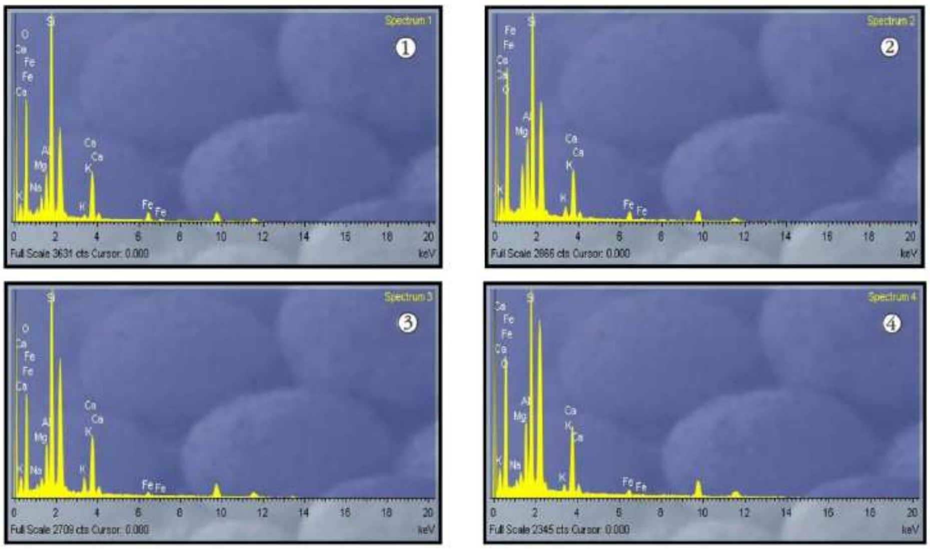

Figure 10. EDX spectrums of the zeolitic tuff Z2

Table 3. Chemical composition of the Zeolitic tuff Z2(wt-%) selected points

	Na	Mg	Al	Si	K	Ca	Fe	Total
Spectrum 1	1.5	5.01	9.84	59.92	1.05	15.63	6.9	100.00
Spectrum 2	-	10.62	15.74	51.63	2.5	13.58	5.9	100.00
Spectrum 3	1.3	2.56	11.07	58.71	3.9	19.66	2.6	100.00
Spectrum 4	1.7	3,28	14.37	53.72	1.7	20.56	4.5	100.00

CONCLUSION

The investigation of zeolitic tuffs from the territory of South Serbia can conclude the following:

The main (basic) mineral composition of the zeolitic tuffs from the territory of South Serbia is the mineral Clinoptilolite with the formula Na, K, Ca) $_{2\text{-}3}$ Al_3 $(Al,Si)_2Si_{13}O_{36}{\bullet}12H_2O$.

In addition Clinoptilolite in tuff Z1 are present as accompanying minerals Quartz and Muscovite.

The tuff Z2 next Clinoptilolite, Quartz, Muscovite recorded the presence of calcium feldspar - Anorthite.

Mineral Clinoptilolite belongs to the group of zeolites due to its outstanding characteristics is one of the most mineral applied in different industries. Thanks to its favorable mineral composition and quality (> 90% Clinoptilolite*)*zeolitic tuffs slowly used in our country for the purposes of agriculture.

Zeolitic tuffs from this region represent an important mineral raw material which application should specifically explore and expand the field of agriculture.

Especially it relates to the production of domestic premix with content Clinoptilolite as a mineral supplement. It is necessary to constantly improving the application as a feed additive premix for livestock and poultry. It is also necessary to find possibilities of increasing use of natural and modified zeolite to produce food for livestock and poultry.

Serious engagement of teams of experts of various profiles (miners, geologists, technologists, chemists, agricultural engineers and good management) zeolites that has our country will be used and applied in the best possible way in agriculture.

Acknowledgements

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INSECTICIDE EFFECT OF NON-TOXIC INORGANIC POWDERS AGAINST BEAN WEEVIL (*Acanthoscelides obtectus)*

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ABSTRACT

Insecticide effect of ZnO, TiO_2, Al_2O_3 and zeolite powders were studied on bean weevil (*Acanthoscelides obtectus* Say, 1831). Mortality of both male and female adults was significantly higher for zeolite and Al_2O_3 powders than for ZnO and TiO_2, while females were less susceptible than males. SEM analysis of the insects treated with Al_2O_3 revealed that disability and mortality of bean weevils can be related to degree of powder coverage of the insects' exoskeleton. All powders showed similar effect to development of F_1 progeny with reduction in larvae number over 50 %, and can be considered for use in organic production.

Key words: eco-insecticide, pest control, organic production, bean weevil, *Acanthoscelides obtectus.*

INTRODUCTION

For the last decades there have been numerous reports of environmental contamination by use of toxic pesticides, mostly organophosphorous and pyrethroid compounds [1]. Their use has been constantly challenged by resistance of insects, consumer's demand for pesticide-free products and restrictive governmental regulations [2]. This led to replacement of the existing chemical insecticides by a new class of non-toxic, nanostructured inorganic compounds, such as silica, alumina, diatomaceous earth and inert dusts [3–6]. Especially these compounds have been reported to be effective in control of stored product insects [1, 5, 6]. Furthermore, they can be applied directly to the grains leaving no toxic residues. This approach was successfully demonstrated in pest control of *Sitophilus oryzae* (L.) and *Rhyzopertha dominica* (F.) by nanostructured alumina [5, 6].

Another type of seed borer, bean weevil (*Acanthoscelides obtectus* Say, 1831) was reported to cause up to 40% losses in stored bean seeds [7]. Since bean is one of the most important nutritive sources in developing countries, its protection in stored conditions has been attracting much attention in past decades. Until now, there have been attempts to investigate the use of essential oils [8] and various plant extracts [9] against this pest. Although effective and non-toxic, these means of protection share some disadvantages, such as volatile nature of insecticide formulations and loss in weight of treated seeds.

On the other hand, the cause of mortality of insects by applying these inert inorganic oxides has not been elucidated yet. However, this approach being cost effective and environmentally friendly is worth further investigations and optimization of the existing formulations. Thus, in this study, commercially available zeolite powder, ZnO, TiO_2 and Al_2O_3 were tested as potential insecticides against *A. obtectus*. The comparison of insecticidal properties was observed for male and female adults and F_1 progeny.

EXPERIMENTAL

Test insects: The adult insects of *A. obtectus* were provided from the Institute for Biological Research "Siniša Stanković" (Belgrade, Serbia). Male and female insects were kept under controlled conditions (27 ºC±1 ºC, relative humidity 65%±5% and photoperiod L16:D8) prior to testing. The adults selected for testing were 48 h old.

Toxicity test: ZnO, TiO_2 and Al_2O_3 (Centrochem doo, Stara Pazova, Serbia) and zeolite powder (Homozel Zeolit – Bilje Borča, Serbia) were mixed with 40 g bean seeds by rotary shaker (Multifix GmbH, Germany) to form 1 % mass concentration of each component separately. Each of four mixtures was further divided into four smaller portions of 10 g bean seeds with 10 male and 10 female insects placed together in a 90/14 mm Petri dish. Apart from that, four control portions contained only untreated seeds with insects. All tests were carried out simultaneously under controlled conditions. Mortality of the insects was checked after each day during 7 days. After 15 days the insects were removed from the Petri dishes and the development of F_1 progeny was investigated.

SEM analysis: After toxicity testing selected insects were analyzed by scanning electron microscopy (SEM, TESCAN Vega TS5130MM) to examine the changes in exoskeleton.

RESULTS AND DISCUSSION

The results of the toxicity test in a period of 7 days were presented in Figure 1. It was clear that zeolite powder was the most lethal against both male and female adult insects, and mortality (M) exceeds 50 % after four days of exposure. Somewhat lower mortality rate was observed for alumina powders, but its efficiency against female insects was significantly lower. The worst insecticide properties against adult insects show ZnO and TiO_2 powders. Taking into account untreated adults, it is clear that female insects live a bit longer, probably due to their final role in laying eggs that were previously fertilized. This trend is also observed for treated insects, leading to a conclusion that females are less susceptible to these substances in general.

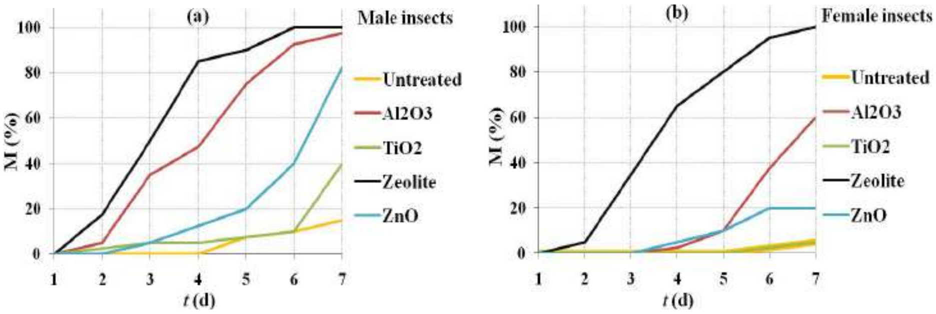

Figure 1. Toxicity test of various powders against male (a) and female insects (b) in a period of 7 days.

It is assumed that such chemically inert compounds attached to an exoskeleton are able to adsorb cuticular lipids, thus causing rapid dehydration of insects [6]. In order to explore this possibility the SEM analysis of untreated and insect treated with Al_2O_3 was performed and presented in Figure 2. By comparing the these images it is easy to notice how Al_2O_3 particles adhere to the exoskeleton of the treated adult. This is more clearly visible on the enlarged image representing the eye of the insect covered with Al_2O_3 particles. Although this analysis gave no evidence of death cause, mortality rate is certainly related to a degree of adhesion of these particles onto the insect exoskeleton. Apart from adsorbing cuticular lipids as assumed, excessive powder coverage may hinder the performance of insect's vital functions as well. Degree of powder coverage depends on factors such as: particle size and shape, specific surface area and concentration of powders, humidity, temperature and insect pubescence [6, 10]. Accordingly, insecticide properties of these powders can be enhanced by optimizing their morphology. The powders used in this experiment were all micro-sized, while by introducing various synthesis methods [5, 6, 11] it is possible to reduce their particle size up to nanoscale and significantly increase their surface area. Such powders could provide higher insecticide efficiency and consequently lower concentrations will be needed to obtain satisfactory eco-pest control especially in organic seed production [12, 13] .

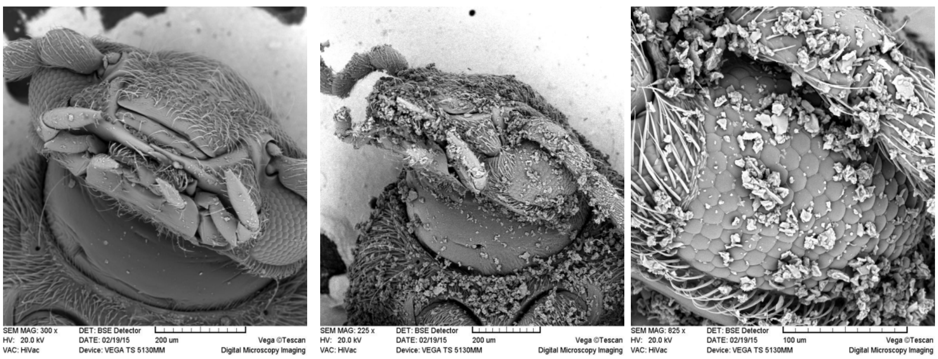

Figure 2. SEM images of untreated (left), treated with Al_2O_3 (middle) and enlarged image of insect treated with Al_2O_3 (right).

As for the development of F_1 generation, all the powders exhibit more or less similar effect (Figures 3a and 3b). The number of larvae hatched from eggs under treated conditions was reduced over 50 %. These results are in accordance with the percentage of damaged seeds as a consequence of larval activity. It is interesting to note that TiO_2 powders, being almost harmless to adult insects, appeared to be as equally lethal against larvae as the other powders. The latter results confirmed the pesticide effect of these non-toxic compounds against *A. obtectus*. Furthermore, the percentage of damaged seeds can be observed as the main indicator in pest control since it dictates the quality and quantity of the stored products. Although the zeolite powder kills the most adult insects, it affects the activity of survived larvae as much as the other powders. Finally, powder concentration of 1 % is probably too low for *A. obtectus* since it is more robust and therefore less susceptible than *Sitophilus oryzae* (L.) or *Rhyzopertha dominica* (F.), whereas this concentration was used as maximal in the work of Stadler et al. [5, 6].

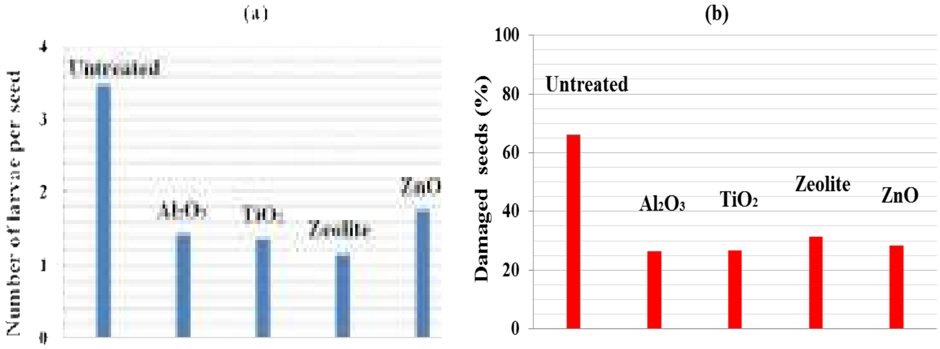

Figure 3. Development of F_1 progeny: number of newborn larvae per seed (a) and percentage of damaged seeds (b).

CONCLUSIONS

In this study, comparative toxicity of various inorganic compounds for *Acanthoscelides obtectus* was successfully carried out. The zeolite powder was the most efficient against adult insects, reaching 100% mortality after 6 days of exposure for males and 7 days for females, compared with 15% (males) and 5% (females) mortality of the untreated insects after 7 days. On the other hand, all the powders exhibit similar toxicity level against larvae and percentage of the damaged seeds was significantly reduced, and therefore can be used in organic production, especially in seed production. It was also observed that TiO_2 poses almost no threat to adult insects, while is lethal against larvae as much as the other powders. Al_2O_3 is promising since it is cost effective and fairly effective against *A. obtectus.* The efficiency of these compounds can be enhanced by introducing various synthesis methods with aim to obtain powders with appropriate particle size and increased specific surface area.

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ECOREMEDIATION - THE CONCEPT OF SUSTAINABLE MANAGEMENT OF NATURAL RESOURCES IN AGRICULTURE

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ABSTRACT

Ecoremediation, as the concept of sustainable management of ecosystem is analyzed in terms of agricultural development in the Republic of Serbia. An integrated approach to the management of biological and water resources and land registers, given by the strategy of agricultural development in the next 10 years, should enable rural development, security of food and energy supplying, with maximum preservation of the environment. Measures of modern agriculture and permaculture in terms of bio-rational use of resources are analyzed. The way to connect ecoremediation and operational objectives of agricultural development was also analyzed in the case of agroenergetic crop production.

Key words: ecoremediation, sustainable development, agriculture.

INTRODUCTION

Word ecoremediation includes two terms: Eco with the same meaning as in ecology or economy and remediation that mean healing, rehabilitation and reconciliation. The first part indicates to the rationally resource management and the second part overcoming the gap between the needs of man and nature resources (ecosystem). The meaning of the term ecoremediation (ERM) is use of natural processes in the protection and improvement of ecosystems. Using of ERM technology can reduce or annul the effects of anthropogenic destruction from tourism, transport, agriculture, industry, urban areas, mining and it provides improvement and remediation of degraded areas and / or protection of natural capital with the "white" and "black" aspect of ecology.

ERM is also a method of integrated ecosystem management that allows the preservation, treatment and improvement of some or all components of the ecosystem, relying on its natural sustainability, through the dynamic change of structure [1].

Aspects of preservation and development of natural resources will be considered in terms of ecoremediation based on facts from the Strategy for the Development of Agriculture and Rural Development of the Republic of Serbia for the period 2014 to 2024th, which includes the protection of the environment, and as one of the five priorities defined the realization of economic, environmental and social goals of sustainable development.

ECOREMEDIATION IN BIORATIONAL USE OF RESOURCES

Although **water** supplying was not affected, water quality is not satisfactory and the water is not used for irrigation of agricultural crops, which is reflected in their yields, especially in the dry season (which are more frequent) and arid areas (which are growing rapidly). Main sources of pollution are: untreated industrial and municipal wastewater, drainage water from agriculture, water from the landfill, as well as pollution related to river navigation and operation of power plants. Less than 10% of the population is covered by some form of wastewater treatment, less than 5% of the population has access to adequate wastewater treatment. For now, there are no regulations to define the nitrate-vulnerable zones, nor the decision to initiate establishing zones that are threatened by nitrates (mainly from agriculture) [2].

Most of these problems can be solved by building ecoremediation facilities for processing moderately polluted wastewater. These facilities, which operate on the principle of natural wetlands and contain biologically active principle based on the synergy of microorganisms and plants activity, are solution that is fully in harmony with the environment, low-cost construction and maintenance, energy and resource efficient. It is particularly suitable for waste water from households and from farms on sites that have enough space. These facilities provide clean water that can be reused (important because of climate change), biomass (use as a fuel) and the protection of surface and groundwater [3].

The area of the Republic of Serbia is characterized by high genetic, species and ecosystem diversity but there is no centralized database or coordinated biodiversity monitoring system at the national level. Genetic resources are very rich and include a large number of indigenous varieties and breeds of cultivated plants and animals. The local agricultural organizations keeps about 15,000 samples of cultivated plants in the form of seed and about 3,500 samples of fruit trees and vines. National ex situ collections of plant genetic resources, managed by the plant gene bank, containing a total of 4,238 samples, and there are about 1000 wild relatives of cultivated plants, *in situ*, in the nature. Nevertheless, more than 400 known species of medicinal plants, 150 protected plant species are registered in the Republic of Serbia , and there is a great potential of plant species (about 1,800 honeybee species) and ecosystems, as well as habitat for pollinators (bees, bumblebees) which are used in agriculture [2].

Forest ecosystems contain 282 tree species, approximately 250 are indigenous,88 wild fruit tree species in 18 genera. 212 seed stands were isolated from a total area of 1865 ha as a form of in-situ conservation of the genetic diversity of forest tree species, as well as its directed use. Animal biodiversity of the forest ecosystem is characterized by the 46 species of amphibians and reptiles, 350 species of birds and 94 species of terrestrial mammals. There are 2.25 million hectares of forests in the Republic of Serbia, which makes 29.1% of the total territory. The condition of forests is unsatisfactory, in terms of forest cover, which is behind the optimum (41.4%) and the lack of overall value of appealing timber volume and annual increment [2].

Abovementioned data clearly show that this sector needs ERM approach. Namely, forest resource is still considered primarily from economic aspect the values is determined only according to tree volume that can be exploited, and other functions of forests, like general usefulness and ecological function, are overlooked. To easier notice and compare real values of forest ecosystems it is necessary to evaluate all values of forests with appropriate methodology, for example according to Viskot that enables economic valorization of the services of forest ecosystem as a whole. This methodology has to be implemented in the forestry development programs [4] [5].

AGRICULTURAL AREAS OF HIGH NATURAL VALUE (HIGH NATURE VALUE FARMING - HNVF)

HNVF areas cover 1.187 million hectares, which corresponds with part of around 19% of total agricultural land and 13% of total territory of the Republic of Serbia. In the Republic of Serbia there are ten types of valuable area connected with agricultural systems: 1) deciduous forests with high content of lawns; 2) winter nomadic pastures on ruder habitats and stubble; 3) semi-natural and man-made meadows used for hay production; 4) semi-intensive grazing of highland semi-natural pastures in the forest zone and at natural lawns above forest area; 5) extensive nomad grazing of highland pastures; 6) extensive grazing at rural outfalls; 7) combined use of mountain pastures; 8) deciduous forests trimmed for lisnik; 9) extensive grazing at light, salty or heavy soils; 10) grazing at moist fields in lowland areas [2].

Contemporary agriculture has two basic goals: maximum productivity and maximum profit. To achieve these goals, a number of agrotechnical measures are used: intensive soil tillage, crop rotation (regular rotation of plant species on a specific field), irrigation, application of mineral fertilizers, complete control of weed including chemical measures, pests and diseases and genetic manipulation of crops [6].Each of these measures has its contribution to productivity increase, and as a system of measures they complement each other and make an interrelated unity. The transition from so called intensive agriculture with the only goal to achieve maximum yield in plant and animal production to permaculture with the goal to maximally use all ecosystem services during a long time period has to find its place in plan documents as well as in consciousness of agricultural manufacturers and food consumers. It should take into consideration that permaculture and organic production are not synonymous. In organic production there are standards that are related only to food production on a certain location. Permaculture (permanent agriculture) insists on ecosystem approach to food production and at the same time using other ecosystem services which achieves ecosystem sustainability [7]. Permaculture is actually reintroduction of culture in agriculture. This method brings lower yields, the production is work intensive, and with choosing this approach we have to take into account all ecosystem services. It should be emphasized that the methods used in systems of sustainable agriculture: intensifying of crop rotation,joining crops, cover crops, introduction of more leguminous plants in crop rotation, etc. The state of agrobiodiversity is seen in the number of newly created sorts and local populations. On a national sort list of the Republic of Serbia there are around 5000 sorts of around 200 plant species that are grouped in the following crop groups:

small grains and corn, industrial plants, forage plants, vegetables and fruits and grapevine. The return of sort agrotechnics with full respect of uniqueness of every genotype and application of proper and timely technology of production is the path to recovery of plant production [8].

Priorities are made for future development of agriculture with – *Protection and improvement of the environment and preservation of natural resources* in unbreakable bond with ecoremediations.

Reforms are necessary for achieving sustainable agricultural practice (agroecological measures, agroforestry, integrated natural resource management, integrated plant protection, soil fertility, sustainable water management, organic agriculture), application of the laws and regulations for pollution prevention, preservation of soil and water, control of non-selective conversion of arable land to other purposes, protection of forests and areas with valuable natural resources.

OPERATIONAL GOALS ARE TIGHTLY RELATED TO ERM

1. *water protection from negative influences of agriculture* – Development of permaculture as well as system for cleaning water, soil and air with application of ecosystem processors – constructed ecosystems that energetically, economically and resource efficiently preserve the qualities of media of the environment.
2. *more application of agricultural practices* (application of agrotechnical measures and technology) good for the environment – primarily reduction of artificial mineral fertilizers use and over-cultivation of land with heavy machinery
3. *establishing and promoting the system of integrated production* – Through the practice of permaculture and maximum respect of national tradition in that field
4. *improvement of organic production,* control system, certification and monitoring in organic production;
5. raising awareness on importance of use of renewable energy sources and production of *energy crops* – Production of energy crops, either agricultural or forest cultures enables valorization, primarily marginal soil that are not suitable for food production and provide local perennial source of energy [9]. In Serbia there is around 30.000 hectares of degraded areas. Their exploitation is insignificant, which has significant impact on domestic agriculture. The dynamics of degraded areas is 4000 hectares of agricultural areas destroyed every year. The most damage to soil is done by mining, surface mining, industry, roads and hydroaccumulations, landfills and barren soil. Production of energy crops, millet and miscanthus as energy crops and willow and poplar as a forest cultures in in the fast opjhodnji is recommended primarily on marginal soil as green technology. The products of burning biomass are cleaner in comparison with products of fossil fuels burning, while in the cycle of growing there is usage of SO_2during photosynthesis, which is an advantage of biomass use as an energy source [10]. Perennial energy crops contribute to preservation and increase of soil quality and they also have clear remediation potentials.

6. controlled *waste management* from primary agricultural production –the remains of primary agricultural production are one of steps in biogeochemical cycles of elements so their use is directed to energy production and organic fertilizers as an alternative to industrial with preservation and improvement of soil and water resources.
7. development and improvement of the system of *food industry byproduct management;*
8. preservation and sustainable management of plant and animal *genetic resources–* genetic resources of an area are a consequence of a long evolution of plant and animal species adaptation to local condition of the environment and traditional selection. The principle of ecoremediation emphasizes local sorts and species because they use natural resources in the most rational way with respect for ecosystem balance and by that they produce biologically more valuable food in comparison to highly selected sorts and species in intensified agriculture [11].
9. landscape preservation, agricultural areas of high natural values and their resources – preservation of area through preserving structure and function of ecosystem, whether they are natural or influenced by human [12].

ERM methods have the following advantages: 1. for their introduction and realization there is no need for significant investments and they don't impact the environment in any way (they are natural in functional and aesthetic manner); 2. they have multipurpose effects: water retention, pollution reduction, regeneration and preservation of ecosystem and biological diversity; 3. they include simple, understandable and environmentally safe and acceptable actions; 4. they act like addition of existing systems for pollution prevention; 5. they enable treatment of potable water and water for recycling (e.g. for irrigation); 6. prevent quick drying out; 7. they establish softening (buffer) area (e.g. air barriers); 8. they also include vegetative zones and swamps besides water flows.

These facts will be used for obtaining financial incentives, as well as a number of activities to increase awareness of producers about the necessity of protection and improvement of the natural resources in the field management. This includes the protection and conservation of soil, air quality, groundwater and surface water, habitats of wild flora and fauna, traditionally rural areas and the agricultural land of high natural value [13].

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DEVELOPEMENT ORGANIC FOOD PRODUCTION IS PARAMOUNT FACTOR VS GENETICAL MODIFICATION FOOD (GMO)

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ABSTRACT

During the period of world, as well as domestic economic crisis every project, like the one which will be presented here, can play an important role in making strategic decisions of society about new developmental programms. Namely, the market instructs us to find the solutions, particularly in the form of enriching the offer of products, which are very important in population nourishment and prevention against the modern seaknesses of humanity. The solutions have to be searched for in the frame of available and renewable resources. Therefore we are faced with an open question of detecting and defining all the relevant factors, which will make the significant contribution to the successful project realization and goal accomplishment. Although the market is one of the relationships regulators in market economy, it does not necessarly mean that the market can solve all the problems by itself. So, there is a need for additional measures, which belong to the state as a system, because the state, by making the proper ambient for work, becomes, more or less obviously, the important partner. Therefore we consider that the concept of sustainable development has to be stressed even more, because the world economic crisis has shown that the neoliberal economy should be directed, in order to achieve the rational exploitation and continual renewal of natural resources. That is particuraly important for developing countries, like the Serbia. The recent acceptance of the project „Plum - national brend“ additionaly confirms that also on the highest state level there is the understanding, recognition and support for such development concepts and strategies.

Key words: organic food, organic food market, the economic crisis, projects of organic food country like a partner

BASIC CHARACTERISTICS OF ORGANIC FOOD

The food produced according to the principles of organic agriculture does not contain any artificially synthesized substances or pesticides. Rather, this food contains larger nutritional values from the food produced by conventional production. Research carried out by German laboratories has shown that organic food products have a significantly higher content of oligo minerals, especially potassium and iron, as well as higher levels of magnesium, phosphorus and vitamin C. Similar results have been obtained by American laboratories, which found that these products have 63% more potassium, 73% more iron and 125% more calcium than the products produced in conventional agricultural production processes.

Organic food, therefore, is based on biological control and the suppression of the use of any kind of chemical substances. That, further, entails a healthy soil, chemically untreated seeds, and the prohibition of using any kind of spraying products. Due to high demands set on the farmers, it is expected that only a smaller number of manufacturers can meet the specified requirements. The goal of organic agriculture is to strengthen the link between the town and the country by recycling nutrients and humus. The two basic characteristics of ecological agriculture are care for the basic functions of nature and the idea of global solidarity.

During the period of seven years, the network of environmental associations has been spreading in Serbia. These are the manufacturers which have opted for a safe production on the one side, and an uncertain placement on the other side. For example, the total organic fruit demand was greater than the supply on the Belgrade market. It is a good sign that the consumers have made a big step forward in determining these kinds of products, so the manufacturers from this production area can count not only on exporting but also on a strong domestic market.

Our experiences are showing us, in the same context, that in the offer of organic food products and their production for the market (and profit as a goal) the costs of production are reduced to an acceptable size. Namely, the fields in which organic soybeans have been planted for the first time in our country were far from industrial sites and lacking in any chemicals, although nearly overgrown by weeds. The average yield results on those parcels were 10t per ha, and the price was about 30 RSD per kilogram, while, for a kilogram of conventional soybeans, the price was 12 RSD. Thus, the demand for organic soybeans certified as healthy products, with no chemicals and polluters, recorded a high growth, which counts as stability and justifies investments.

And equally, on the other hand, the manufacturers of raspberries with organic production certificates, had no problems with exporting and the price on the European and world markets. Thus, various protests are only a waste of time and energy, while specialization of organic production brings profit.

In the Worldwatch Institute's report for the previous year, special attention was paid to the wasting of arable land and the waste of cereals via inefficient use. For the nutrition of the world population, about one quarter of the arable land would be sufficient. On one ha of land, 50 kg of beets or 4,000 kg of apples, 8,000 kg potatoes, 10,000 tomatoes or 12,000 kg of celery can be produced.

Meat consumption in the world has increased dramatically, as great forests are being destroyed to extend pasture lands. On the other hand, a half of the world's harvest is spent on fodder. In industrial countries, the share of fodder is a huge two thirds of the production. About 60% of the total import of fodder comes from developing countries, where about 40,000 children starve to death every day, and 1.3 billion people suffer from malnutrition, while in one year, 50 million people starve to death, or are dying from a disease caused by starvation (Source: FAO- Food and Agriculture Organization of the United Nations).

About 90 million ha of global land will have to be transformed into agricultural lands until the year 2011, in order to achieve a global food supply. A half of these lands will be deforested, which may have negative consequences on the global climate conditions and biodiversity. In the present conditions, another danger for the planet is the loss of agro-biodiversity, and that, apart from the other factors, causes pesticide usage and conventional fertilizers which contain toxic substances.

ORGANIC FOOD PRODUCTION IN THE WORLD, WITH A SPECIAL REFERENCE TO FRANCE

Organic food is produced either fresh or processed, depending on the processing method.

Fresh unprocessed organic food, like fruits and vegetables, can be bought directly from the manufacturers at market places, supermarkets, health food markets, health food stores, etc. Unprocessed products such as products of animal origin, meat, eggs, milk, etc., can rarely be found fresh.

Most of the products which can be found in the supermarkets are considered to be processed organic food. Occasionally, it happens that organic food is placed together with conventional food, but they differ by price, organic food being more expensive. The better part of organic food comes from major food manufacturers which also produce and sell canned food, frozen fruits and other types of conventional food stuff.

In the world, processed organic food occasionally contains only organic elements without artificial additives and is produced by applying several methods and special materials under special conditions. This process does not involve chemical and conventional methods of processing. These products are potato chips, cookies and different types of snacks, as well as oat flour, buckwheat flour, etc.

Demands for this type of food are growing on the world organic food market. Even if it took only about 1% of the total world market, a large increase would be noted in numerous segments of its consumption. A profit of some 45 billion dollars has been noted per year from organic food (Source: FAO).

About 31 million ha is used for growing organic food in the world. Regarding leading countries with a high technical, technological and health culture, a large part of their credit potential is directed towards creating smaller or bigger farms. According to FAO data, at this moment in the world some 120 countries are producing organic products. This involves about 0.7% of arable land, which means that there are 634,000 farms on this land.

In the world, organic food development trends are clearly defined. This is understandable, say the experts, considering the measures and the processes which are used in conventional production: intensive land treatment, growing only one sort over the large areas (contempt for crop rotation), mineral fertilizers use, chemical control of weeds, pests and diseases, and genetic manipulation of cultivated plants, as they have as a goal productivity increase. But these activates question the conditions which will contribute to the long term maintenance of soil fertility.

Table 1. The countries with the largest areas where organic food is grown

Country	Areas under organic agriculture (ha)
Australia	11,800,000
Argentina	3,100,000
China	2,300,000
USA	1,600,000
Italy	1,200,000
Brazil	845,000
Germany	700,000
Austria	300,000
Switzerland	110,000
Hungary	105,000
Serbia	6,000 +9,000= 15,000
Bosnia and Herzegovina	1,150
Croatia	120
Europe – total	6,900,000
European Union	6,000,000

Source: *FAO, EBRD, World Bank.*

Regarding Serbian indicators, the size of 6,000 ha and plan for an additional 3,000 ha, and the 6,000 ha which are under investigation and monitoring, is not satisfactory. Compared to the total area of 4.2 million ha of arable land, this is a mere 0.3%.

The growth of the area under organic food is the most marked in North America and Europe. The structure of the products under organic food is:

- Organic citrus...Italy
- Coffee...Mexico
- Cocoa..Dominican Republic
- Grapes...Italy, Spain, France
- Olives..Spain, Tunisia

With government support, the natural potential, and due to culture and tradition, developed countries lead in the development of organic food production. Besides 31 million ha of arable land, wild fruits also grow on the 62 million of uncultivated land. The biggest part is taken up by bamboo shoots (36% of the total fruits), wild and berry fruits (21%) and different kinds of nuts (19%).

Serbia has the potential to be the world leader in collecting organic juniper, as well as ecological grapes, soybeans, and some other kinds of agricultural crops (cabbage, peppers).

Organic agriculture in Europe

At the beginning of the 90ies, a rapid development of organic food production started in European countries. Since the year 2005, development has increased. On 6.9 million ha in Europe, organic food was produced on 160,000 farms. In the European Union, 6.3 million ha (on 160,000 farms) was cultivated, this being 3.9% of the total farming land. The country with the largest number of farms and the largest areas under organic food is Italy.

Support for organic agriculture in the European Union includes grants within the program for rural development, legal protection which gives a recently reviewed regulation on organic economy and the realization of the European Action Plan for Organic Food and Farming from the year 2004. The countries which are not co-opted into the European Union had similar support.

Table 2. Organic food world markets in millions of Euros

Markets	Retail in 2003 Euros	Percent of organic food sales (assessments)	Expected annual growth in 2003 - in percent
France	1,300	1.0-1.5	5-10
Germany	3,100	1.7-2.2	5-10
Great Britain	1,750	1.5-2.0	10-15
USA	13,000	2.0-2.5	15-20

Source: Yussefi@Willer, 2003, p. 24.

Switzerland has the largest share of organic food on the market, and the biggest consumers of organic food in the world are the Germans, the Italians and the French. The citizens of Switzerland spend 100 Euros per person on organic food.

But on the other hand, the development of the European market has the going rate of 10-15% per annum. The value of the organic food market in Europe is estimated at 15-16 billion Euros.

Features of the French organic food market

The consumption of organic food in France has definitely shown dramatic growth, thanks to French consumers. After 1980, the position of France as a leader of organic agriculture had gradually decreased, until the middle of the 90ties. That reduction, however, is a consequence of nonexistent government support, a decline in demand, an inefficient manufacturing and processing sector, and a high level of ineffectiveness as well as a poorly developed distribution system. Furthermore, this sort of situation lasted until the mid-90ties. A five-year French government action plan stimulated the expansion of organic manufacturing, and the number of farmers and arable land transformed into organic agriculture increased dramatically during 1998 (USDA – American agricultural service report 1999).

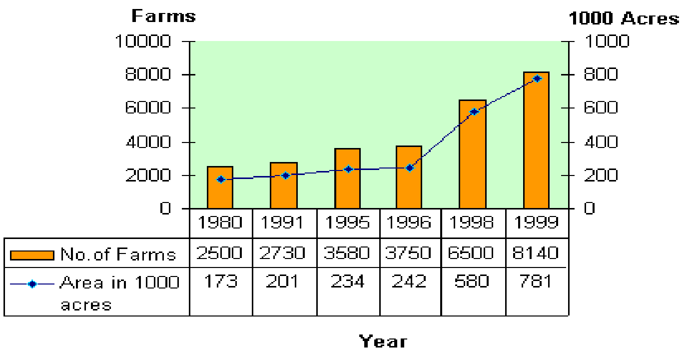

Figure 1. The number of farmers and arable land transformed into organic agriculture

Even with the food manufacturing growth in France, there is still a need to import large amounts of organic grain (mostly from Central Europe) in the aim of satisfying these demands. Otherwise, this country is on the fourth place in Europe regarding organic agriculture, after Italy, Germany and Austria.

The newest research of the Association for Organic Food in France shows that with 10 ha of organic manufacturing, high incomes on 100 ha of conventional production could be reached.

Production and the organic food market in Serbia

Organic food production projects in Serbia are mostly innovative. The total fund of arable land in Serbia is about 4.2 million ha. From that amount, 6,000 ha are already cultivated for organic food production and 9,000 ha have implemented works for the preparation of oil for that type of production, so soon there will be about 15,000 ha. This is by no means a big number, but it is important that it is a beginning and that improvement will ensue. However, if we compare this with the European average, it is 13 times less.

Regarding the structure, organic certification of soil is carried out on 2.400 ha. There are 2.155 ha under conversion (transferring organic standards). If we consider that Serbia has a huge experience in crop production, that it has good climate conditions and land potential for organic food production, it can be said that it has a good base for a dynamic production development.

In order to obtain a certificate for organic production, the soil should not be treated with chemicals for at least three years. Instead, it should be treated and primed with organic fertilizers, either biological or fluid, and furthermore, recently, great results have been obtained by soil treatment with zeolites. These are minerals which, as great absorbers, reduce the time of soil purification. Serbia is rich with zeolites, and they are also among the best in the world, nearly on the same par as those from Australia.

In the report by the Ministry of Science and Environmental Protection for the year 2002, it is claimed that 651,000 ha are fit for organic production. On the sample of 868ha of the examined land, satisfying results have been observed, meaning there are no heavy metals, pesticides, or residues of classically produced mineral fertilizers. Moreover, the soil is not polluted or acidified. This especially relates to hilly and mountainous areas, and brands can be created such as: "Ivanjica potato", "Zlatibor prosciutto", "wine from Rajac breweries", "Futog cabbage", "Leskovac paprika", etc.

If, on the other hand, we look at the development concept of organic production, we can ascertain that such an approach can reduce the differences between our underdeveloped or less developed areas and those which have a highly developed conventional, and now also organic food production. The dispersion of organic food production would significantly impact the export products' performances, which would, via constant production improvement (by way of educating manufacturers) exert some influence on consumer awareness and the potential habits in the consumption of this type of effective agricultural production.

However, Serbia is deficient in knowledge of the work organization system, and not only in the mentioned activity. Namely, organic production requires an exact division of labor, from production to consumption. Researchers from this project were pleasantly surprised by the realization that there is a huge interest for interest-based associating. Not even the start-up production funds were a problem. The manufacturers, or future manufacturers, only insisted on the facilitating of placements. They had their own resources for the purchasing of the machines and devices, and are ready to reimburse the experts which will follow the annual production on all levels (there is a possibility of three harvests per year in certain production areas). As the winegrowers are recompensing enologists as well, they can also remunerate experts for insight into field and vegetable crops. Moreover, some 20,000 to 40,000 people of different professional groups can be employed on these projects, from the primary production to the market and products consumption.

The biggest percent of the land under organic production in Serbia grows vegetables (about 70%). Vegetables are grown on the farms which are not highly specialized, which in effect are the majority of the small farms. The normal use of these products is about 500 g per person and in Serbia, this amount is about 150-200 g. Due to a lack of basic vitamins, metabolic diseases occur, and it is a well known fact that nutrition impacts human health. Also, vegetable production is located in the valleys of the major rivers as well as in the lowlands and nearby cities, where there are shopping malls which trade with the largest amount of these products. The highland areas reduce the types of vegetable crops which can be grown, but the microclimate in those areas reduces the appearance of some diseases and pests which can cause big problems in these areas.

STANDARDS, CERTIFICATIONS AND ACCREDITATIONS

In 2006, the institutional frameworks in the world had a very important task in the area of developing legal regulations for organic agriculture. The process of revising UN Rule Book 2092/91 about organic agriculture attracted the attention of experts and international institutions. The adopting of this document has enabled more than 60 countries in the world to benefit from the Law on Organic Manufacturing, including Serbia.

Within the current activities, 395 organizations around the world offer services for certifying organic food manufacturing. Most of these organizations are in Europe (160), in Asia (93) and in North America (80). The countries which have the largest number of certifying bodies are the USA, Japan, China and Germany. Numerous certifying bodies act outside of their mother country, 40% of them are confirmed by the European Union, 32% possess 180 85 (code) accreditation, and 28% are accredited on the basis of the US national organic program.

Considering the fact that there is no unification of accreditation documents, this represents a huge problem in further commerce development, market development as well as in establishing trust between the various factors on the market. Thus, this is the reason why the Accreditation Program of IFOAM which estimates certifying bodies according to IFOAM norms (the basic standards of organic agriculture) is an important initiative for international harmonization. At this moment, 32 certifying bodies which act in more than 70 countries around the world have accepted the process of IFOAM accreditation. Also, recently formed was an international body for harmonization and uniformity in organic agriculture which as its goal the achieving of a general consensus on the harmonizing of private standards and regulations with those issued by the governments of certain countries and the world at large.

CONCLUSIONS

1. Modern global trends regarding healthy nutrition and the production of those kinds of products are becoming more and more significant.
2. In this context, Serbia has taken appropriate measures and it is the first time for us not to be late on the world market.
3. In Serbia there are conditions for practicing organic food manufacturing of the most different scope and types of products.
4. From 4.2 million ha, around 610 thousand ha is available to be, in a short timeframe, directed towards organic food production.
5. Today in Serbia, organic food is produced on about 15 thousand ha, which represents a mere 0.3% of arable land.
6. With an appropriate upgrade of the system conditions of economic activity on the side of the state and eventually, by establishing partner triangular relations (manufacturer, market, state) exporting and a foreign exchange flow could be achieved.
7. The organic product prices on the domestic and international markets are higher by about 30-40% compared to the prices of conventional products.
8. Human resources for this kind of production do not exist.
9. There are also all types of planting materials.
10. It is necessary to carry out a regionalization of the production of certain crops, as it is already done with viticulture, raspberries, plums, etc.
11. The support of the system's economic activities (subventions and other support) can be done with the help of the following parameters:
    - 200 euro/ha for the costs of certifying
    - 600 euro/ha for biological protection equipment
    - 800 euro/ha for an increase of labor costs
    - 350 euro/ha for marketing costs
12. A tax amount of 8% in the beginning of the production process.
13. A tax amount of 8% for marketing and promotion activities.
14. The mark-up should be limited to a maximum of 25%.
15. Display of goods on the market shelves and organized green markets should be provided at 30% of the available retail space.
16. The interest rate for the procuring of machines and planting material should be around 1.5-2% per year.
17. For larger investment activities in the production part, a grace period of 3-5 years should be provided, depending on the type of production and the beginning of product exploitation.
18. The organization of organic production products should be accomplished through interest associations of the cluster type, which, with joint policies, can compete on the international market.

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EFFECT OF MICROBIAL FERTILIZER APPLICATION ON YIELD OF BEAN (*Phaseolus vulgaris L.*) IN ORGANIC PRODUCTION SYSTEM

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ABSTRACT

Research was conducted in organic production system in location of Backa Topola with two bean varieties. Experimental field trial was set by split-plot model in four repetitions. Varieties were on big plots and on sub-plots were three variants: control, application of liquid microbial fertilizer by soil treatment and two times during vegetation. Data were statistically analysed by analysis of variance using two factorial split-plot experiment, and significance of differences between the treatments was tested by LSD test. The aim was to determine influence of genotype and effect of microbial fertilizer application on grain weight per plant and 1000-grain weight.

Key words: 1000-grain weight, beans, microbial fertilizer, organic production, yield.

INTRODUCTION

Bean is one of the basic vegetable cultures used in human diet. By its nutritional values, bean is one of the richest aliments with plant proteins, carbon hydrates, fibres and minerals (Fe, Ca, Sn, Mo), and it is biologically the most valuable in human diet [1]. In structure of total vegetable consumption in Serbia, bean takes 4.3%. World level of bean consumption is 2.4 kilograms. In Europe consumption is very low and it is 0.7 kilograms, which is for 4.5 kilograms lower than in Serbia. Bean consumption is increasing in Serbia [2].

Organic production is based on modern scientific understanding of ecology and agriculture and completely supports and follows technological development and mechanization. Products grown this way are of high quality, safe for human health and the production itself contributes to environment protection. That is why is evident the increase of number of researches that are oriented to application of alternative measures in plant production to avoid unwanted consequences. One of the measures is application of microbial fertilizers [3]. Intensification of soil biological activity is also contributed by microorganisms which have defensive and stimulating effect on plant growth and development and its yield as well. In our country, until now, soybean was the most common legume in stubble crop sowing [4, 5]. Numerous researches show that one part of soybean could be replaced by bean, especially from point of view of higher economic effect [6, 7].

Application of microbial fertilizers represents inoculation of living organisms in soil with aim of improvement, providing necessary nutrients to plants. This way can increase availability of nitrogen, phosphorus, potassium, iron, sulphur and plant growth stimulators. Organic matter transformation accelerates. Besides these stimulators they contribute to: more rapid and direct decomposition of plant residues, nitrogen fixation, decrease of carbon dioxide concentration in soil, decrease of root affixation possibility, release of elements from difficult available to easily available forms.

The aim of this work was to determine influence of bean variety (genotype) and effect of liquid microbial fertilizer application on grain weight per plant, 1000-grain weight, correlation dependence of important bean properties and define optimal variant of bean treatment by effective microorganisms, which will enable high and stable yield in organic production system. Also, the aim was to determine which genotype is advisable in organic production for agroecological conditions of the North Backa county.

MATERIAL AND METHODS

Two varieties of beans were used, created at the Institute of Field and Vegetable Crops in Novi Sad:

Maksa, late low variety, suitable for two-phase mechanized harvesting. The grain is cylindrical in shape, approximately 1.5 cm, white. 1000-grain weight is 440 g. It has satisfactory yield even in the stubble production. Germination percentage is 97%. Has a low branching bushy tree. Long flower stalks, flowering and pod setting is largely outside the foliage.

Zlatko, determinant growth, the length of vegetation season of up to 75-80 days. Flowering lasts for two weeks. The stem is erect, up to 45 cm. Ripe pods do not crack. The grain is golden yellow in colour, cylindrical shape, large. 1000-grain weight is about 450 g. Cooked beans retain their shape, and the seed coat do not slip off.

Experimental field trial was set on experimental plot of Faculty of Biofarming in Backa Topola, on calcareous chernozem after potato as preceding crop. The trial was set by split-plot method in four repetitions, where on big plots were varieties (Maksa and Zlatko), and on sub-plots: treatments with liquid microbial fertilizer containing mixture of different kinds of microorganisms (lactic acid bacteria, photosynthetic bacteria, yeasts, actinomycetes, mushrooms). Soil was treated with microbial fertilizer, dose of 30 lha^{-1}, one week before sowing, and during vegetation in pheno-phase of three to four trifoliate leaves and at the beginning of flowering period with 4 lha^{-1} .

Before sowing and after harvesting N-min analysis of soil was conducted, to determine content of mineral nitrogen in 30 cm depth. During the botanical maturity 10 plants from middle rows were chosen for analyses.

Data were statistically analysed by analysis of variance using two factorial split-plot experiment, and significance of differences between the treatments was tested by LSD test in program GenStat (Trial version). Correlation analysis was conducted between some of tested properties, as well as regression analysis of mineral nitrogen content and bean yield per plant and 1000-grain weight (Statistica 12.0).

RESULTS AND DISCUSSION

Weather conditions

Impact of ecological factors, especially climate, on yield of all vegetable crops is generally well known. Weather conditions were not favourable for growth and development of bean. Especially during the flowering phase and grain filling, when the temperatures were high and air humidity and soil moisture were low. In 2013 average monthly air temperatures were significantly deviating from multy-year averages. July with 26.1 ºC was extremely warm and during that period location of experimental trial had tropical climate (the end of July), which had unfavourable impact on bean (Fig. 1). During the mentioned period the experimental field was irrigated. Precipitation sum for vegetation period, May-August 2013, was 257.9 mm and comparing to multy-year average of 242.8 it can be considered as dry year. Amount and distribution of precipitation were not satisfactory in July and August during pod formation and filling. According to temperature values and drought intensity during vegetation period, May-August 2013, it was one of extremely warm and dry years in past few decades.

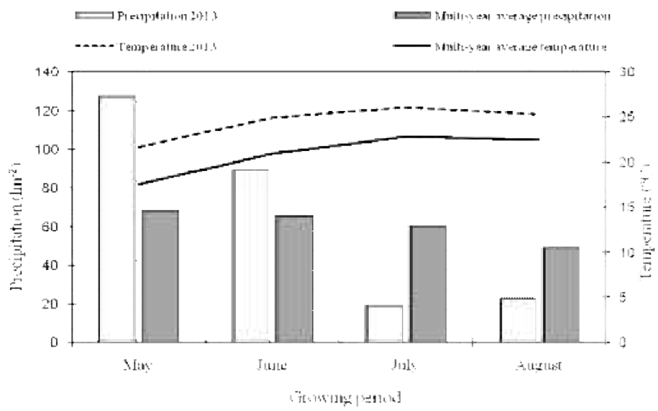

Figure 1. Weather conditions

Table 1. Relative humidity during growing beans (%)

Month	2013	Multy-year average
May	67	69
June	66	68
July	51	64
August	56	65
Average	60	66.5

Relative air humidity is important climatic factor in bean cultivation and has direct impact on yield. Reduction of relative air humidity and high temperatures are unfavourable for bean during the flowering and pod set period. In July and August relative air humidity was extremely low comparing to multy-year average (Tab. 1).

Grain weight per plant

Priority in each agricultural production is to achieve high and stable yield of satisfactory quality. In the most important characteristics of the varieties we include their production potential, grain yield, safe food quality and environment protection and preservation by using the new safe technologies in plant growing.

Table 2. Grain weight depending on the variety and microbiological fertilizer (g).

Microbial fertilizer (B)	Variety (A)		Average	Factor	LSD	
	Zlatko	Maksa	B		1%	5%
Control	10.3	11.9	11.1	A	3.3	1.8
Treatment of land	7.8	18.0	12.9	B	8.2	6.0
Treatment in vegetation	7.8	23.0	15.4	AxB	11.6	8.5
Average A	8.6	17.6	13.1	BxA	10.4	7.7

Grain weight per plant is important yield component, in other words yield per plant. Average grain weight per plant in this experiment was 13.1 g (Tab. 2.). The highest grain weight per plant had variety Maksa (23 g), and the lowest variety Zlatko (7.8 g). Variety Maksa had statistically significantly higher ($p<0.01$) average grain weight than variety Zlatko and it was higher for 105%. Similar results in their research state [8]. Application of effective microorganisms two times during vegetation showed the highest grain yield per plant (15.4 g), and soil treatment before sowing 12.9 g, which is more comparing to control which had the lowest yield per plant (11.1 g). However, determined differences were not statistically significant. Interaction AxB was statistically significant ($p<0,05$), because at variety Maksa significant difference was determined between the treatment during vegetation (23.0 g) and control (11.9 g). Interaction BxA was highly significant because variety Maksa had higher grain weight per plant in vegetation treatment than variety Zlatko. In soil treatment it was only significant, while control did not show any statistical significance.

1000-grain weight

Examined varieties had 429.9 g average 1000-grain weight (Tab. 3). The highest average 1000-grain weight had variety Maksa (471.3 g) and the lowest had variety Zlatko (356.1 g). Variety Maksa (460.5 g) had statistically significantly higher grain weight than variety Zlatko (399.3 g) and it is for 15.3%. Results which show that variety Maksa had higher 1000-grain weight were determined in researches of [9]. Variant where soil was treated with microbial fertilizer shows statistically significantly lower ($p<0,05$) 1000-grain weight comparing to other two tested variants.

Table 3. 1000-grain weight depending on the variety and microbiological fertilizer (g)

Microbial fertilizer (B)	Variety (A)		Average B	Factor	LSD	
	Zlatko	Maksa			1%	5%
Control	423.9	455.3	439.6	A	84.6	46.1
Treatment of land	356.1	454.8	405.5	B	45.0	33.2
Treatment in vegetation	417.8	471.3	444.6	AxB	63.7	47.0
Average A	399.3	460.5	429.9	BxA	72.0	52.5

Interaction AxB was significant at variety Zlatko, because in soil treatment variant 1000-grain weight was significantly, that is to say highly significantly lower (356.1 g) comparing to the other two variants (417.8 g i 423.9 g). Interaction BxA was also significant in variants where microbial fertilizer was applied. In that case variety Maksa had statistically significant larger sized grains with higher absolute weight. Control variant had no statistically significant differences.

According to results obtained during the examined year it can be concluded that application of adequate agro-technical measures, favourable climatic conditions and application of microbial preparations have positive effect on increase of grain weight, that is 1000-grain weight. 1000-grain weight, of bean mainly, is determined by genotype. Besides genotype, local climate factors also have impact on absolute grain weight.

Correlation dependence of examined properties

Correlation coefficients were calculated between following bean properties: number of symbiotic nodules (NSN), weight of symbiotic nodules (WSN), plant height (PH), number of pods (NP), number of grains (NG), grain weight (GW), 1000-grain weight (1000-GW) and yield (Y).

Table 4. Coefficients of correlation

Variable	NSN	WSN	PH	NP	NG	GW	1000-GW	Y
NSN	1.00	0.96*	1.00**	0.96*	1.00**	0.95 ^{ns}	-0.11 ^{ns}	0.98*
WSN	-	1.00	0.93^{ns}	1.00**	0.93 ^{ns}	0.82 ^{ns}	-0.39 ^{ns}	0.87 ^{ns}
PH	-	-	1.00	0.93 ^{ns}	1.00**	0.97*	-0.02 ^{ns}	0.99**
NP	-	-	-	1.00	0.93 ^{ns}	0.82 ^{ns}	-0.39 ^{ns}	0.87 ^{ns}
NG	-	-	-	-	1.00	0.97*	-0.04 ^{ns}	0.99*
GW	-	-	-	-	-	1.00	0.21 ^{ns}	0.99**
1000-GW	-	-	-	-	-	-	1.00	0.11 ^{ns}
Y	-	-	-	-	-	-	-	1.00

^{ns}non significant *significant at $p<0.05$ **significant at $p<0.01$

Strong positive correlation was determined between plant height, number of grains and number of symbiotic nodules. And also between number of grains, yield and plant height. Yield and grain weight per plant were in highly significant positive correlation (Tab. 4). The same results state [10]. Similar conclusions were obtained in researches with soybean by [11].

Mineral nitrogen in soil and examined properties

Regression analysis showed that with increase of mineral nitrogen content in the soil profile 0 to 30 cm after harvest grain weight per plant was slightly increasing, as well as 1000-grain weight. Higher mineral nitrogen content in soil after harvest, higher yield per plant and higher 1000-grain weight implicate more intense nitrogen fixation. When nitrogen fixation is more intense yield per plant and 1000-grain weight are higher and more mineral nitrogen remains in soil. Researches with soybean show higher yield with increase of mineral nitrogen content in the soil profile 0 to 90 cm before sowing [12].

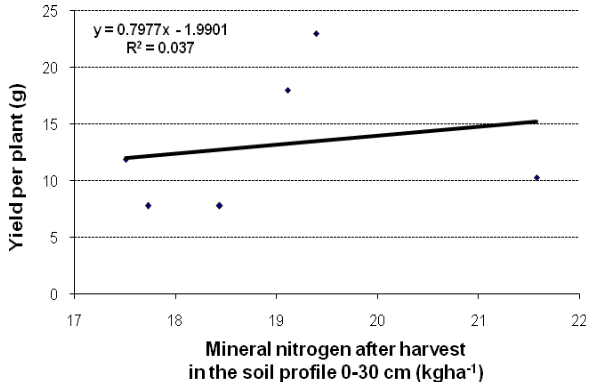

Figure 2. Dependence of yield per plant of mineral nitrogen in the soil

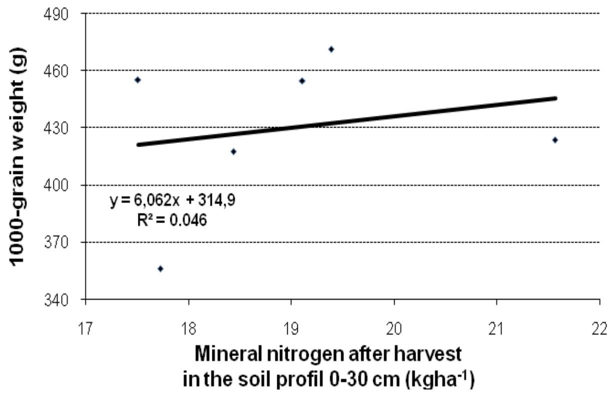

Figure 3. Dependence of 1000-grains weight of mineral nitrogen in the soil

CONCLUSIONS

Organicl beans production, as plant production with respect of environmental principles and standards, as well as specific local agroecological conditions, has its priority.

Application of modified and new technologies in crop production tends to the production of safe food, which would affect the human health in a positive way.

Ecological way of beans production has impact on the environment.

Aknowledgement

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MICROORGANISMS INDICATORS OF THE BALANCE IN THE AGRO-ECOLOGICAL SISTEM

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ABSTRACT

Microorganisms are the predominant portion of the soil's biological phase and they are indicators of soil health and quality. The primary microbial population starts to decompose herbicides several days after their arrival into the soil. The secondary population produces induced enzymes and decomposes herbicides after a period adaptation. Effect of heavy metals on soil microbial activity depends on the element, their concentration, microbial species, as well as physical and chemical soil properties.

The aim of experiment was to study the influence of herbicides, used in soybean cropping, on soil microbiological activity.

Key words: soil, herbicides, microorganisms.

INTRODUCTION

The man constantly changing nature and forms of self, and the results are negative pressures on the ecosystem. The most vulnerable resource is land. In the soil can come inorganic pollutants (fertilizers, acids, heavy metals, radionuclides, etc.), organic (oil and its derivatives) and halogenated organic substances and various xenobiotics (pesticides and polycyclic aromatic hydrocarbons, PAHs). Anything that threatens the health of the land, endangers the health and survival of man, which from the land use energy for their life and work. The land consists of four sub-systems of which one gives him the dynamics of living systems. This component is a biological character and make the microbes. Microbes as the largest group of living organisms in the soil, provide an informative assessment of health and quality of land and soil ecotoxicity [1,2]. In total transformation in the soil, microorganisms account for 60-80%. They allow cycling of matter (carbon, nitrogen, phosphorus, sulfur and other elements) and immobilization of toxic substances. Some types of microbes can be used in bioremediation, also certain types are biosensors toxic substances in soil.

Persistence of herbicides depends not only on the adsorption of herbicide in soil for organics and colloids clay, but from the activity of microorganisms that play an important role in the metabolism of herbicides. Most microorganisms of the soil has the ability to decomposition of herbicides, using them mostly as a source of carbon and other biogenic elements. The degradation of some pesticides are ranging from 9 to 116 years, and without microorganisms in the soil use of these compounds would have negative consequences for the entire living world. The primary population of microorganisms degrades herbicides after a few days of the introduction in the soil, while a secondary population to produce enzymes which to decomposition of these chemicals after a period of adaptation. Carbofuran decompose Pseudomonas, Arthrobacter and Bacillus sp. and use it as a source of carbon. The atrazine may be source of carbon or nitrogen source [3]. Ecotoxicity effects of these compounds enhance the mutual interaction with enzymes or microorganisms. Phenol compounds which produces *Pseudomonas acidovorans*, depending on the concentration and chemical structure of the pesticide, can decrease or increase the phytotoxicity of the herbicides lenacil. In research, it has been found that high doses of lenacil stop the growth of cells *Azotobacter chroococcum*, whereas lower doses have been changed form of the cell result in a decrease of synthesis of slimy substances [4].

Bearing in mind the need to use herbicides in crop production for the problems is the ability to set indications ecotoxicity of soil based on the number and activity of microorganisms.

MATERIALS AND METHODS

The five-replicate trial was set up in a randomised block design on slightly calcareous chernozem in the experimental field of the Maize Research Institute, Zemun Polje at Zemun Polje. All cropping practices were done in due time and very of high quality. Prior to sowing, the soybean seeds were inoculated with Nitragin microbiological fertiliser that encompasses highly efficient strains of *Bradyrhizobium japonicum*.

Four herbicides were applied within the crop control system in the following recommended rates: H1- flumetsulam+trifluralin, H2-oksasulfuron, H3- clomazone, H4-alahlor+linuron.

All applied herbicides are selective wide spectrum herbicides that provide lasting protection to legumes against all more important broad-leaf and grass weeds.

Soil sampling for microbiological analyses was done from the soybean root rhizosphere. Samples were taken on the 3rd, 14th and 90th day upon the herbicides application. The dynamics of the microorganisms abundance was determined on the basis of the following parameters: The total number of bacteria (UBB), distribution of *Azotobacter* (Az), abundance of actinomycetes (ACT), fungi (F) and dehydrogenase activity (DHA).

Standard microbiological methods on selective mediums were used to determine basic parameters of all alterations in soil [5]. Dehydrogenase activity was realized by modificated method [6].

RESULTS AND DISCUSSION

The applied herbicides influenced differences in amount of microorganisms and their enzymatic activity, depended on microorganism variety and reactional persistence.

The differences in reactional array of herbicide treatment were estimated by microorganisms' number (Tab. 1). The increased physiological activity and mortality of microorganisms was noted as reaction on the majority of herbicides [7]. Some microorganisms species could reduce the toxic effect of herbicides, what depend on constituents of microbiological population; physical and chemical soil properties [8].

Results confirmed in Figure 1. approve herbicide influence in examined periods, i.e. they decreased total quantity of microorganisms, in general. However, after 30 days of herbicide application H3-clomazone, H4-alachlor+linuron reduce their amount, opposite to other herbicide treatments, in which amount was increased to 5.9 do 14.2%.

Herbicide application decreased *Azotobacter* amount (Fig. 1). Hence, this bacteria is very sensitive and reacts with quantity on inhabit shift, it is good prove of all soil alterations. *Azotobacter* was reduced with the application of herbicides of type quizalofop-p-tefuryl, also found that the negative efect of prometryne on the growth and development of azotobacters was higher in the soil under sunflower than in the soil under soyabeen [9,10].

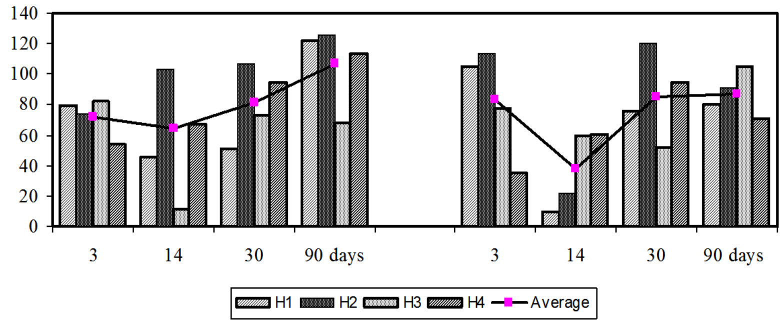

Figure 1. The effect of herbicides on the dynamics of the number of total microorganisms and *Azotobacter* (%)

It could be recognised that high amount of this nitrogen-fixator was decreased, especially after alachlor+linuron and clomazone application. The results of researchers also prove that imezatapir appliance had negative influence on noticed group of bacteria, particularly after 14 days; clomazone in combination with bentazonom reduced amount of this group to 53-80% [11,12].

The applied herbicide were reduced the number of fungi to the 14th day, H4-alachlor + linuron an average of 10-14%, but after that period they have a stimulating effect (Fig. 2). The average use of inhibited growth of the fungi to 30th day. The highest inhibitory effect was recorded on the 14th day, which is why at the end of the study period the application of this herbicide was influenced on reducing their numbers. Additionally, the herbicides stimulated *Actinomycetes* number: already, after 14 days the number was increased, continually to 30th day, with values higher to 13.7 and 20.9%. The biggest negative impact on the number of actinomycetes was with the treatment of clomazone. It is important to determine dynamism of *Actinomycetes* amount in soil, since they produce vitamins of B group and could participate in activation of physiological processes of other microorganisms.

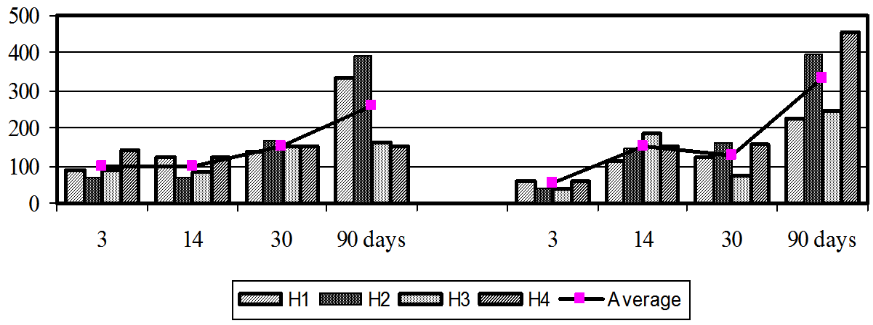

Figure 2. The effect of herbicides the dinamics on fungi and *Actinomycetes* (%)

The fungi and *Actinomycetes* are resistant to pesticide influence [13].

The herbicides generate decease of sensitive microorganisms, reverse to herbicide decomposition, supported by enzymes of microbiological population, who yielded on noted compounds and their metabolites as resources of biogenic elements [7]. It could be recognised, that primary group of microorganisms decay herbicides even after few days, while the secondary group produce adequate enzymes to rot co-products after period of adaptation.

The significan decrease of dehydrogenase activity was observed in 30^{th} day after herbicide use (Tab. 1).

Table 1. Dehydrogenase activity (μTPF.10 g soil^{-1})

Herbicides	after 30 days	
	μTPF.10 g soil^{-1}	Index level
Control	916	100
H1- flumetsulam+trifluralin, H2-	589	64.30
oxasulfuron,	626	68.34
H3- clomazone,	823	89.84
H4-alachlor + linuron	686	74.89
Average	681	74.35

The applied herbicides have contributed to the reduction of dehydrogenase activity by an average of 25.65%, which is comparable with the dynamics of the total number of microorganisms and other groups.

In field conditions show a decrease in dehydrogenase activity in soil after application dichloropropane (13%) and glyphosate [14].

The representation of the majority of microorganisms is returning to baseline after 30 days [15,16]. Disorder of ecological balance occurs if it is found reduced microbial activity after 60 days.

The tolerance of bacteria *Pseudomonas spp, Azotobacters sp*. and *Rhizobium sp.* on the pesticides endosulfan, carbofuran and maltion depends on the concentration [17]. *Pseudomonas spp.* is tolerant to the concentration of endosulfan 800 μg.ml^{-1} and the concentration of malathion 1600 μg.ml^{-1}.

Microbial activity is a good indicator of presence of heavy metals that may be present in pesticides. High concentrations of heavy metals negatively affect the soil microbial activity, and the degree of inhibition depends on the group or species of microorganisms [18]. Metal like nickl (Ni) at a concentration of 2 $mg.kg^{-1}$ soil largely stopped the growth of microbiological parameters except Azotobacter [19]. The bacteria Alcaligenes eutrophus affects the solubility of Zn, Cd, Cu and Pb [20].

In reducing the toxicity of soil can be used *Pseudomonas, Rhodococcus, Bacillus, Arthobacter, Acinetobacter, Streptomyces*, fungi *Aspergillus* and *Penicillium*.

Dominant genera of microorganisms that degrade hydrocarbons of petroleum are: of the bacteria: *Nocardia, Pseudomonas, Acinetobacter, Flavobacterium, Micrococcus, Arthrobacter, Corynebacterium, Achromobacter, Rhodococcus, Alcaligenes, Mycobacterium* i *Bacillus,* of the yeast: *Rhodotorulla, Candida, Sporobolomyces* and *Aureobasidium*, and of the mold: *Fusarium, Aspergillus, Mucor, Penicillium, Trichoderma* i *Phanerochaete* [21,22].

CONCLUSIONS

Microorganisms are constituting of the environment. Their abundance, enzymatic activity and biodiversity are good indicators of the balance in the agroecological system. To use microorganisms as indicators of changes in soil biological activity, it is necessary to find most reliable detection methods and most effective microbial strains. Microbiological research should be focused on isolating microbial strains which, on application, effectively decompose herbicides, irrespectively of the natural microbial population in the soil.

Aknowledgement

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HEAVY METALS FRACTIONATION IN AGRICULTURAL SOILS FROM THE IBAR RIVER VALLEY (SOUTHERN SERBIA): BIOACCUMULATION BY *Solanum tuberosum L.*

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ABSTRACT

In the present study, BCR sequential extraction procedure was introduced to assess mobility of heavy metals (HMs) in agricultural soils along the Ibar River Valley in the historically industrial region. Furthermore, the potato samples grown on these soils were estimated for their bioaccumulation ability. The concentrations of Pb, Zn, Cd, Ni, Cr, and Cu in soil and plant samples were determined by the ICP-OES method. The results indicated that industrial Pb/Zn production over the years significantly increased not only the total concentrations of HMs in the soil, but also their mobile and potentially bioavailable amounts. The order of the bioconcentration capacity in potato samples were Cu>Zn>Cd>Pb>Ni>Cr.

Key words: Heavy Metals; Agricultural Soil; Mobility; Potato; Pb/Zn Industrial Region.

INTRODUCTION

Mining processes, chemical industries, metal ore processes, beneficiation processes, metallurgical operations, generate various categories of industrial waste, *i.e.* mine waste low-grade ore, overburden, barren rocks, tailings, dump and heap leachings, acid mine water, *etc*. These wastes, disposed off in surrounding land, are major sources of heavy metal (HM) contamination in soil [1]. Once agricultural soil is polluted by HM, they could be accumulated into the crops, which occasionally lead to chronic and acute diseases in animal or humans.

In order to estimate the mobility of HMs in soil, it is necessary to determine their chemical forms in different soil phases along with the total metal contents [2]. This is essential because the total metal contents in soils provide, in most cases, limited information on their mobility and bioavailability [3]. The widely used way for the determination of the forms of HMs is the sequential extraction procedure (SEP) proposed by the European Community Bureau of Reference (BCR). In the BCR three-step SEP, successive application of extractants of increasing reactivity provides the selective dissolution of certain, specifically associated forms of HMs.

The region covered by present study hosts one of the most important base metal ore fields in Europe, namely the Trepča district, where Pb and Zn ores were mined extensively exploited during the past century. The legacy of all of these activities in the study area are eight tailing ponds, which cover a total area of around 170 hectares and a total weight of 44.64 million tons of tailings from the production of lead and zinc concentrates and 2.75 million tons of tailings from the production of copper and magnetite concentrates [4]. The majority of these tailings are located next to the Ibar River flow and directly threaten the environment. In this context, the objectives of the present study were (i) to determine the distributions of various HMs (Pb, Zn, Cd, Ni, Cr and Cu) in the agricultural soil using the modified BCR three-step SEP, and hence to ascertain their mobility, (ii) to define the origins of the HMs in soil based on their fractionation and correlation analysis and (iii) to investigate the relationships between HM fractions in soil and their concentrations potato tuber (*Solanum tuberosum* L.).

MATERIALS AND METHODS

Sample collection and procedures

A total of 44 soil and plant samples were collected from agricultural sites in the Ibar River Valley. The sites were selected on the presumption of a progressive decline in HMs contamination with increasing distance from the industrial facilities and the route of the Ibar River. Given this, the soil and plant samples were divided into two groups: (i) samples taken from alluvial plains (Soil 1) and (ii) samples taken at the distance from the River watercourse (Soil 2). Sampling was performed during harvesting in 2013 from the crop fields which were uniform in size and cultivated plant species. Composite soil samples (0–30 cm depth) were obtained by applying „systematic random sampling" described in IAEA [5]. Simultaneously, potato samples were collected randomly on the plot from where the soil samples were taken.

Laboratory treatment and analytical methods

The pseudo total HM concentrations in the soil and in the potato samples were determined after digestion with aqua regia and an acid mixture of HNO_3 and H_2O_2, respectively using a Milestone ETHOS One Advanced Microwave Digestion System. Analysis of the HMs contents in plant samples was performed on the peeled potato tubers. In the present study, the modified BCR three-step SEP was used for HMs partitioning into the acid-soluble/exchangeable (F_{exc}), reducible (F_{red}) and oxidisable (F_{oxi}) fractions. The performed extraction steps with the employed reagents and operating conditions for the modified BCR SEP can be found elsewhere [3]. For validation of the analytical methodology, a certified reference material (CRM-BCR® 701) was used. Both the digests and extracts were analysed by the Inductively Coupled

Plasma Optical Emission Spectrometry (ICP–OES) method on a iCAP^{TM} 6500 instrument. All chemicals and reagents were of analytical reagent grade.

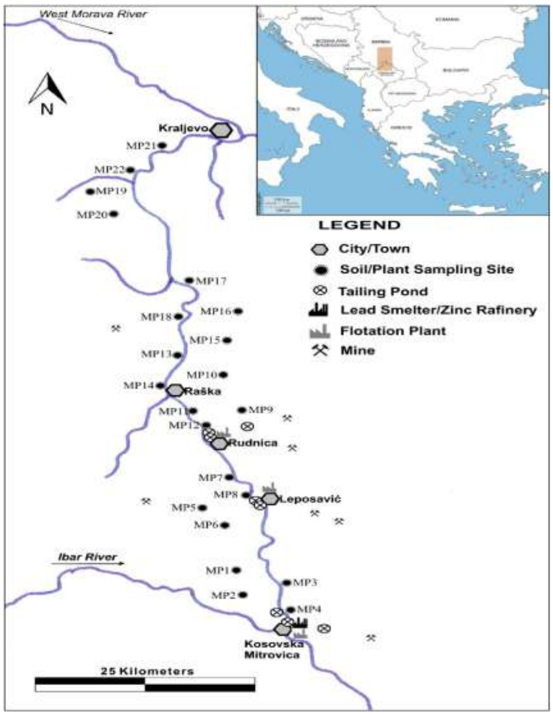

Figure 1. Map of study area

Data analysis

The Student's *t*-test and the Mann–Whitney *U*-test were used to test statistical hypotheses. Inter-element relationships in the soil as well relationships between the HMs concentrations in the potato samples and those in soil fractions were determined by either the Pearson linear correlation coefficient or Spearman rank correlation coefficient according to the normality of the data distribution. Statistical processing of the data was performed using SPSS 20.0 software for Windows.

RESULTS AND DISCUSSION

Pseudo-total metal contents in the soils

The pseudo-total concentrations for all studied metals had a wide range of values. In general, the Pb concentrations varied from 11.6–969.8 mg/kg and significantly exceeded the New Dutch List [6] target value, *i.e.* 85 mg/kg. Zn concentrations ranged from 51.9–716.6 mg/kg as well as Pb significantly exceeded the corresponding New Dutch List target value of 140 mg/kg. The most elevated concentrations of Pb and Zn in the soils were recorded in samples taken in the vicinity of the industrial hotspots: MP4=969.8 mg/kg; MP8=228.8 mg/kg and MP12=472.6 mg/kg for Pb, and MP7=543.2 mg/kg; MP8=716.6 mg/kg and MP9=650.3 mg/kg for Zn (Fig. 1). Furthermore, the Cd contents in all soil samples were 2 to 56 times higher than the target value of 0.8 mg/kg with the peak concentration of 45.1 mg/kg at the sampling point MP9 (Fig. 1). Ni and Cr levels were in the ranges of 92.7–1251.4 mg/kg and 34.2–944.6 mg/kg, respectively. However the highest concentrations of Ni and Cr were detected in northern sector of the study area that could not be associated with industrial production or industrial waste dumping: MP19=1251.4 mg/kg and MP20=1076.1 mg/kg for Ni, and MP18=400.7 mg/kg and MP19=944.6 mg/kg for Cr (Fig. 1). Cu concentrations ranged from 22.3–993.5 mg/kg significantly exceeded the corresponding New Dutch List target value of 36 mg/kg. Highest Cu concentrations were found at the sites near industrial hotspots: MP1=560.7 mg/kg, MP8=310.4 mg/kg and MP9=993.5 mg/kg (Fig. 1). The obtained results of the *U*-test indicated that the total Pb and Zn concentrations were significantly higher in the fluvial soils than those distant from the River flow: p=0.041 and p=0.048, respectively. In the case of Cd, Cr, Cu (*U*-test) and Ni (*t*-test), no statistically significant differences were found.

Correlation analysis

Inter-element relationships could provide information on the sources and pathways of HMs in soil. According to the values of the Spearman's correlation coefficient Pb and Zn were highly correlated (r=0.778; p<0.001). Cd showed significant positive correlations with Pb (r=0.456; p<0.05) and Zn (r=0.474; p<0.05). Significant correlations were also found between Cu and Pb (r=0.599; p<0.01) and Cu and Zn (r=0.626; p<0.01). These findings are in agreement with the geochemical affinity of these elements, which occurs naturally with lead and zinc in the sulphide ores galena (PbS) and sphalerite (ZnS). These facts suggests a common origin of these metals and, therefore, the mining and smelting activities and industrial waste dumping could be indicated as the sources for the soil pollution by these elements. On the other hand, Cr significantly positively correlates only with Ni (r=0.673; p<0.001). A strong relationship was observed between Cr and Ni indicating an independent origin of these two elements in the soil. Additionally, Cr and Ni are known to be geogenically influenced and originate from natural sources *e.g.* weathering and erosion of Jurassic and Cretaceous serpentinite and ophiolite rocks, Palaeogene flysch and Neogene clastic series that are enriched in these elements [7].

Chemical fractionation of the HMs in the agricultural soils

The accuracy of the analytical procedures was checked using certified reference material CRM BCR®–701. The obtained recovery values for the Cd, Cr, Cu, Ni, Pb and Zn concentrations were in good agreement with the certified ones and found to be acceptable (95.5–106.1 %). The determined HMs concentrations in various fraction of the BCR three-step SEP for the soil samples taken with respect to the Ibar River flow are illustrated in Fig. 2.

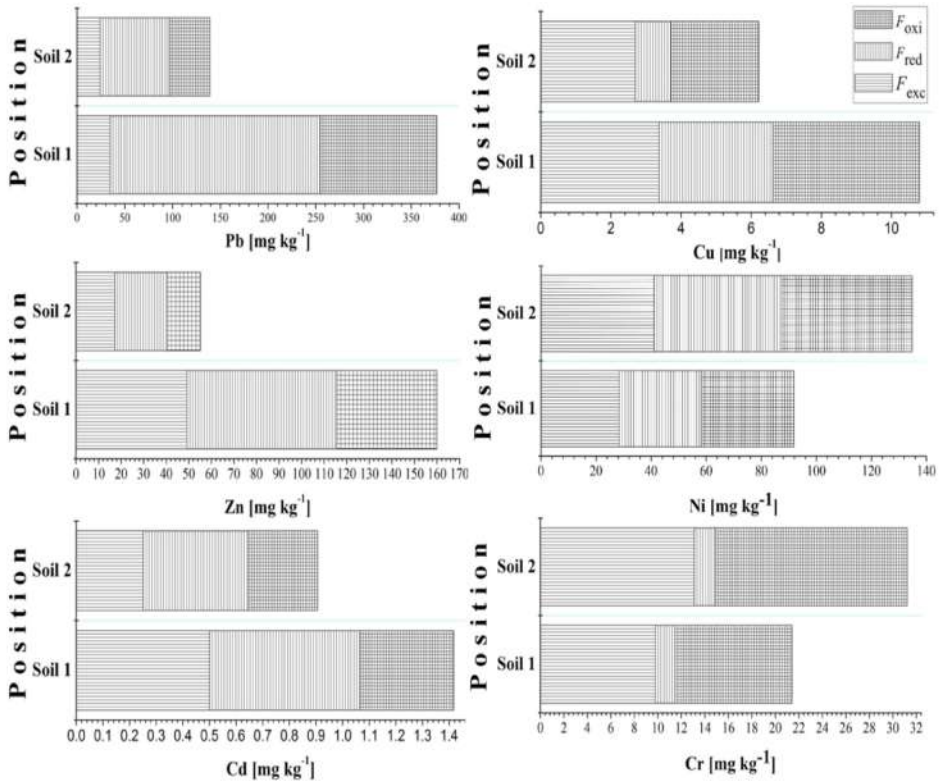

Figure 2. Distribution of HMs in the sequentially extracted fractions of soils; Soil 1-the fluvial soils; Soil 2-soil samples collected at a distance from the Ibar River watercourse

HMs associated with F_{exc} include weakly adsorbed metals retained on the solid surface by relatively weak electrostatic interactions and could be released by ion-exchange processes. F_{exc} is considered as the most mobile and the most dangerous for the environment taking into account that the HMs in this fraction are readily bio-available [3]. In the present study, Zn was the most extractable metal in F_{exc}, with concentrations ranging from 1.41–141.58 mg/kg (Fig. 2). The Zn_{exc} and Cd_{exc} concentrations were significantly higher in the Soil 1 than in the Soil 2 samples (*U*-test, p=0.041 and p=0.048, respectively). In general, anthropogenic Cd and Zn were preferentially associated with carbonate minerals [8]. Cadmium forms a carbonate mineral (otavite, $CdCO_3$), which may occur in soils heavily contaminated by this element, while Zn_{exc} was probably related to carbonates, such as Zn-rich calcite and/or smithsonite ($ZnCO_3$) [9]. The concentrations of Pb and Cu associated with F_{exc} ranged from 0.16–112.38 mg/kg and 0.38–7.98 mg/kg, respectively, were found to be markedly higher in the Soil 1 than in the Soil 2 samples (Fig. 2). Contrary to this, the Ni_{exc} and Cr_{exc} concentrations were evidently higher in the Soil 2 than in the Soil 1 samples, as was the case in the other extraction steps (Fig. 2), as well in the pseudo-total contents.

Metals released in F_{red} are bound to Mn and Fe oxides/hydroxides, which are excellent scavengers of metals in soil. The surfaces of Fe and Mn oxides/hydroxides have special affinity for metal cations at neutral pH values [7]. Any change in the anoxic soil conditions could cause desorption of metal cations [9]. In the analyzed soils, Pb was most extractable metal in F_{red}, ranging from 5.53–700.31 mg/kg with statistically significant difference in favor of the Soil 1 samples (*U*-test, $p<0.05$). In addition, Pb was predominantly extracted in this fraction relative to the other fractions ($F_{red}>F_{oxi}>F_{exc}$; Fig. 2). As in the case of Pb, the Zn in the analyzed soils was predominantly extracted F_{red} ($F_{red}>F_{exc}>F_{oxi}$; Fig. 2) with concentrations ranging from 3.57–138.31 mg/kg. The Zn_{red} concentrations in the Soil 1 samples were significantly higher than those in the Soil 2 samples (*U*-test, $p<0.01$). Similarly, concentrations of Cu in F_{red} were significantly higher in the Soil 1 than in the Soil 2 samples (*t*-test, $p<0.01$). As was the case for Pb and Zn, Cd was mainly extracted in F_{red}, relative to the other fractions ($F_{red}>F_{exc}\geq F_{oxi}$; Fig. 2).

HMs released from F_{oxi} (bound to organic matter and sulphides) are relatively stable under normal soil conditions [3]. HMs in F_{oxi} are assumed to remain in the soil for longer periods but may be mobilised by decomposition processes. Under oxidising conditions, organic material tends to be degraded, leading to the release of adsorbed metals. In the analysed soil samples, the concentration of Pb in F_{oxi} ranged from from 0.25–658.68 mg/kg were pronouncedly higher in the Soil 1 than in the Soil 2 samples (Fig. 2). The concentration of Zn in F_{oxi} ranged from below detection limit (<DL) to 138.00 mg/kg in the analyzed soils showed a statistically significant difference between fluvial and non-fluvial soils (*U*-test, $p<0.05$) (Fig. 2). In relation to all the other fractions, Cd was at least released in F_{oxi}, ranging from <DL–0.93 mg/kg (Fig. 2). Ni and Cr were mainly extracted in this fraction compared to the other fractions, indicating their prevalent association with organic matter ($F_{oxi}>F_{red}>F_{exc}$ and $F_{oxi}>F_{exc}>F_{red}$, respectively, Fig. 2). In fluvial soils Cu was predominantly extracted in the oxidisable fractions F_{oxi} ($F_{oxi}>F_{exc}>F_{red}$), while for the Soil 2 samples the order was $F_{exc}>F_{oxi}>F_{red}$ (Fig. 2). Taking into account that HMs from anthropogenic sources are mainly associated in the earlier fractions of the extractions, while those from lithogenic sources are present in the residual fraction [8], the obtained results clearly indicate significant influence of the Pb/Zn industrial production on the Pb, Zn, Cd, and Cu mobility and bioavailability in soil.

HMs accumulation in Solanum tuberosum L.

The order of the bioconcentration capacity in potato tuber calculated as the ratio of the HMs concentrations in the potato tuber to the pseudo-total HMs contents in the soil was: Cu>Zn>Cd>Pb>Ni>Cr. As elements with essential metabolic roles in plants Cu and Zn were the most abundant metals. According to guidelines for food contaminants proposed by FAO/WHO [10], Zn concentration in the all plant samples was far below maximum allowed level of 100 mg/kg. The Pb concentrations in the potato samples ranged from <DL–2.90 mg/kg. The highest Pb concentrations were recorded in the samples from the sampling sites near flotation tailing ponds, MP4=2.9 and MP11=1.2 mg/kg. The proposed level for Pb in peeled potato given by the EU Commission Regulation (EC, № 1881/2006) is 0.1 mg/kg. The obtained results of Pb contents in the

plants were significantly above the proposed ones. The levels for Cd in potato samples ranged from from <DL–0.08 mg/kg. Majority of recorded values were below the maximum level of 0.05 mg/kg proposed by the EU despite the high total Cd concentrations in the soil. The highest Cd concentration in potato samples was recorded at sampling point MP4=0.0810 mg/kg. The concentrations of Ni, Cr, and Cu in the analyzed plants were below the recommended levels proposed by the WHO (10 mg/kg, 1.3 mg/kg, 10 mg/kg, respectively). Significant positive correlations between the Pb, Cd, Ni, Cr and Cu concentrations in potato and in the different soil fractions were found. Significant positive correlations between the concentration of Cr in the potato tubers and those in the F_{red} and F_{oxi} fractions were found (r=0.427; p<0.05 and r=0.441; p<0.05, respectively). Significant negative correlation was found between the Pb in the F_{oxi} fraction and in the potato (r=–0.508; p<0.05). Taking into account that Cu and Ni are essential elements for plants supplies of these elements according to the present research were mainly from the F_{red} and F_{oxi} (r=0.690; p<0.01 and r=0.517; p<0.01 for Ni and r=0.427; p<0.05 and r=0.441; p<0.05, respectively). On the other hand, the Cd content in the potato tubers significantly correlated with the most mobile fraction (F_{exc}). Finally, no significant correlation was found between the Zn content in potato and its concentration in the soil fractions.

CONCLUSIONS

The results obtained in the present study showed that the highest pseudo-total contents of Pb, Zn and Cd in the agricultural soils were found in the vicinity of Pb/Zn industrial hotspots. In general, the Pb, Zn and Cd pseudo-total concentrations found in the soil significantly exceeded the corresponding New Dutch List target values. There were significant differences between the Pb and Zn concentrations in the fluvial soils and those taken at a distance from the Ibar River flow. Correlation analysis revealed significant positive correlations among Pb, Zn and Cd as well Pb, Zn and Cu in the agricultural soil samples, indicating a common origin of these elements. Taking into account that the heavy metals from anthropogenic sources were mainly contained in the earlier extractions of the BCR three-step SEP, the obtained results clearly indicate significant influence of the Pb/Zn industrial production on the mobile and potentially bioavailable amounts of Pb, Zn, Cd, and Cu in the soil. Significant positive correlations were found between the Pb, Cd, Ni, Cr and Cu concentrations determined in *Solanum tuberosum* L. samples and in different soil fractions. Correlation analysis suggested that the various fractions of heavy metals in the soil represented different sources for accumulation during the plant vegetation period. The highest Pb concentrations in the plant samples were recorded in the samples from the sampling sites near flotation tailing ponds. The Pb concentrations significantly exceeded the proposed maximum levels for potato plants in the majority of the analyzed samples. The results of the present study indicated that the intensive industrial production of Pb/Zn over the years and permanent pollution were responsible for the environmental contamination by heavy metals in the study area, particularly by Pb, Zn, and Cd. The quantity of the mobile and potentially bioavailable heavy metals in the studied soils threatens the quality of *Solanum tuberosum* L. crops, with a real risk that these elements could enter the food chain.

Acknowledgement

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IMPROVEMENT OF SEA IMPLEMENTATION IN URBAN PLANNING IN SERBIA

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ABSTRACT

Strategic Environmental Assessment (SEA) is an instrument for ensuring appropriate environmental protection during the preparation of planning documents. The paper reflects the experiences and problems faced in the SEA implementation in Serbian practice over the years, and the goal was to present the opportunities for improving the implementation of the SEA in urban planning. Based on the experiences made and supported by the GIZ-project "Strengthening of local land management in Serbia" the authors developed a guide for SEA in urban development planning with the aim of supporting a better integration of the SEA into the planning process in the future as well as an improvement of the SEA process itself.

Key words: Strategic Environmental Assessment, Urban planning, Serbia.

INTRODUCTION

Strategic Environmental Assessment (SEA) is an instrument for description, evaluation and assessment of possible significant impacts of planning solutions on environment arising during the realization of a plan, program or project.

SEA in EU-countries represents a constitutive part of issuing programs and plans in cases in which their implementation could have more significant impacts on environment. In the European Union SEA was introduced 2001 through the adoption of Directive 2001/42/EC on Strategic Environmental Assessment, which bonded the member states to institute SEA in national legislation. As a part of Serbia's EU approximation, the Government of Republic of Serbia has already introduced SEA through adoption of a national law on SEA in 2004.

Urban plans, according to the Law on Planning and construction, should be, as early as possible –at the level of decision on plan drafting - examine their environmental impacts. The implementation of SEA in urban planning opens up the possibility of consideration and prevention of negative impacts and changes in the urban space and environment. In this way, SEA can contribute to achieving sustainable development according to principles of environmental protection.

PROBLEMS AND LIMITATIONS REGARDING THE PROCEDURE OF STRATEGIC ENVIRONMENTAL ASSESSMENT IN SERBIA

The main Problems and limitations regarding the procedure of Strategic Environmental Assessment in Serbia are:

Limitations regarding opinion giving about the necessity of developing a SEA – competent authorities for environmental issues do not often posses enough information about planned spatial interventions, targets and effects of planning proposals and their potential environmental impacts. As a basis for giving of the opinion, there are mostly used criteria defined by the Annex of the I. Law on Strategic Environmental Assessment ("Official Gazette of RS", No. 134/04, 88/10) and the Decision on the Type of Developing Plan, which disables the possibility, to consider environmental protection and preservation in right way (at this stage), but also complicates the cooperation between processors of strategic assessment and competent authorities (at later stages);

Limitations regarding existing legislation–discordance between existing laws has led to confusion about the development, adoption process and understanding of the purpose of SEA, which is often understood as an imposed obligation, and not as a necessity for planning solutions to be defined and implemented in a way, which would not endanger the environment;

Limitations regarding obtaining of the technical opinions and environmental information – due to the fact that most of local authorities do not have local monitor networks, the environmental information has to be taken from other sources such as national institutions.

The problem of correct determination of indicators and absence of methodology for selection of indicators – during the development of Strategic Environmental Assessment (SEA), experts in charge of carrying out the SEA are facing the fact that there is still no uniform methodology and selection of available indicators. After the adoption of the Law on Strategic Environmental Assessment, besides existing dilemmas about volume and content of the SEA, another question arose regarding the selection of appropriate indicators. Experiences and examples from EU-countries are mostly about indicators of global significance and could hardly be applied in the local context.. At the same time, simple and very specific indicators do not give possibilities for quantification of particular cases. The By-law on the national list of environmental protection indicators ("Official Gazette of RS", No.37/11) national list of environmental protection indicators has been prescribed, applicable at national and international level. Although some of these indicators could be applied at local and regional level, it is necessary to define a clear and unified list applicable for all plan types and administrative areas, in order to achieve a more efficient implementation of the Plan and Report on SEA;

Insufficient public participation or participation of interested authorities or organizations – The public is often not enough informed about the implementation of the Strategic Environmental Assessment, its significance and objectives, so the public participation is mostly only formal. In the most cases, there are no examples available how more efficient methods of consultations and active participation of interested parties could be applied. This is why they are not being implemented in practice;

Refusal of the request for consent – in the Law on Strategic Environmental Assessment the procedure on refuse of consent on the SEA Report has not been defined. This leads in practice to the fact that the competent authority for preparation of the plan refers the plan to further procedure without obtained consen on the SEA-Report. So, it should in any case be possible to give opportunity for amendments and supplements to be incorporated in the Report within an appropriate deadline.

Insufficiently clear connection between the plan and Strategic Environmental Assessment - The Law on Planning and Construction does not define that the Report on Strategic Environmental Assessment is a constituent of the urban plan, but only "documentation basis of spatial plans" (in the last amendment of the Law on Planning and Construction from 2014). This does not imply that proposals of the Report on Strategic Environmental Assessment for urban plans are as well incorporated in the plan. Moreover, there is no common procedure for the adoption of the plan. It also stays unclear, why it is not stipulated, that at least one member of the planning commission should be an expert for environmental protection issues, or why it is necessary to form a separate commission for the evaluation of the report, which increases costs for the party ordering the plan and Report, although in the Annex II of the Law on Strategic Environmental Assessment("Official Gazette of RS", No. 135/04 and 88/10), there are consisted criteria for its evaluation.

PREPARATION PHASE OF IMPLEMENTATION OF THE STRATEGIC ENVIRONMENTAL ASSESSMENT

The preparation phase of implementation of the Strategic Environmental Assessment includes: issuing of the decision on the necessity of developing a strategic environmental assessment ("screening" phase), and defining of the content and volume of strategic environmental assessment ("scoping" phase).

Issuing of the decision on the necessity of developing a SEA ("Screening" Phase)

A competent authority for urbanistic issues, according to the previously obtained opinion of a competent authority for environmental issues, makes a decision on the necessity of developing a Strategic Environmental Assessment. The competent authority for environmental issues gives its opinion according to criteria for defining of potential significant impacts consisted in the Annex I of the Law on Strategic Environmental Assessment.

In order to enable the competent authorities to make a preliminary assessment of possible environmental impacts of the planned activities in an appropriate way and to give the opinion on the necessity to carry out or not to carry out a SEA, it is necessary to provide information on:

- quality of the environment in the planning area (quality of the air, water, soil, drinking water, noise level, condition of natural and cultural goods);
- guidelines and measures for environmental protection related to the planning area, defined by panning documents of higher hierarchy level;
- guidelines for lower hierarchy levels defined by strategic assessment of impacts of higher plans in the hierarchy;
- planned contents and activities in the framework of the plan and their possible impacts.

Definition of content and volume of the SEA ("scoping" phase)

The definition of content and volume of strategic environmental assessment is a procedure, in which experts for the Report on SEA, planners, authorities in charge for environmental protection and urban issues, and also other relevant institutions should be included. This procedure starts after the resolution on plan formulation.

When the content and volume are being defined it is necessary to consider:

- general purposes and aims of the plan development, possible solutions for development of the spatial unit (and urban renewal), and effects of the planning (facts about planned contents and activities, which could significantly impact the quality of environment);
- facts from measuring locations of local and national monitor network (quality of the air, water soil, drinking water, noise level);
- planning documents and Strategic Environmental Assessments of the higher hierarchy level;
- Opinions and conditions of competent institutions (authorities, organizations and public enterprises, authorized to defined conditions for spatial preservation, landscaping and construction).

In this phase it is useful to organize meetings with all interested parties, in order to ascertain the quality of the environment at the planning area and possible negative or positive impacts, that planning solutions could have on complete spatial condition. The aims of such meetings are:

- establishing contacts with representatives of planning processors, competent authorities, local public enterprises and institutes for health protection and representatives of other interested authorities and organizations as well;
- gathering of necessary documentation, whereby it is important to find out: Which facts are available, and which have to be collected? Which variant solutions are considered in the planning concept? How detailed each environmental factor should be analyzed? Which methodology would be used? Is it necessary, to make additional measuring and which indicators would be used for the evaluation of the condition? Involving of representatives of health

institutions and of the health protection is very important, because in this way the insight in health condition of people is gained and consequences of all possible negative impacts on health of local people are recognizes.

As well, in this phase is defined the space, which is going to be the subject of the examinations. It could be bigger than the planning area, if there are possible impacts on environment also out f the area, or if it is expected that impacts could come from the environment (e.g. in cases of floods of a river, which is out if the area, or emissions of an industrial complex out of the area).

REPORT ON STRATEGIC ENVIRONMENTAL ASSESSMENT

The Report on Strategic Environmental Assessment is a document, where results of the examination of environmental impacts are represented. The Report is being developed during the development of the planning document, and its purpose is foreseeing of possible impacts and planning solutions evaluation from the aspect of environmental protection.

The report includes: definitionof the general and special purposes of Strategic Environmental Assessment, representation of evaluated environmental impacts of variant solutions; representation of evaluated environmental impacts of planning solutions, measures for reduction of negative impacts, guidelines for lower hierarchy levels and a program for environmental condition monitoring.

Definition of general and special objectives of Strategic Environmental Assessment is made on the basis of requirements and purposes from other plans and programs, targets of the environmental protection defined at the national level and targets of the environmental protection defined by international documents. For the implementation of general objectives, special objectives are defined in special fields of protection. Special objectives are defined according to specificities of the plan and they represent specific, quantified statements of general objectives, given in form of guidelines for changes and actions that are going to be used for realization of these changes.

Environmental impact assessment of variant solutions is related to all solutions defined in the "scoping" phase with obligatory impact assessment of the variant solution "non-adoption of the plan". It is necessary to consider this variant, if the plan wouldn't be adopted and implemented (if the development goes on according to previous trend) or if the plan would be adopted and implemented (if the development goes on according to planned planning solutions). This is the most important comparison of variant solutions in order to represent the choice of the most beneficial solution from the aspect of environmental protection.

Environmental impact assessment of planning solutions is made on the basis of a previously defined evaluation matrix that could be in form of a table, written text or combination of the both. It is necessary to asses the environmental impacts on the basis of quantity (critical, extremely negative, less negative, positive, beneficial, very beneficial), significance (global, national, regional, municipal, local) and characteristics (reversible, irreversible, cumulative, synergic, direct or indirect).

Measures for reduction of negative impacts are defined for the purpose of limitation and compensation of negative consequences that the plan realization could have on environment or human health. These measures could be related to some of environmental factors (protection of water, air), or they could be defined as compensation measures that recover consequences of development.

Guidelines for lower hierarchy levels are defined on the basis of guidelines for implementation taken from the plan.

Program for environmental condition monitoring is defined on the basis of estimated negative environmental impacts and necessity for some environmental factors and human activities to be followed, that could have negative impacts on the planning area. At defining of monitoring it is necessary to answer: What would be followed (What are targets and indicators for the following)? Who follows (state agencies, local authorities, local public and communal enterprises, project holders)? How often all these would be followed? What are critical values and when should be some actions taken?

EARLY PUBLIC PARTICIPATION AND PUBLIC PARTICIPATION

Early public participation is an amendment introduced by the Amendments on the Law on planning and construction from 2014. It is in spirit of the "Aarhus regulation". After issuing the decision on the plan development, the local authority responsible for the formulation of the plan informs the public about general objectives and aim of the plan, possible and alternative solutions and effects of the plan.. Early public participation is announced to the public according legal requirements and lasts 15 days. All objections and suggestions are to be documented and they could have impact on the planning solutions. As stated in the law "the public must have a possibility to declare, and recorded suggestions could have impact on planning solutions" (Article 45a, Law on planning and construction).

Public participation in Strategic Environmental Assessment happens simultaneously with the public participation of the draft plan according to article 19 of the Law on SEA and article 45a of the Law on planning and construction. The SEA-Report is exposed to public participation after the professional review, in order to provide participation of all interested parties in the process of decision making and adopting of the Report on Strategic Environmental Assessment. The public is given a possibility to actively take part in the decision making process related to environmental protection by means of delivering opinions, comments and suggestions to the competent authority. Moreover,, in this process it is important to ensure that the SEA is harmonized with other environmental impact assessments and plans and programs related to environmental protection.

Well planned and implemented process of the public participation and consultations incorporating all relevant stakeholders is very important for the SEA procedure. It enables acquiring valuable information about alternative solutions to be considered and significant impacts of the plan and necessary protection measures.

The final evaluation and adoption of the Report on SEA is made after completed public participation. If needed, the department for environmental protection can request opinions of the relevant public institutions for environmental issues.

Moreover, they can establish a committee for professional review and evaluation of the SEA-Report.

CONCLUDING REMARKS

With the intention to contribute to better understanding of the SEA, the authors prepared a Guide for Strategic Environmental Assessment in urban development planning. Providing technical information on the procedure itself, the content and methods to be used, its final aim is to improve the quality of SEA and, with that, the quality of urban plans. The guide focuses on the integration of SEA in urban plans. It mainly targets planners and local self-governments and intends to support them in the formulation of urban plans in the most environmentally sensitive manner.

The guide is a result of intense cooperation between planners and environmental experts from the Ministry of Traffic, Construction and Infrastructure, the Ministry of Agriculture and Environmental Protection, the University of Belgrade, local self-governments and experts from abroad and is based on experiences made in various urban planning projects in Serbia and in Germany.

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EFFECT OF SO_2 ON THE QUALITY OF AMBIENT AIR IN BOR

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ABSTRACT

This paper provides an analysis of the data on the quality of ambient air for a one-year period for two monitoring stations in Bor.The atmospheric level of the following pollutants SO_2, NO_2, CO, suspended particles up to 10 µm and up to 2.5 µm was monitored. The paper provides an analysis of mean daily, monthly and annual concentrations that were compared with the limit values stipulated by the law and with some critical locations in the world. Based on the pollutant concentration data, the quality of ambient air was determined for the analysed locations in Bor.

Key words: air quality, monitoring,sulfur dioxide,copper production,Bor.

INTRODUCTION

Clean air is the basis for the health of people and the entire ecosystem. Air pollution sources may be of natural origin or of anthropogenic origin, such as stationary sources of pollution (in rural area, related to agriculture; in industrial area, such as electricity production, production and processing of metal and non-metal raw materials; and in urban area, originating from heating plants, individual furnaces, waste combustion, etc.) and mobile sources of pollution (road transport and other transport)[1−4].The most common types of atmospheric matter are sulfur dioxide (SO_2), nitrogen dioxide (NO_2), carbon monoxide (CO), suspended particles up to 10 µm (PM_{10}) and up to 2.5 µm ($PM_{2,5}$) in diameter.

Sulfur dioxide after being emitted in the air, it can further be oxidised by photochemical effect into sulfates and sulfuric acid, creating an aerosol that, with the atmospheric moisture, and often turning into precipitation. Anthropogenic emission of SO_2 mostly comes from the combustion of fossil fuels containing sulfur (accounting for more than 67% of the total emission of SO_2), and also is a by-product of numerous industrial processes (smelting ores containing sulfur). Natural sources of SO_2 are volcanoes and oceans, contributing around 2% to the total global emission. The total emission of sulfur compounds in the air from all sources is estimated at 195 million tons per year[3,4]. SO_2 can be transmitted through the atmosphere over long distances, causing transboundary air pollution. Since the SO_2 emission is mostly the result of fuel combustion, the best practice for emission reduction boils down to using fuels with lower sulfur content, using alternative fuels and improving the emission reduction techniques. Its compounds are removed from the atmosphere by wet or dry deposition. The most pronounced sources of SO_2 in Serbia in 2012 were thermal power plants for power production and distribution, metal processing plants and chemical industry, followed by heating plants and individual furnaces and road transport. The total emission of SO_2 was 376.95 kt[3,4].

The Regulation on the Conditions for Monitoring and Requirements Regarding Air Quality stipulates mandatory monitoring the level of the following pollutants in the atmosphere: SO_2, NO_2, CO, PM_{10}, and $PM_{2.5}$[3−8].The air quality assessment is performed based on the criteria defined by the Air Protection Law, the Decree on the Conditions for Monitoring and Requirements Regarding Air Quality[*7*], according to the pollution level, and starting from prescribed limit values (LV) and tolerance values (TV).

The limit value (LV) is taken to be the tolerance value for any matter for which no tolerance value (TV) is prescribed. The limit value is the highest allowed level of pollution in the air, determined based on scientific findings, while the tolerance value is the limit value plus the margin of tolerance[3,4].

This paper aims to provide an analysis of the results of monitoring the quality of ambient air in Bor (Serbia).

MATERIALS AND METHODS

The monitoring of air quality in the territory of the Republic of Serbia was established by the Air Protection Law [6−8]. Pursuant to this Law, a state network of automatic air quality monitoring stations and stations was created. In June 2012, the network comprised a total of 36 automatic stations) distributed across several areas (urban/industrial (U/I), suburban (SU), industrial (I), and rural (R)).

In order to more properly inform the general public about the status of air quality, in 2011 the Environmental Protection Agency defined the SAQI_11 (Serbian Air Quality Index), which is in compliance with the air quality categorisation and provides a direct status assessment based on the pollutant concentration level. The SAQI_11 comprises five classes, depending on the concentrations, with the first three classes–"*excellent*", "*good*" and "*acceptable*"–corresponding to Category I of air quality, the "*polluted*" class corresponding to Category II, and the "*very polluted*" class corresponding to Category III of air quality [3] The numerical values of parameters by SAQI_11 class are shown in Table 1.

Table 1. Definition of the Quality Index, [$\mu g/m^3$][3]

Period	Pollutant	LV	TV	Exellent	Good	Acceptable	Polluted	Very polluted
24h	SO_2	125	/	0-50	50.1−75.0	75.1−125.0	125.1−187.5	>187.5
Year	SO_2	50	/	0−30	301-40	40.1−50.0	50.1−75.0	>75.0

This paper provides an analysis of the data on pollutants for a one-year period, i.e. from 1 October 2012 until 30 September 2013, at monitoring stations in Bor (City park (Bor-GP) and Institute (Bor-Inst)). The main polluter in Bor is the Bor Mining and Smelting Basin, i.e. the copper smelter where sulfide ore is smelted.

RESULTS AND DISCUSSION

Based on the mean daily concentrations of SO_2, the mean monthly concentrations were calculated, which is shown in Table 2.A579.19 µg/m^3 maximum daily concentration of SO_2 was recorded at the Bor-GP. At the Bor-INST monitoring station, the maximum daily concentration of SO_2 reached381.70 µg/m^3(on 19 October 2012), which was three times the concentration permitted by the law.

Table 2. Mean monthly concentrations of SO_2 at monitoring stations in Serbia,[µg/m^3]

Measuring station	Okt	Nov	Dec	Jan	Feb	March	Apr	May	June	July	Aug	Sep
Bor GP	202.48	344.96	277.40	231.07	**579.19**	190.20	222.82	295.90	176.74	189.54	303.68	60.73
BorInst	102.76	164.92	78.39	104.49	51.48	36.84	87.11	61.85	56.56	96.16	106.37	70.82
LV[a]	125											

Figure 2 shows mean daily concentrations of SO_2 at monitoring stations in Bor for January 2013. January was chosen as the most critical month in the analysed period. For SO_2, it is 125 µg m^{-3} at the daily level.

In addition, the SO_2air pollution level in the winter and summer seasons was analysed at a four-month level. November, December, January and February were analysed in the winter period, while the summer period includes May, June, July and August. We can see in Figure2 that the maximum concentration of SO_2in Bor, both in the winter period and in the summer period, was at the Bor-GP monitoring station (358.16 µg/m^3 for the winter period and 241.47 µg/m^3 for the summer period), from which we conclude that the city heating plant has no significant impact on the air pollution although it uses coal.

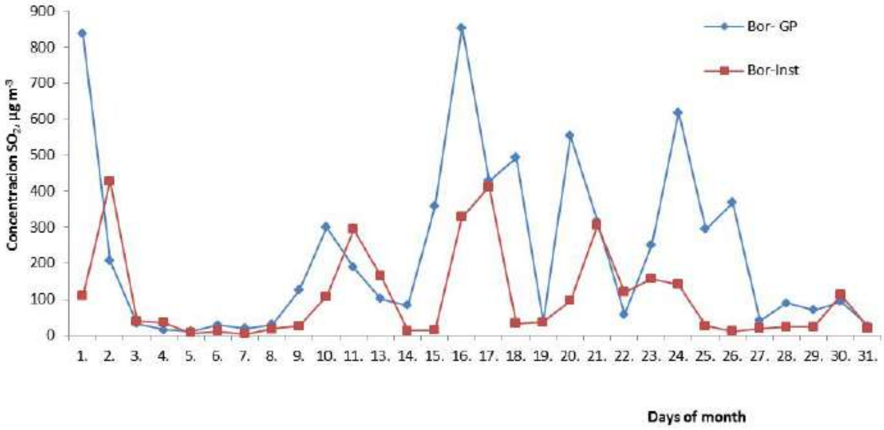
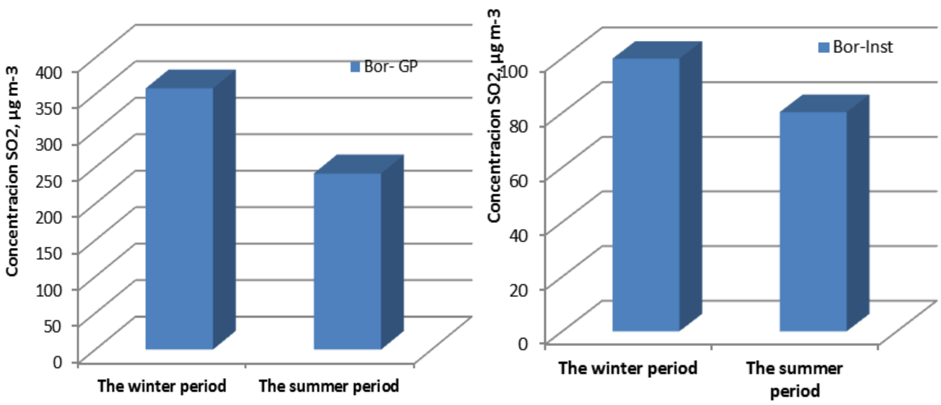


Figure 1. Mean daily concentrations of SO_2 at monitoring stations in Bor for January 2013

Figure 3 shows daily concentrations of SO_2 at monitoring stations in Serbia, also for January 2013. January was chosen as the most critical month in the analysed period. The limit value of the pollutant SO_2 in the air is 125 µg/m^3 at the daily level for SO_2.



a) b)

Figure 2. Mean 4-month concentration of SO_2 during the winter and summer seasons at monitoring stations: a) Bor–GP; b) Bor–Inst

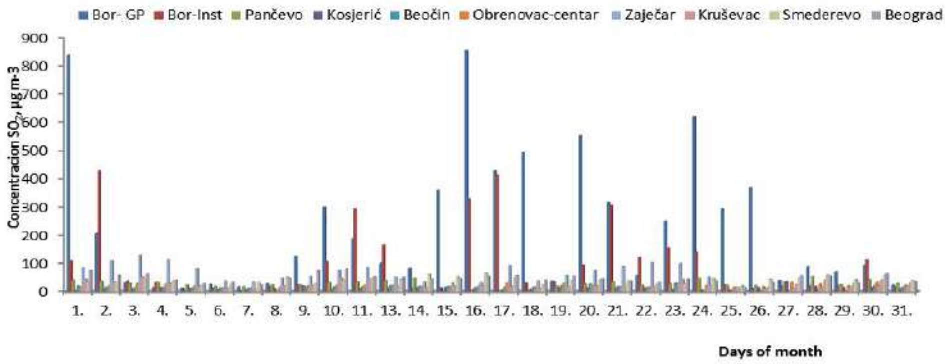


Figure 3. Daily concentrations of SO_2 at monitoring stations in Serbia for January 2013.

The analysis of the data on the mean daily, monthly and annual concentrations of SO_2 in Serbia shows that the LV was exceeded in Bor. According to the available literature, the daily concentration of SO_2 in Anshan, China, was around 25.5 µg m^{-3} in the period 2004−2006 [9]. The maximum daily concentration of SO_2 in Huelva, Spain, was 150 µg m^{-3} in 2004−2005 [10]. For example, the concentration of SO_2 was almost three times as high in January as in July in Puertollano, Spain, where the main sources of pollution are transport, individual furnaces, chemical industry, a mine and two thermal power plants (the data were collected from February 2002 to August 2003) [11].

CONCLUSION

Based on the data on mean daily, monthly and annual concentrations of pollutants compared to the data from the literature, we may conclude that the LV was only exceeded in Bor. The main source of pollution in Bor is the Bor Mining and Smelting Basin. By comparing the seasonal data it may be seen that the concentration is high both in the winter period and in the summer period,which means that the Heating Plant has no significant impact on the level of pollution by SO_2.

The processed results of the automatic air quality monitoring indicate that the annual LV and TV of pollutants were exceeded in 2012. The SO_2 pollutant emission poses a serious environmental pollution problem.

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ANALYSIS OF THE BIOLOGICAL SPECTRUM OF FLORA OF THE QUAY IN NOVI SAD

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ABSTRACT

The life form is a set of adaptation features of a species to environmental conditions and it is determined by climate. This study is an analysis of the presence of life forms in the studied areas of the quay in Novi Sad, where a total of 167 plant species were found divided into eight classes of life forms. It was found that the largest number of species (35.32%) belong to the life form of hemicryptophytes. A significant number of therophytes (26.34%) were recorded, including a large number of species with an invasive character. The great share of therophytes indicates instability of the quay habitats and a significant human impact on the flora of these grasslands.

Key words: biological spectrum of the flora, life forms of plants, quay, Novi Sad**.**

INTRODUCTION

Quays are areas by the rivers, and their function is primarily water protection (flood protection). Rivers, canals and lakes in built up urban areas serve as green corridors by linking urban green areas into an integrated system. An increasing number of residents choose these places for active recreation. The biological spectrum represents a percentage share of all life forms of plants in the flora of an area or in a plant community (1). The life form is a structural-functional response to environmental impacts (2). The life form is a result of adjustments during the evolution of a species. It reflects environmental conditions and is determined by climate (1,2). Climatic factors with the highest impact on the composition of flora in certain areas are precipitation and temperature (1).

Novi Sad is located at 45° 20'00" north latitude and 19° 51'00" east longitude, in the central part of the autonomous province of Vojvodina, on the border of Bačka and Srem in northern Serbia. The city lies on the banks of the Danube River, between the 1,252nd and 1,262nd kilometer of the watercourse. The lowland part of the city is located on the left bank of the Danube (Bačka), while the slopes of Mt. Fruška Gora as the hilly part of the city are on its right bank (Srem). The altitude on the Bačka side ranges from 72 to 80 meters, while in Srem it reaches from 250 to 350 meters. The climate in Novi Sad ranges from moderate-continental to continental. The dominant wind in the autumn and winter periods is the so called east wind. The average air temperature in the city is 10.9 °C, the mean temperature is -1 °C in January, while in July it reaches 21.6 °C. The average annual rainfall is 578 mm and the number of days with precipitation is 122 (3). The quay in Novi Sad extends over a length of 5 kilometers, serving as a public green area, with a significant impact on the psychological and physical characteristics of people (4). The quay with the Strand city beech belongs to the category of urban parks (5).

MATERIALS AND METHODS

The floristic research of the quay in Novi Sad was carried out in the period from 2010 to 2012. It included grasslands of the Belgrade quay and the Sunny quay in the area from the mouth of the Danube-Tisa-Danube Canal into the Danube to the Štrand city beech.

The structure and the floristic composition of the investigated area of the Novi Sad quay were determined by the Braun-Blanquet method (6). The determination of plant species was carried out according to the following literature sources: Josifović et al., Ed. (I-X) (7), Sarić, ed. (8), and Javorka & Csapody ed. (9), and Tutin et al., Ed. (I-V) (10). The nomenclature of plant species is in line with the "Flora Europaea" (11).

The life forms of plants were determined according to the Raunkiaer system (12). According to this classification, there are five basic classes of life forms: phanerophytes (P), chamaephytes (Ch), hemicryptophytes (H), therophytes (T) and Cryptophytes (K) which include geophytes (G) and helophytes and hydrophytes (HH). In addition to these life forms, the paper lists the following types of life forms: woody chamaephytes (wCh), nanophanerophytes (Np), therophytes/hemicryptophytes (Th), and skandentophytes. Invasive species were determined according to the preliminary list of invasive species in the Republic of Serbia (13).

RESEARCH RESULTS

The presence of 167 plant species was recorded in the research areas of the quay in Novi Sad. The analysis of life forms in the investigated areas indicated the presence of eight types of life forms: hemicryptophytes, therophytes, the joint group therophytes / hemicryptophytes, phanerophytes, geophytes, nanophanerophytes, skandentophytes and woody chamaephytes.

A total of 59 plant species, i.e. 35.32%, belong to hemikryptophytes, making it the most dominant life form in the total biological spectrum of flora in the investigated area. High-quality grasses such as *Lolium perenne, Poa pratensis, Agrostis stolonifera*, *Agrostis capillaris*, *Festuca arundinacea* and *Poa angustifolia* belong to these life forms. In addition, four species with an invasive character, including *Aster lanceolatus*, *Artemisia vulgaris*, *Cichorium intybus* and *Urtica dioica*, belong to hemikryptophytes.

The life form of therophytes includes a total of 44 species, accounting for 26.34% of the total biological spectrum of flora in the investigated area. A significant number of species (10 species) belonging to this life form have an invasive character, including *Amaranthus retroflexus, Ambrosia artemisiifolia, Atriplex patula, Chenopodium album,* *Echinochloa crus-galli, Polygonum aviculare, Portulaca oleracea, Veronica persica, Xanthium italicum* and *Xanthium strumarium.*

The therophytes/chamaephytes group includes 35 species, accounting for 20.1%. A large number of species that belong to the family of legumes have been observed within this group, including *Melilotus albus, Vicia grandiflora, Vicia sativa, Vicia villosa, Trifolium campestre, Medicago lupulina* and *Medicago minima*. Two species, *Conyza canadensis* and *Erigeron annuus,* have an invasive character.

Eleven species (6.59%) were found in the group of phanerophytes and 11 belong to the group of geophytes. In the researched areas the life form of phanerophytes comprises seedlings of woody species, including three species with an invasive character, i.e. *Acer negundo*, *Ailanthus altissima* and *Morus alba.* Other recorded seedlings of woody species like *Populus alba*, *Salix alba* and *Fraxinus angustifolia* represent coastal vegetation. Species with an invasive character have also been recorded among the life forms of geophytes. A total of 4 such species were recorded, including *Aristolochia clematitis*, *Asclepias syriaca*, *Cynodon dactylon* and *Sorghum halepense*.

The life form of nanophanerophytes is represented with 4 species, accounting for 2.39% of the total biological spectrum. Half of the species belonging to this life form (2 species) have an invasive character (*Rubus caesius*, *Amorpha fruticosa*).

A total of two species (*Hedera helix*, *Vitis vinifera*) belong to the life form of skandentophytes, accounting for 1.2% of the total spectrum of biological flora.

The life form of woody chamaephytes is represented with one species (*Solanum dulcamara*) accounting for 0.6% of the total biological spectrum of flora in the investigated area.

DISCUSSION

Eight classes of life forms were observed in the study areas of the quay in Novi Sad. The largest number of species belong to the life form of hemicryptophytes (59 out of a total of 167 recorded species). The share of hemicryptophytes in the investigated areas corresponds to the share of these life forms in the flora of Serbia. Hemicryptophytes are the largest group of life forms, accounting for 46.8% of the total number of recorded species in the flora of Serbia. Hemicryptophytes are numerous, both in lowlands and hilly and mountainous, subalpine and alpine zones (1). According to Stavretović (14) the largest number of species of the grasslands in Belgrade belong to the life form of hemicryptophytes.

The life form of therophytes is in the second place with 44 species, i.e. 26.34%. Considerable presence of this life form can be explained by the specific anthropogenic conditions in the investigated areas. Out of 44 species belonging to this life form, 10 species have an invasive character. The share of therophytes in the investigated areas corresponds to the share of this life form in the flora of Serbia. Therophytes grow in different habitats and are the most abundant in lowlands and hilly areas. Most often they occur in open habitats with plenty of light and warmth, i.e. in places where there are conditions for the spread of these species (1). The places with a high impact of the anthropogenic factor in ruderal habitats display a more pronounced increase in the number of annual plants compared to biennial and perennial plants (15, 2). A total of 577 plant species in the flora of Serbia belong to the life form of therophytes (1). Stavretović & Obratov (16) recorded a considerable share of therophytes in Belgrade parks. A large number of perennial plants in the mowed lawns indicates a bad state of these lawns and their poor maintenance (14).

The joint group of therophytes/chemicryptophytes involves 35 species, accounting for 20.1%, and ranking third in the total biological spectrum of the flora in the investigated area. A total of 110 species belonging to this group were recorded in the flora of Serbia, accounting for 3.5% of the total number of species. These plants can be both annual and biennial, but also triennial depending on the local environmental conditions (1).

The life forms of phanerophytes and geophytes share the fourth place in the overall spectrum of the flora in the studied area with 11 plant species each (6.59% each). The representatives of phanerophytes in the investigated areas are seedlings of woody species. Out of a total of 11 species belonging to the life form geophytes, 4 species have an invasive character. According to Jovanović (15) geophytes are represented with 38 species in the ruderal flora of Belgrade. Geophytes account for 10% of the flora in Serbia, and they include 311 species (1).

The fifth place belongs to the life form of nanophanerophytes represented with 4 species, accounting for 2.39% of the overall biological spectrum. Two species from this group (*Rubus caesius*, *Amorpha fruticosa*) have an invasive character. The presence of the species *Rubus caesius* indicates an absence of tending and care measures in the lawns (15). The percentage of nanophanerophytes in the flora of Serbia amounts to 4%. This life form occurs in different terrains and habitats, ranging from lowlands up to an altitude of 2200 meters, i.e. places of marginal conditions for forest trees (1).

The life form of skandentophytes is represented with two species (*Hedera helix*, *Vitis vinifera*) in the studied areas and is ranked sixth in share (1.2%). Jovanović (15) recorded 20 species belonging to the life form of skandentophytes in the ruderal flora of Belgrade. Stavretović & Obratov (16) also recorded the presence skandentophytes in the flora of three parks in the city center of Belgrade. According to Stavretović (14), this life form is represented by 10 representatives in the grasslands of Belgrade.

Woody chamaephytes are the life form in the seventh place, being represented by only one species (*Solanum dulcamara*), accounting for 0.6% in the total biological spectrum of the flora in the investigated area.

CONCLUSION

The analysis of the floristic composition of the investigated area of the Novi Sad quay revealed the presence of 167 plant species, distributed in eight types of life forms. The largest number of recorded species (35.32%) belong to the type of hemicryptophytes. Therefore, it can be concluded that the biological spectrum in the studied area has hemicryptophyte character.

The presence of therophytes, accounting for 26.34% is also significant. The highest number of invasive species (10 out of 44 invasive species) can be found in this life form. Besides having an invasive character, the species *Ambrosia artemisiifolia* also has exceptionally allergenic properties, which makes its presence undesirable in green areas of walking trails both in general and in the area of Novi Sad quay. The higher the anthropogenic factor, the greater the share and spread of annual plats (therophytes) on account of biennial and perennial plants (Jovanović, 1994). A significant number of invasive species (24 out of 167 species) indicates a low level of maintenance in the studied area. The lowest number of species in the total biological spectrum belongs to the life form of woody chamaephytes (1 species - 0.6%)

In conclusion, much more attention should be paid to green areas in general, including promenades. Their benefits to cities are reflected in the health status of urban population. Designed and properly maintained green areas have a positive impact on the health of residents, indirectly affecting their physical and mental state.

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SPATIAL USE AND THE NEEDS OF VISITORS OF PARK-FOREST KOSUTNJAK IN BELGRADE

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ABSTRACT

Park-forests contribute social, aesthetic, ecological, recreational and economic benefits within cities. This paper analyzes the Košutnjak park-forest in Belgrade, with a special emphasis on the needs of its visitors and usage of urban forest. The aim of this paper is to understand the needs of users and the integration of their opinions and attitudes in the process of planning, management and improvement of recreation area. A survey among 70 visitors was conducted in park forest Košutnjak via random sampling. The results shows the highest number of visitors coming from surrounding neighborhoods, mainly for walking and enjoying nature or for active recreation. More than a half of the respondents (63,40%) were satisfied with the management and maintenance of the area. Nevertheless, they offered suggestions for improvements. The results provide practical solutions related to the management and maintenance of the park forest and emphasize the importance of communication with users in order to raise awareness of the importance of urban forests.

Key words: public involvement, urban forest, visitor needs, landscape architecture, green areas.

INTRODUCTION

The rapid development of cities have significant influence on green area, which have every day an increasing number of visitors. Urban forests and especially those located in the city center have become an increasingly important element in the daily life of an individual. Therefore, one of the important goals in managing green areas is understanding the user needs. Research by many authors (2,7,8) indicate that for achievement these objectives it is necessary to consider relationship between people and places and integrate the opinions and views of stakeholders in the planning, designing and improving certain areas.

Park forest is usually linked to the achievement of social, health, aesthetic and recreational uses in industrial cities (1). Today, the park forest are very important for the people as symbols of personal, local and cultural meanings and have significance for the local community also (1). An understanding of the character of an area, the distribution of the forests, and the distribution of the open spaces is a prerequisite for functional planning of different uses that will not endanger natural features of forest. The users in a given recreational areas have different notion regarding how the landscape should be designed depending on their personal characteristics and needs. Some visitors prefer a park-like spatial design, whereas others prefer a more natural look (2). However, visitors are not a homogenous group and have different needs and perceptions so the need for a long-term observation and research are needed. This paper present an analysis of the usage of the Košutnjak park forest in Belgrade, with a focus on the importance of the use by, and needs of, the visitors to this forest.

METHODOLOGY

Study location

The Košutnjak Park Forest covers an area of 330 ha and is situated in municipalities Rakovica and Čukarica. Urban forest Košutnjak is within the State Enterprise "Serbia Forest", the management unit "Košutnjak forest" and in the form of green fragments belongs to hillside forest complex Šumadija (3). Košutnjak is the most visited forest park in Belgrade with the valuable cultural and historical monuments, many catering, sports and recreational facilities, as well as protected natural area - a general nature reserve (community oak and hornbeam) near Topčider Fountains (4). Near the sports center Košutnjak is fitness trail, equipped with a supporting props for amateurs and notification panel. The start point of trail is located across the Republic Institute for Sports Medicine (Kneza Višeslava 72 street). The trail route is circular, 1200 m length, with 16 stations for practice.

Primary data

Primary data were collected through a survey conducted among visitors of Košutnjak urban forest. The survey respondents were selected via random sampling and the survey contained a combination of different types of questions. The combination of different types of questions was employed to investigate the various dimensions of the views of the respondents and, particularly, to ensure that accurate information was obtained (5). The questionnaire has 20 questions and can be classified in 4 groups. The first group of questions was related to socio-demographic characteristics, including gender, age group, occupation and knowledge. In the second group, the questions were related to information about reasons for their visits and how the area is used.

The third group of questions addressed the extent to which the respondents were satisfied with the condition of the area, their structual elements and the management of the area. This group of questions employed a Likert scale corresponding to a 1–5 rating (very bad, bad, acceptable, good, and very good). The last section was about getting personally involve in the design process as well as the possible need for the existence of a greater number of these areas in the city. The survey was conduct in september 2011 and june 2012. for 4 days (2 was work days and 2 weekend). The data were analyzed using Microsoft Excel and then presented in graphs and tables.

RESULTS AND DISCUSSION

1. Socio-demographics structure of visitors

Among all participants, 44 were male and 26 were female. The main socio-demographic characteristics are presented in Table 1. The largest number of respondents at Fitness Trail Košutnjak (26) was in the 25-34 year age group, following by 18-24 year age group (14). The oldest group (over 64 years) was represented at least, only 3 visitors. In terms of their proffesions, most of respondents (29) were employed, 19 were students and schoolchildren were at least, only 5 visitors. Most respondents were high school graduates (30), whereas primarly school graduates were at least (3).

Table 1. Socio-demographics characteristics of respondents

Age (years)	no	%	occupation	no	%	education	no	%
<18	4	5,71	schoolchildren	5	7,14	Primaly school	3	4,28
18 – 24	14	20	students	19	27,14	Secondary school	30	42,86
25 -34	26	37,14	unemployed	10	14,28	college	10	14,28
35 -44	10	14,28	employed	29	41,43	university	27	38,57
45 -54	7	10	penzioner	7	10			
55 -64	6	8,57						
> 64	3	4,28						

2. Reasons for visiting Košutnjak Park Forest

The results showed that most of visitors (64,30%) come from surrounding neighborhoods, municipality Čukarica (suburb Banovo Brdo, Žarkovo, Cerak, Filmski grad), 24,30% come from municipality Rakovica (suburb Vidikovac, Petlovo brdo), whereas 8 visitors came from other part of the city. Most of the participants come on Fitnes Trail Košutnjak with friends (57,10%), following by respondents come with family (18,60%) or alone (17,10%), whereas 5 people come with partner (5).

More than a half of the respondents (41) visit the park forest quite often or very often. Only 4 respondents visit the forest very rarely . The results showed that most of the visitors equal come during the working days and weekend (47). Also, most of participants stay 1-3 hours on Fitnes Trail (52), while 9 of them stay 1 hour as well as those staying more than 3 hours (9). Most of visitors come on Košutnjak Trim Trail by own car (29), whereas 8 participants come using bicycles.

The main reason for visiting the park forest, as stated by the respondents, was enjoy walking (31,50%), followed by active recreation (28,70%), and leasure-time (20,40%) (Figure 1). As stated by many authors (7-10) walking and enjoying nature are the dominant reasons for visiting the park forest.

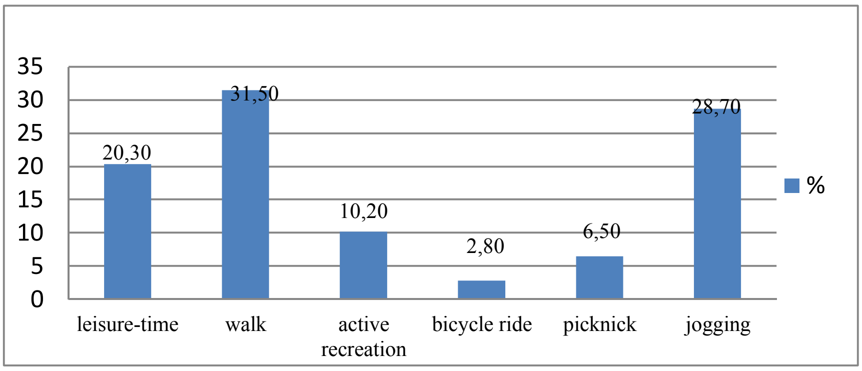

Figure 1. Reasons for visits the Košutnjak park forest

Availability as a main reason for coming specific on this Fitness Trail was stated by half of respondents (51,00%), followed by landscape (32,90%) (Figure 2). Visitors answers shows that the least represented reason for coming specific in Košutnjak park forest (5,70 %) is sanitary-hygienic conditions of an area.

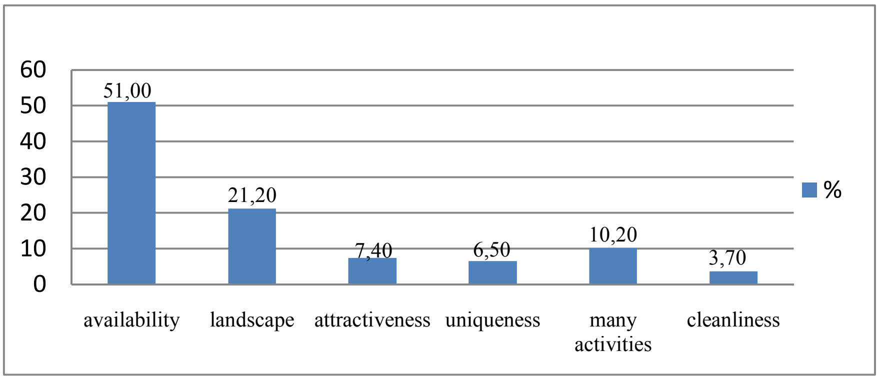

Figure 2. Reasons for specific visits the Košutnjak park forest

3. Satisfaction with the management of the Košutnjak Park Forest

More than a half respondents (63,40%) are satisfied with the condition of Fitness Trail Košutnjak. The average rating of visitors satisfaction in terms of attendance rates as very good, while infrastructure and safety rate as good (Figure 3). Crime and social conflict are a serious concern in some urban parks and forests and often cause less attendance (6). In the case study of Košutnjak Park Forest, we obtained the opposite results, and visitors are satisfied with Košutnjak Park Forest in terms of safety. The average rating of visitors satisfaction in terms of equipment, lawns and greenery rate as acceptable.

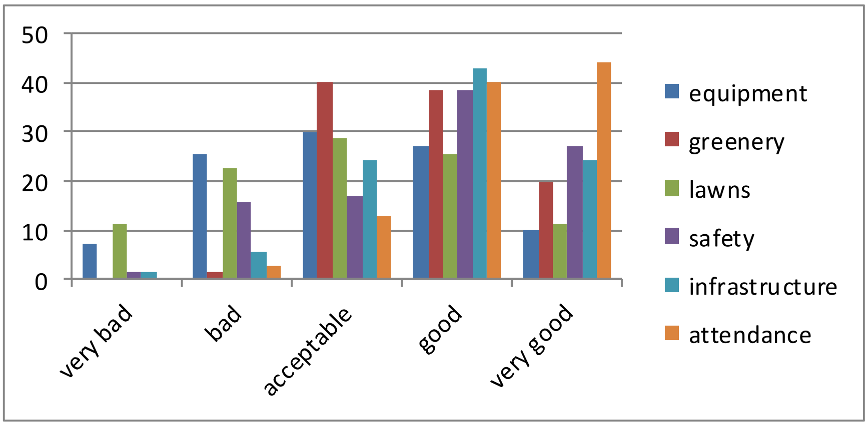

Figure 3. Satisfaction of visitors in the Košutnjak park forest

The most important aspect of maintenance on trim trail Košutnjak, by surveyed respondents, are improvements of equipment (33,90%), and hygiene (32,30%) (Figure 4). Improvement of infrastructure is less important according to participants (3,20%).

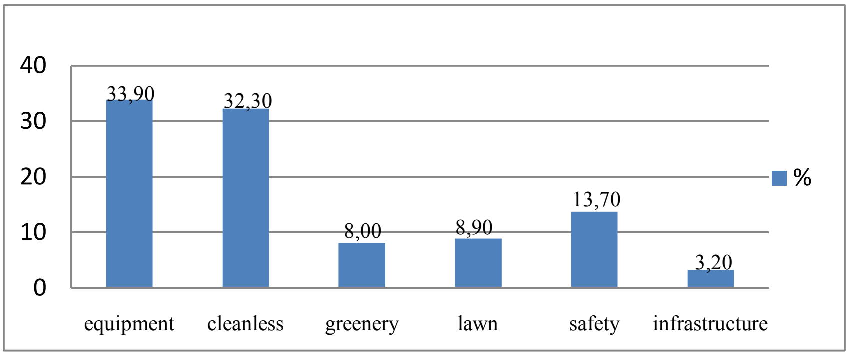

Figure 4. Research results showing user reviews of maintainance measures in the park forest

4. The visitors relation to the improvement of recreation areas

Most of the surveyed visitors (74,28%) would be willing to get personally involved in practical activities in the park forest Košutnjak while 96% of visitors have postitive perceptions of green areas and care about them. For the last question in which visitors had the option to provide personal comments about Košutnjak park forest, they state the need to light the trim track, the lack of potable water fountains, benches and garbage cans, the need to set up mobile toilets and solve the problem with stray dogs. Visitors also note the need to control vehicles parking because users often parked their motor car on the lawn next to the Trail.

CONCLUSION

Park Forest are valuable places of social interaction that brings together people of different age groups, cultural and social beliefs. Planners and urban designers should involve all categories of users of green areas, their needs and expectations in making decisions on planning and management of green areas. Location of recreation area affects the users structure and the way of using the place. The research results showed that the most of visitors came from the surrounding neighborhoods mostly for walking and enjoying nature but for active recreation also. The results produced information for solving practical problems related to maintenance and management of urban forests and emphasize the importance of communication with visitors to develop awareness of the importance of urban forests.

Acknowledgements

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LAWNS OF THE PARK IN BANOVO BRDO

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ABSTRACT

This paper analyzes the presence of plant species, and invasive and potentially invasive plant species, in the lawns of the Banovo brdo park in Belgrade. A total of 39 plant species were recorded in five sites of this park. Two species, *Stenactis annua* and *Robinia pseudoacacia* are characterized as invasive and potentially invasive. The measures of tending and maintenance of the lawns in the park are at a lower level than required. This conclusion is suggested by a marked presence of plants that were not sown in the analyzed lawns.

Key words: lawns, invasive species, parks.

INTRODUCTION

Lawns are the most vulnerable and sensitive part of urban greenery. They are subject to great changes due to intensive use and the maintenance of low intensity, therefore being a fertile ground for the emergence of weeds and invasive species. A growing number of scientists investigate invasive species, as they have become a major problem and an impediment to the conservation of biodiversity (Sala i sar., 2000, McNeely i sar., 2001, Cronk i Fullers, 2001, Sukopp, 2001, Cox, 2004). In addition to being a threat to native biodiversity, the number of invasive species that seriously threaten human health is increasing, while their presence in and around residential areas is highly undesirable. The aesthetic and urban values of city lawns are the most prominent in the parts of residential areas characterized by high population density (Stavretović, 2002).

This paper analyzes the lawns of the park in Banovo brdo, partly located along Požeška Street and partly on the border with apartment blocks. On the basis of the results of this research, conclusions were reached on the presence of invasive and potentially invasive species. The percentage share of invasive species was determined, as well as the relationship between these invasive species and other species. In addition, the residential area characterized by the highest presence of these invasive species was determined.

MATERIALS AND METHODS

The analysis of the structure and floristic composition of plants was performed using the standard Mid-European Braun-Blanquet phytocoenological method (1964), with the exception that communities were not determined. The following scale was used for the abundance and coverage in all phytocoenological records (Braun-Blanquet, 1928): + (the species is rare), 1, 2, 3, 4 and 5 (the highest mark shows the dominance of a species in terms of abundance and coverage).

The determination of plants was carried out according to the following literature sources: Flora SR Srbije I-X (The flora of SR Serbia I-X) (1970-1986)), Flora Europaea I-V (1964-1980), Javorka and Csapody (1934), Kojić (1990), Šarić (1991) and Stavretović (2008).

The data on the naturalization of species in Central Europe were used to determine the presence of invasive species, and they were taken from three relevant "online" databases. These databases are "Delivering Alien Invasive Species Inventories for Europe" (www.europe-aliens.org) which covers 63 countries / regions including 39 islands and marine and coastal areas, "CPS SKEW Schwarze Liste und watch-list Invasive gebietsfremde Pflanzen" (www.cps-skew.ch) and the Global Invasive Species Database (www.issg.org/database). Before designating a species as invasive, their status was checked in the databases with respect to the countries in the region, i.e. Hungary, Romania, Bulgaria, Croatia. If, at least in one of these countries, its character was designated as invasive (designation alien / established), it was also designated as invasive in the study area. In addition, the lists of authors were also used: Vrbničanin et al. (2004), Boršić et al. (2008) and Kaufman et al. (2007).

RESULTS AND DISCUSSION

The park in Banovo brdo borders Pere Steve Todorovića Street, Žarka Vukovića-Pucara Street and the very busy Požeška Street. This park is the most significant park area of the Municipality of Čukarica. The part of the park located along Požeška Street is representative, and its central part also shows a high level of organization and maintenance. The central part of this park is designed for children's play, gatherings and passive forms of recreation. The specificity of this park is reflected in its higher parts along Žarka Vukovića-Pucara Street. This part is influenced by the nearby forest of Košutnjak displaying many of its features, including a dense canopy, narrow crowns, tall stems and the like.

The floristic composition and lawn structure in the park of Banovo brdo are presented in a table which combines 5 phytocoenological records from the following sites:

1. Decorative lawn at the entrance to the park on the side of the green market in Banovo brdo;
2. Lawn on the slope next to the apartment blocks, near the children's playground;
3. The park lawn above record 2;
4. Lawn in the shade above the amusement park, often visited by children from the nearby kindergarten;
5. Decorative lawn at the entrance to the park from Požeška Street, close to the French bakery.

Table 1. Location: Park on Banovo Brdo estate

		area (m)	**300**	**75**	**105**	**900**	**120**
specie	**specie**	**Lawn high (cm)**	**25**	**30**	**30**	**20**	**30**
No	**No in**	**Lawn covery (%)**	**90**	**90**	**95**	**50**	**85**
	group	**slope (n)**	**2**	**60**	**/**	**3**	**2**
		exposition	**NW**	**EN**	**/**	**NW**	**NW**
A	**B**	**No of species in record**	**11**	**17**	**19**	**18**	**15**
		No of record	**1**	**2**	**3**	**4**	**5**
		I quality grass:					
1	1	*Lolium perene*	3.2	2.2	1.2	1.2	3.2
2	2	*Poa pratensis*	2.2	1.2	3.2	1.2	2.2
3	3	*Agrostis alba*	1.2	2.2	1.2		
4	4	*Agrostis vulgaris*					1.2
5	5	*Poa trivialis*	1.2				
		II bad grass:					
6	1	*Poa annua*	1.2			1.2	+
7	2	*Dactylis glomerata*			R	R	R
8	3	*Hordeum murinum*	1.2				
9	4	*Poa bulbosa sp. Vivipara*				+	
10	5	*Agropyrum repens*		R			
		III leguminose:					
11	1	*Trifolium repens*	1.1	+	1.1	1.1	2.1
12	2	*Trifolium pratense*		1.1	1.1	1.1	R
13	3	*Trifolium campestre*			R		
		IV other herbs					
14	1	*Taraxacum officinale*	+	+	R	1.2	R
15	2	*Capsella bursa pastoris*	+	+	+		+
16	3	*Bellis perennis*		2.1	2.1	R	+
17	4	*Stenactis annua*		R	R	R	R
18	5	*Plantago lanceolata*		1.1	1.1		+
19	6	*Plantago media*	+		+		1.1
20	7	*Stellaria media*	+		+		
21	8	*Geum urbanum*		R		R	
22	9	*Verbena officinalis*			R		R

23	10	*Glechoma hederacea*		1.1			
24	11	*Carex divulsa*			R		
25	12	*Achillea millefolium*					R
26	13	*Ranunculus repens*		R			
27	14	*Potentilla reptans*		R			
28	15	*Convolvulus arvensis*		R			
29	16	*Artcium lappa*				R	
30	17	*Linaria vulgaris*				R	
31	18	*Hypericum perforatum*				R	
32	19	*Ranunculus arvensis*		R			
33	20	*Ajuga reptans*				R	
34	21	*Geranium robertianum*			R		
35	22	*Prunella vulgaris*			R		
36	23	*Symphitum officinale*				R	
37	24	*Anagalis arvensis*			R		
		VI woody seedlings					
38	1	*Fraxinus ornus*				R	
39	2	*Robinia pseudoacacia*				R	

A total of 39 species were observed in the analyzed lawns of the park in Banovo brdo (Table 1). The largest number of plants present belong to the fourth quality group "other herbaceous plants", i.e. 24 of them (Figure 1, 61.54%). A much smaller number of plants belong to other groups of plants. However, the maximum coverage of the soil surface is provided by quality grass species (*Poa pratensis, Lolium perenne* and *Agrostis vulgaris*). According to Table 1, there is a marked presence of annual meadow grass (*Poa annua*), which is widespread in most of the analyzed sites. A significant presence of the species *Hordeum murinum* can be seen on the sunlit surfaces of the park along the road or in a small improvised playground for sports on the grass (football). Orchard grass (*Dactylis glomerata*) is present in a number of sites, whereas its presence is insignificant, which speaks of the level and quality of the lawns. The major legumes present are white and red clover (*Trifolium repens, Trifolium pratense*). Among other herbaceous plants, the highest coverage ratings were recorded for *Taraxacum officinale, Capsella bursa pastoris* and *Bellis perennis*. The lawns of this park display a high coverage of areas, the exception being the lawn in the shade in site 5 (Table 1). The average coverage of lawns in this park is 82%, while the average lawn height is 27 cm. Therefore, they can be characterized as unmowed lawns with a relatively low coverage.

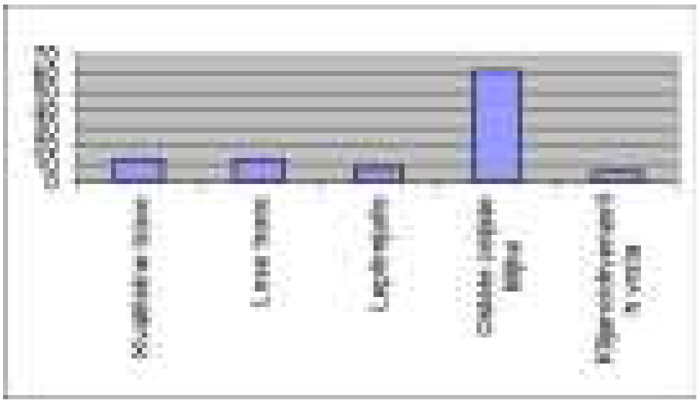

Figure 1. The spectrum of plant species present in the lawn of park Banovo Brdo by quality groups

CONCLUSION

The research of lawns was carried out in several sites of the Banovo brdo park in Belgrade. A total of 39 plant species were observed within the park area. A large number of observed plant species indicates a low intensity of care and maintenance in these lawns. The analyses revealed two invasive species in the lawns of the residential area, i.e. the herbaceous plant *Stenactis annua* and the seedlings of *Robinia pseudoacacia*. The low coverage of the lawns makes them a potential habitat for invasive species. The restoration of old, poor lawns, as well as their regular and proper maintenance can reduce the presence and potential appearance of invasive species in the lawns of both parks in Belgrade and in general.

Acknowledgements

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LAWNS OF THE RESIDENTAL AREAS OF BELGRADE
(The suburbs Cerak and Vidikovac)

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ABSTRACT

This paper analyzes the presence of plant species, and invasive and potentially invasive plant species, in the lawns of the residential areas Cerak and Vidikovac in Belgrade city. A total of 113 plant species were recorded in five sites. Within the researched localities eight species are characterized as invasive and potentially invasive and four are very aggressive plant species. The measures of tending and maintenance of the lawns in the park are at a lower level than required. This conclusion is suggested by a marked presence of plants that were not sown in the analyzed lawns.

Key words: lawns, invasive species, residential areas.

INTRODUCTION

Lawns are the most vulnerable and sensitive part of urban greenery. They are subject to great changes due to intensive use and the maintenance of low intensity, therefore being a fertile ground for the emergence of weeds and invasive species. A growing number of scientists investigate invasive species, as they have become a major problem and an impediment to the conservation of biodiversity (Sala i sar., 2000, McNeely i sar., 2001, Cronk i Fullers, 2001, Sukopp, 2001, Cox, 2004). In addition to being a threat to native biodiversity, the number of invasive species that seriously threaten human health is increasing, while their presence in and around residential areas is highly undesirable. The aesthetic and urban values of city lawns are the most prominent in the parts of residential areas characterized by high population density (Stavretović, 2002).

This paper analyzes the lawns of the residential areas Cerak and Vidikovac in Belgrade city suburbs.

MATERIALS AND METHODS

The analysis of the structure and floristic composition of plants was performed using the standard Mid-European Braun-Blanquet phytocoenological method (1964), with the exception that communities were not determined. The following scale was used for the abundance and coverage in all phytocoenological records (Braun-Blanquet, 1928): + (the species is rare), 1, 2, 3, 4 and 5 (the highest mark shows the dominance of a species in terms of abundance and coverage).

The determination of plants was carried out according to the following literature sources: Flora SR Srbije I-X (The flora of SR Serbia I-X) (1970-1986)), Flora Europaea I-V (1964-1980), Javorka and Csapody (1934), Kojić (1990), Šarić (1991) and Stavretović (2008).

The data on the naturalization of species in Central Europe were used to determine the presence of invasive species, and they were taken from three relevant "online" databases. These databases are "Delivering Alien Invasive Species Inventories for Europe" (www.europe-aliens.org) which covers 63 countries / regions including 39 islands and marine and coastal areas, "CPS SKEW Schwarze Liste und watch-list Invasive gebietsfremde Pflanzen" (www.cps-skew.ch) and the Global Invasive Species Database (www.issg.org/database). Before designating a species as invasive, their status was checked in the databases with respect to the countries in the region, i.e. Hungary, Romania, Bulgaria, Croatia. If, at least in one of these countries, its character was designated as invasive (designation alien / established), it was also designated as invasive in the study area. In addition, the lists of authors were also used: Vrbničanin et al. (2004), Boršić et al. (2008) and Kaufman et al. (2007). On the basis of the results of this research, conclusions were reached on the presence of invasive and potentially invasive species. The percentage share of invasive species was determined, as well as the relationship between these invasive species and other species. In addition, the residential area characterized by the highest presence of these invasive species was determined.

RESULTS AND DISCUSSION

As a part of research sites the settlement Cerak, Cerak Vinogradi and Vidikovac were monitored. Cerak Vinogradi and Vidikovac were slightly younger date then settlement Cerak. The settlements are connected or separated by streets. Kadinjačka street separates the settlements Cerak and Cerak Vinogradi, while Vinogradski Venac Street separates settlements Cerak and settlement Vidikovac. These settlements are located in the southern part of the city and adjacent to the settlements Žarkovo, Labudovo brdo, Kneževac and Rakovica.

The floristic composition and lawn structure in the residential areas Cerak and Vidikovac are presented in a table which combines 11 phytocoenological records from the following sites:

1. The lawn on a slope at the bus stops No 52, street Cerski venac.
2. The lawn inside the housing block, street Cerski venac No 9.
3. The lawn near the record 2, street Cerski venac No 11.
4. The lawn with two cascades, street Cerski venac.
5. High-maintained green areas between the buildings in Žitomislinačka Street.
6. Lawn in the residental area old Cerak, in front of building on the corner Petefijeva and Kosmajska street.
7. Lawn in front of Primarly school Branko Ćopić in Vidikovac residental area.

8. Lawn in Vidikovac settlement, Partizanska street, between the buildings near heating plant.
9. Lawn inside the Primarly school Branko Ćopić in Vidikovac residental area.
10. Lawn near "Maxi" shop, Partizanska street.
11. Lawn on playground between Partizanska and Susedgradska street.

A total of 113 species were observed in the analyzed lawns of the residential areas Vidikovac and Cerak. The average coverage of lawns in this park is 78%, while the average lawn height is 21 cm. On the lawns of researched areas six life forms of phanerophytes are presents. They are presented with seedlings of very used plant in town green spaces but extremely weed species also (*Rubus caesius*). In addition, two creeping chamaephytic *Vinca major* and *Vinca minor* are present which are used as a ground cover. In locations where they were observed, these plants are crossed boundaries on parts of the green areas in which they are planted and are spreading on the lawns (creepers, vines, sites 4, 5, 8). Spreading of individual flower species on the lawn explains the lack of care measure lawn edge BS 7370). The same is with the species *Calendula officinalis* and *Viola tricolor* which are out of the planting areas.

The total of 14 species of plants within the group of bad grasses and leguminoses are presents in the researched lawns, while 73 plant species are belonging to the group of other herbs. A large number of leguminoses indicating the low intensity of lawn care and closeness of agricultural land from which encourages greater number of plants. The most common leguminoses are *Medicago sativa* and *Vicia sativa*, and *Agropyrum repens* of the bad grass, which are cultivated plants and their weeds. Among other herbaceous plants are also present representatives of the most important weeds of agro ecosystems (according to Kojić, 1998). The large presence of species *Erodium cicutarium* confirms the fact that these species in certain circumstances can be used as a ground cover (Stavretović & Obratov, 1994).

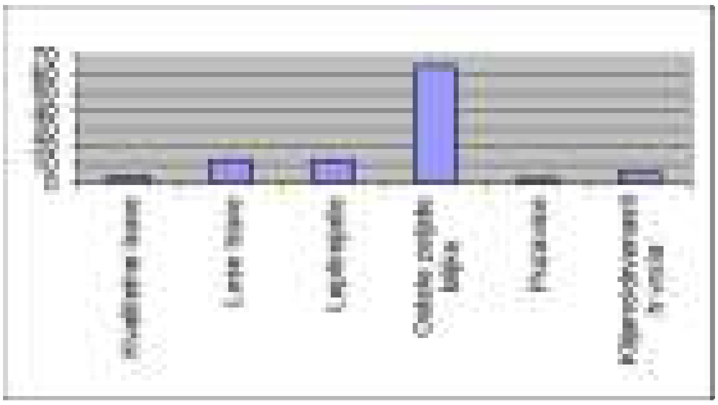

Figure 1. The spectrum of plant species present in the lawn of Vidikovac and Cerak residential areas by quality groups

On the study sites the invasive species with a small cover and abundance were observed (*Bromus tectorum, Sorghum halepense, Veronica persica, Stenactis annua, Oxalis stricta, Orlaya grandiflora, Cichorium intybus* and *Bidens tripartite*) and four very aggressive and expansionary species (*Cynodon dactylon, Polygonum aviculare, Artemisia vulgaris* and *Rubus caesius*).

CONCLUSION

A total of 113 plant species were observed within the Cerak and Vidikovac residential areas. A large number of observed plant species indicates a low intensity of care and maintenance in these lawns. The analyses revealed eight invasive species and four very aggressive plants in the lawns of the residential area. Law lawn cover represents a potential habitat for invasive species, restoration of old, poor lawns and regular and proper care can reduce the presence and potential invasive species in the grasslands of Belgrade and settlements in general. In residential areas a large number of people are living, among whom were a large number of children, so the care for green spaces of residential areas should be better.

Acknowledgements

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AIR QUALITY MONITORING BY USING EPIPHYTIC LICHENS IN THE URBAN PART OF PIROT (southeastern Serbia) 2002– 2014

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ABSTRACT

The field work consisted of collecting and identifying lichens and then, on the basis of the samples, index of air quality (IAP) was calculated for each investigated spot. On the basis of the calculated value of IAP index, lichen zones were described as "struggle zone" and "lichen desert". "Normal zone" has not been observed.

Based on research from 2002, 2009 and 2014, comparing the results, it was concluded that the zone "lichen desert" was increasingly present as a result of intense air pollution in Pirot.

Key words: index of air quality (IAP), lichens, air pollution, lichen zones.

INTRODUCTION

Human domination on Earth cause changes in its appearance, structure and functional characteristic. There is no ecosystem on which people do not have an influence. (Glavač, 1999)

Pollution is every qualitative or quantitative change in physical, chemical or biological characteristics of food, air, land or water leading to the destruction of ecosystems (Cvijan, 2000).

Air pollution first appeared with the appearance of fire and significant pollution occurs with the development of industry.

Bioindicators are biotic systems which are used for indication of changes in environment.

Lichens as bioindicators are very useful because of their sensitivity on changes in environment. Pirot is a town in south-eastern Serbia with temperate continental climate. The average maximum temperature is 18.42˚C and the average minimum temperature is 5.95˚C.

MATERIALS AND METHODS

The field work consists of collection of materials radially, from the city center to the periphery (Stamenković, 1997.): Lichen material is collected from certain points, the substrate from which the sample is taken is noted and then lichens ground cover is measured. After the determination of lichen based on the lichens ground cover, the index of atmospheric purity (IAP) can be calculated. (Stamenković, 2002.):

$$\boxed{\mathbf{IAP}= \frac{\mathbf{1}}{\mathbf{10}} \sum\nolimits_{1}^{n} (Qxf)}$$

IAP- index of atmospheric purity
Q- ecological index of every species
f- coefficient that represents the prevalence of finding each species as well as its cover at each point (counted from 1 to 5)

After the mathematical part, researched area is mapped while separating 3 zones:
- "Normal zone", where concentration of Sulfur-dioxide is low and the air is clean
- "Struggle zone", where concentration of Sulfur-dioxide is higher
- "Lichen desert", where the air is very polluted

Physico-chemical monitoring involves measuring the amount of nitrogen oxides, Sulfur-dioxide and soot using a machine PROEKOS AT801X2 in three places: the residential and administrative zone,the residential and recreational zone (Institute of Public Health Pirot) and industrial zone.

RESULTS

On 27 investigated spots 17 species from 12 genuses are collected. The most common species was *Xanthoriaparietina* (59.26%) and *Physciaadscendens* (59.26%).

Table 1. The substrat from which lichen material is collected and spots where the substrats are

The substrat	Investigated spot
Aesculushipocastanum	5, 6, 9, 16
Juglansregia	19
Malusdomestica	22, 23
Morus alba	18
Populussp	13, 25
Prunusdomestica	20, 21, 27
Robiniapseudoacacia	1, 2, 17, 24
Tiliasp	3, 4, 7, 8, 10, 11, 12, 13, 14, 26

Table 2. IAP on investigated spots, lichen species found on each spot and their cover (1-12)

investigated spot / species	1	2	3	4	5	6	7	8	9	10	11	12
Buellasp			1									
Candelariellaxanthostigma								2		2		
Everniaprunastri												
Hypogymniaphysoides	5									2		
Lecanoracarpinea									1			
Lecidellasp				1						2		
Lecidellaelaeochroma		1										
Melaneliaexasperata												
Parmeliasulcata	2	1	4					1				
Parmeliatiliacea	1										2	3
Phaeophyscia orbicularis	3	3	1	2	1	4	3	1	2		2	3
Physciaadscendens	4	2			1	2	3	2	1	3	4	
Physciaaipolia												
Physciastellaris			1									
Physconiagrisea								2				
Physconiaentheroxantha	4	2	3	4		2		3			3	
Xanthoriaparietina		4	1		3	2	2	1		1	2	
I A P	**6**	**5**	**4**	**2**	**2**	**3**	**3**	**4**	**1**	**4**	**4**	**2**

Table 3. (sequel of table 2) IAP on investigated spots (13-27)

investigated spot / species	13	14	15	16	17	18	19	20	21	22	23	24	25	26	27	%
Buellasp																3,7
Candelariellaxanthostigma						2				2	1			2		22,2
Everniaprunastri				3					2							7,40
Hypogymniaphysodes		1	1		1											18,52
Lecanoracarpinea				2					2							11,1
Lecidellasp																7,40
Lecidellaelaeochroma									3							7,40
Melaneliaexasperata							2	1	2			1				14,81
Parmeliasulcata									2	1				1	1	29,63
Parmeliatiliacea	1		2													18,52
Phaeophyscia orbicularis	1		1							2			3	1		59,26
Physciaadscendens	1	2				3				3	1				2	55,56
Physciaaipolia								3	2							7,40
Physciastellaris							3	3								11,1
Physconiagrisea				2												7,40
Physconiaentheroxantha						2						1				33,33
Xanthoriaparietina		1	3		3	3				2	1			3	1	59,26
IAP	**1**	**2**	**2**	**3**	**2**	**3**	**1**	**2**	**5**	**3**	**1**	**1**	**1**	**3**	**1**	

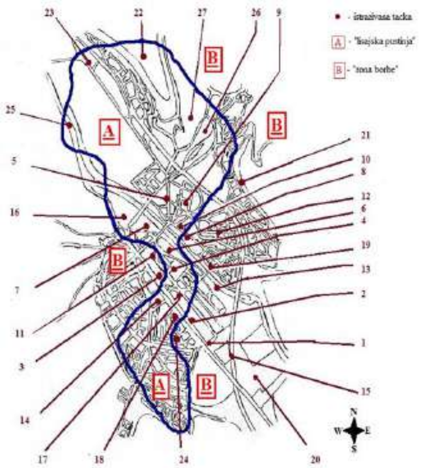

Figure 1. Map with investigated spots and lichen zones

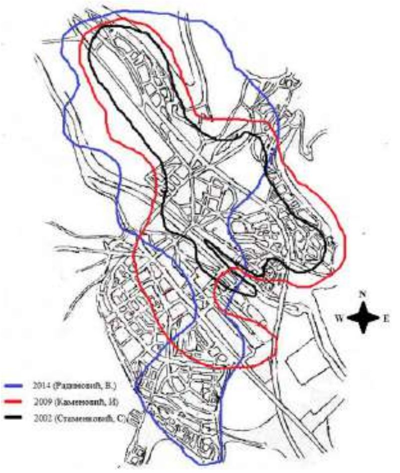

Figure 2. Simultaneous display of lichen zones (2002, 2009, 2014)

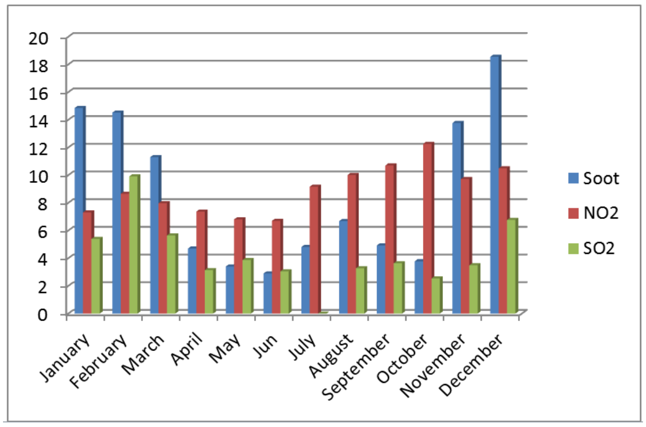

Figure 3. Concentration of soot, Sulfur-dioxide and Nitrogen-dioxide for year 2013

DISCUSION

Based on Fig. 1, we can see that the biggest part of Pirot is a "lichen desert" which indicates that the air in the urban part of Pirot is very polluted. By comparing the results of previous researches (Fig. 2) increase of a 'lichen desert" can be seen through time. First, it occupied just a small area around the Industrial zone "Tigar" (2002) but by 2014. it has expanded to the city center which is a consequence of increased production from "Tigar" and increasing number of motor vehicles.

Lichen fungi decreases through time. In 2002 it was registered 27 species from 14 genera, in 2009 it was registered 22 species from 11 genera and in 2014, 17 species from 12 genera.

One characteristic thing about the research in 2014 is that the "Normal zone" is not present. The cause of decreasing of lichen fungi may be reinforced by cutting of the substrate.

The results which are given by the Institute of Public Health Pirot and the results of the biological monitoring may be in mild opposites, which is primarily related to the time of air quality monitoring. Physical-chemical monitoring shows the current concentrations while the biological monitoring shows the cumulative effect of the concentrations of pollutants on organisms (lichens). Also, physical-chemical monitoring shows that the air quality is at low level in the winter months and that has to do with the increased combustion and heating. Indicative fact is that the air quality is the worst around the "Tigar"corporation.

CONCLUSION

Pirot is a city with about 60.000 inhabitants settled near mountain of Stara.

The air quality in Pirot is decreasing and without necessary protection methods it can be predicted even rapider decreasing.

The analysis of the results can be concluded that the concentrations of sulfur dioxide and soot measured in Pirot had the seasonal nature of increase, so are increased in the heating season.

According to the results of the Institute for Public Health Pirot, the air is relatively clean over the year, while concentrations of sulfur dioxide, nitrogen oxides and soot grow during the winter because of the increased heat and smoke discharge from households. The results obtained by the Institute for Public Health and the data presented in this paper does not fully agree and the reason is the cumulative effect of pollutants that tracks biological monitoring.

In addition to the physical-chemical monitoring it is necessary to develop a biological monitoring, obtain objective data and propose adequate protective measures.

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OVERVIEW OF THE RECONSTRUCTION OF SQUARE OF JOVAN SARIC IN KRALJEVO CITY

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ABSTRACT

Taking into that cities are being filled with buildings, architectural elements and hard–surfaces, the aim of this research is to determine vitality and visual aspect of the existing plants on the square of Jovan Saric in Kraljevo city and also to create a proposal for reconstruction of sustainable green space area based on it's current condition. The result of the research has confirmed that considerable amount of the square's surface is paved (75,15%), consequently, green space area must be increased. With that in mind, number of the woody plants must also be increased which will ease climate extremes, create shade and lower the insolation. Functionality and visual value of the green space area is correlated with the selection and application of taxa which is restricted by their bio ecological characteristics. In order to preserve biodiversity, culture and history, and because of their adaptive ability, use of the autochthonous species is recommended. Reintroduction of specie *Syringa vulgaris* L. and it's lower taxa is specially proposed because of vicinity of valley of the Ibar river which is also known as the Valley of lilacs.

Key words: landscape architecture, dendroflora, reintroduction, autochthonous species, lilac.

INTRODUCTION

In populated places plant material plays an important role and has positive effect on an environment by having sanitary, technical, urban–architectural, aesthetic, cultural, psychological, and other functions (Anastasijevic, 2007). Cities have large areas covered with hard–surfaces, while there is little vegetation. Therefore, it is important to plan plant material that can improve state of an environment, coordinated by ecological conditions and biological plant requirements. Dendroflora of Serbia consists mostly of autochthonous species. Alien species are usually planted in urban areas. Exotic species are used on green space areas because of their decorative effects, fast growth or bio reclamation features. However, most of the woody plants (two–thirds) planted in the urban areas of Serbia are alien species (Vukicevic, 1996) that must not be neglected but instead chosen and nurtured carefully. Most of parks and green space areas do not include autochthonous, relict or endemic species. Research of dendroflora of Belgrade city shows that most of the trees, shrubs, and climbing plants have an alien origin (Ocokoljic, 2006; Jovanovic, 2007). It is important to use more autochthonous species to protect and conserve biodiversity of Serbia.

The aim of this study is to give a proposal for reconstruction of green space areas of square of Jovan Saric based on vitality and visual aspect value of the plants and their distribution by origin.

STUDY AREA AND METHODS

Square of Jovan Saric (Image 1) is located in the downtown of Kraljevo city, right next to the town hall (43°43'29" и 20°41'17"). In the north part, square borders Car Dusan's Street and in the south Car Lazar's Street. Surrounding buildings are built in the style of socialist realism. Total area of the square is 3167 m^2 and green space area spreads on 787 m^2. Medium altitude is 210 m. Most of the soil near Kraljevo city is pseudogley (Sikiriš et al, 2013). Due to urbanisation soil is mostly anthropogenic. Climate is described a transition between mild ocean climate in the Western Europe, Mediterranean and harsh continental climate in the Eastern Europe and is determined by great oscillations of meteorological elements. The area of square was once covered by phytocoenoses of Hungarian and Austrian oak forests (*Quercetum frainetto-cerris* Rud.). In the Ibar river valley, Lilac (*Syringa vulgaris* L.) forms permanent plant community of primary characteristics *Syringetum vulgaris serpentinicum* Jov et Vuk (Vukicevic, 1996; Tomić, 2004). Uros I planted lilacs with decorative flowers (Stojicic, 2010) in the Ibar river valley, along the road, to solemnly and royally welcome his future wife which she used to arrive to Kraljevo city. From that point lilac represents the symbol of Ibar River.

During analysis of the researched area, different values were given for vitality and visual quality of the existing plants and functionality of the square. Vitality and visual quality were graded with numbers from 0 to 5, 0 being plant with no aesthetic values and 5 being plant with great visual qualities and good health. Field research included measuring height of the trees according to Blume Leissov's measuring scale and also ground covered by shrubs using a measuring tape. Reconstruction and selection of the new planting material has been nominated according to current plant layout and architectural elements present in the field.

RESULTS AND DISCUSSION

There are 11 different taxa of woody plants recorded in the area of square of Jovan Saric. 4 different taxa of woody plants are recored within 16 trees. There are two taxa from the division of *Pinophyta*, *Pinus strobus* L. (2 specimens) and *Juniperus virginiana* 'Skyrocket' (1 specimen). There are two tree taxa, *Tilia tomentosa* Moench (8 specimens) and *Magnolia grandiflora* L. (4 specimens) from the division of *Magnoliophyta* (Table 1). There are also seven shrubby taxa recorded in the green space area of the square: *Syringa vulgaris* L., *Berberis thunbergii* 'Atropurpurea', *Cotoneaster horizontalis* Decne. *Lonicera pileata* Oliv., *Euonimus japonicas* 'Aureomarginatus', *Pyracantha coccinea* M.Roem. and *Rosa polyantha* Carr.

Comparative analysis, on the individual level, of plant heights shows that *Pinus strobus* L. is the highest taxa (17 m) in the researched area, and on the other hand *Juniperus virginiana* 'Skyrocket' is the lowest (1,2 m). Analysis of the vitality and visual value, on the individual level, shows that *Tilia tomentosa* Moench has the highest grades

(4,87); *Juniperus virginiana* 'Skyrocket' has the lowest grades (1) of all the researched plants which is why it is suggested for removal (Table 1). Vitality grades of shrubby taxa are ranged from 3 to 5, and visual values grades are ranged from 2 to 5 (Table 1). Taxa with the highest grade of vitality and visual value is *Syringa vulgaris* L., while *Euonimus japonicas* 'Aureomarginatus' and *Pyracantha coccinea* M.Roem has the lowest, which is why evergreen spindle with variegated leaves and firethorn are suggested for removal.

Diversity of the autochthonous dendroflora is small. Researched area contains only two autochthonous taxa (*Tilia tomentosa* Moench and *Syringa vulgaris* L.), which represent 18,18 % of all taxa present on the square. There are 81,82 % of allochthonous taxa.

On the green space area of the square in front of the town hall, first lilac was ceremoniously planted by tennis player Novak Djokovic. In front of the lilac there is informational panel set at top of the stone plinth. Researched area should be dominated by the first *Syringa vulgaris* L., which also represents the main motif of Kraljevo, city of lilacs. However, to make that lilac dominant, stone plinth with informational panel must be removed and replaced with smaller one, closer to the ground level. To form open space dominated by the lilac, it is recommended to replant taxa *Cotoneaster horizontalis* Decne. from current position to space currently occupied by the firethorn. Taxa *Berberis thunbergii* 'Atropurpurea' should be replaced with specie *Berberis vulgaris* L.

By comparative analysis of current situation in the field, environmental conditions, and purpose of green space area of the square of Jovan Saric it is suggested to: build wooden pergolas in style complemented by architectural elements of the town hall building, increase shaded area and upgrade open space from aesthetic point of view but also improve area with special meaning and symbolism. Decorative elements of pergolas should be similar in style with sun-breakers on the front of the building. Existing benches should be modified to look closer similar to the style of the pergolas. Pergolas are designed with openings to direct view on lilacs. Beside existing lilac in the analysed area, it is planned to symmetrically plant five more shrubs of the same species. Each in front of the different opening in pergolas. It is suggested to use cultivar *Syringa vulgaris* 'Frederick Law Olmsted', which has white flowers — contrasting flower colour of the shrub planted by Novak Djokovic and boarder of lavender (*Lavandula angustifolia* Mill.) on short sides of the green space area (Image 2). This way, main focus is directed at existing lilac. Green space area with the lilacs should be illuminated by night. Lighting should be in the form of reflectors, directed at the pergolas and lilacs.

For greening of peripheral parts of the square it is suggested to use *Picea omorika* (Pančić) Purk., endemic and relic species distinctive for Blakan peninsula, with narrow pyramidal shape, endemic and relic *Pinus peuce* Griseb. with dense and conical shape and relic *Corylus colurna* L. with conical habit (Ocokoljic&Ninic–Todorovic, 2003). To improve aesthetic quality of the green space area, it is recommended to use autochthonous shrubby species like evergreen *Prunus laurocerasus* L. and *Cotinus coggygria* Scop. with ornamental cotton like fruit. Their use will also greatly affect biodiversity conservation of our country.

Landscape architectural elements are in great condition and their number should not be changed. Analysis of the lawn led to conclusion that its vitality, visual quality and functionality grades are very low because of the presence of barren patches and weeds.

Lawn needs to be reconstructed and established of the highly decorative lawn mixture made out of two species: *Festuca rubra* L. (60 %) and *Poa pratenis* L. (40 %).

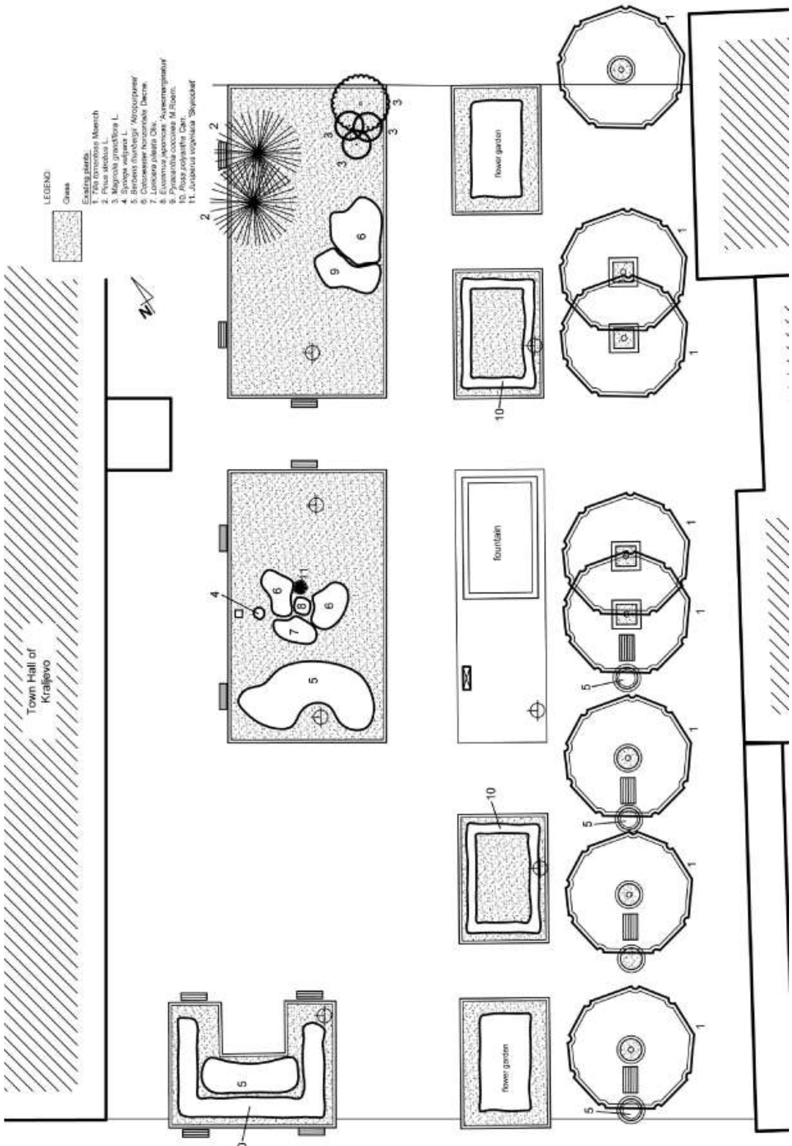

Figure 1. Layout plan of the square of Jovan Saric in Krajevo city

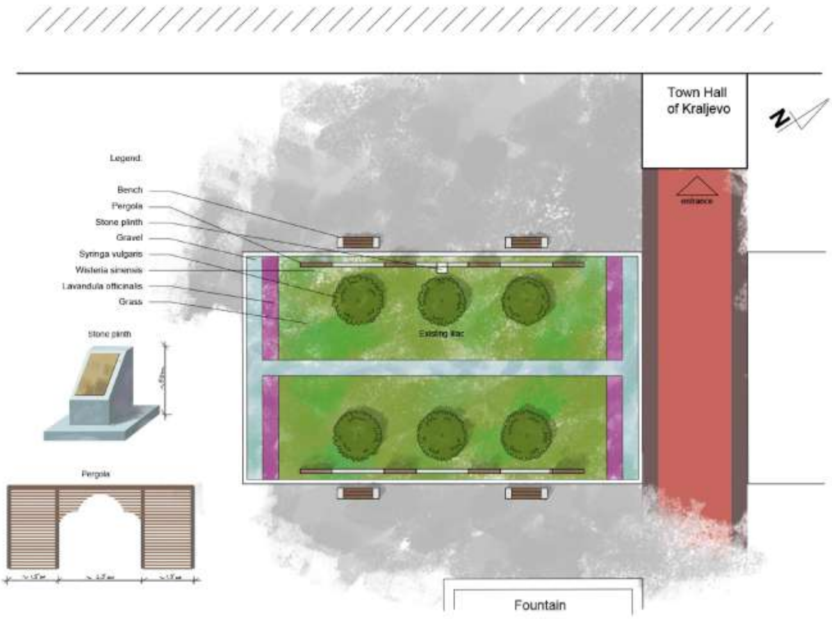

Figure 2. Plan of reconstruction of the green space area portion on square of Jovan Saric in Kraljevo city

Table 1. Analyzed parameters of dendroflora on square of Jovan Saric in Kraljevo city

Taxa	**Plant height [m]**			**Area [m^2]**			**Vitality grade (1-5)**			**Visual value grade (1-5)**		
	Min	$\bar{x}$	**Max**	**Min**	$\bar{x}$	**Max**	**Min**	$\bar{x}$	**Max**	**Min**	$\bar{x}$	**Max**
1	**2**	**3**	**4**	**5**	**6**	**7**	**8**	**9**	**10**	**11**	**12**	**13**
Juniperus virginiana 'Skyrocket'	1,2	1,2	1,2	-	-	-	2	2	2	1	1	1
Magnolia grandiflora L.	4	5,75	9	-	-	-	3	3,5	5	2	3	5
Pinus strobus L.	17	17	17	-	-	-	4	4,5	5	4	4,5	5
Tilia tomentosa Moench	8	15	14	-	-	-	4	4,87	5	4	4,87	5
Berberis thunbergii 'Atropurpurea'	-	-	-	1,06	9,56	30,47	3	4	5	3	3,67	4
Cotoneaster horizontalis Decne.	-	-	-	4,88	7,92	12,8	3	3	3	3	3	3
Euonimus japonicas 'Aureomarginatus'	-	-	-	1,12	1,12	1,12	2	2	2	2	2	2
Lonicera pileata Oliv.	-	-	-	4,12	4,12	4,12	3	3	3	3	3	3
Pyracantha coccinea M.Roem.	-	-	-	8,66	8,66	8,66	3	3,5	4	2	2	2
Rosa polyantha Carr.	-	-	-	14,94	19,3	28,02	4	4	4	4	4	4
Syringa vulgaris L.	-	-	-	0,4	0,4	0,4	5	5	5	5	5	5

CONCLUSIONS

There are 11 different woody taxa found in the area of square of Jovan Saric: four are trees and seven are shrubs. Analysis of the vitality and visual quality has shown that average grade for vitality is 3,58, and visual quality 3,37. The diversity of autochthonous woody taxa is small. There are only two autochthonous taxa present in the researched area. The reintroduction of autochthonous species, especially *Syringa vulgaris* L and its lower taxa *Syringa vulgaris* 'Frederick Law Olmsted', is recommended to enrich dendroflora and protect biodiversity of Serbia. Openings on well–lit pergolas direct views to lilacs, which will become the symbol of recognition of Kraljevo city. Percentage share of the domestic species will increase from 18,18 % to 57,14 % by using taxa like *Syringa vulgaris* L., *Picea omorika* (Pančić) Purk., *Pinus peuce* Griseb., *Corylus colurna* L., *Prunus laurocerasus* L. and *Cotinus coggygria* Scop. and removing alien species with low vitality and visual quality. After the reconstruction, number of alien species will be 42,86%. Vitality, functionality and visual quality of the existing lawn is negligible, thus it needs to be reconstructed using the lawn mixture of *Festuca rubra* L. и *Poa pratenis* L.

Suggested reconstruction and plants are determined on the basis of current plant material and architectural elements position and their relationship. It is also in accordance with rich history of the Ibar river valley.

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NEW URBAN REALITY: HYBRID MEGALOPOLIS

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ABSTRACT

Modern city emerges in a process of expansion of urban areas, due to intensive migrations and growth of urban population. The generation of new urban forms (metropolitan areas, city regions, megacities) and appearance of conurbations, polycentric urban agglomerations, represent the most important evolutional rise of the cities in the twentieth century. The networking of these large cities created megalopolises, initially interpreted as a phase in urban overdevelopment, the development leading to social abyss with inability to efficiently manage the city area, and subsequently regarded as a geographic indicator, the inevitability of market economy, and even as a desirable form of population concentration, as opposed to the endless zones of suburban typology with low density. The new challenges of urban areas are created by radical changes in technology, particularly in its economy, ecology and energy. Today's progressive megalopolises are to be thanked for the development of dual city nature through combination of real, physical urban reality and the virtual, technological one. This paper considers these phenomena of new urban reality as a new postulate for discussion about the city.

Key words: city; megalopolis; hybrid; real and virtual space.

INTRODUCTION

Cities around the world are getting bigger, more versatile and fluid. The unrestrained expansion of urban areas alienated these agglomerations from traditional understanding of the city. Namely, according to the United Nations' data on world population, more than half of the world population (51.6 percent) lives in the cities today. Also, this percentage is expected to rapidly increase and amount to 67.2 percent by 2050 [1]. According to these forecasts, the world population in the cities would grow from current 3.5 billion to 6.2 billion by 2050, and almost entire growth is expected in least developed countries. At that time, 73 percent of world's population will be comprised of urban population in Asia and Africa. By 2020, there will be 30 cities in the world with more than 10 million inhabitants, the biggest will be Tokyo with 38.71 million, and by 2050 more than one billion people will live only in Chinese cities.

Mass urbanization and quick expansion of cities and megalopolis regions worldwide represent the most important phenomena of our planet's transformation. This explosive growth is mostly unplanned. The cities in the developing countries are not prepared for absorbing several million people from poor rural areas coming to cities, and direct consequences of such population inflow imply the appearance of informal settlements with substandard living conditions [2]. Although the largest part of urban transformation is almost finished in the developed societies, there is a real concern about the phenomenon of expansion of low density zones i.e. increase of their harmful ecological impact. These long-ranging demographic and economic transformations are followed by geographic changes which are particularly important at the time of global climate changes. The expansion of city area increasingly consumes arable and other land. This global trend of constant expansion of city agglomerations can be considered as an inevitable process taking into account the pressure and size of population wave towards the cities.

European demographic trends are also full of different challenges. Namely, the number of people over 60 years of age has been increasing in the EU by 2 million per year. In certain EU member states, the detailed regional analyses indicate the demographic forms concerning mobility and migrations, and the modest growth of population is usually justified by migration waves. According to the UN data, the European urban population grew by 91 percent between 1950 and 2010, whereas the total number of citizens increased by nearly 35 percent. Despite generally negative demographic trends, the increase of urban population at the European continent will be 10 percent in the period 2010-2050 [1]. At the same time and according to the same forecast, the overall European population will start to decrease as soon as from 2020 or 2025, and negative ratio between the total number of inhabitants between 2010 and 2050 will be 2.6 percent.

GLOBAL INSTANT URBAN EXPANSION: PATH FROM CITY TO MEGALOPOLIS

The notions of city, metropolis and territory are now extended to new meanings in line with their own spatial mutations, by new urban forms and modified role of architects in city formation. In the process of consideration of urban future or redefinition of urban concepts we must respect this essentially changed urban lexicology. Cities are therefore constantly changed, built, renewed and reformed, inhabited by different groups of citizens, and used for different purposes. In search for better spatial organization and optimization, more efficient economy and other benefits provided by urban agglomerations, cities experience differently graded social differentiation. In most urban areas of the developed world, despite social heterogeneity and spaces with mixed purposes, it is relatively easy to discern the spread spatial segmentation to different functions [3]. This indicate the urgent need for new, sustainable approaches to urban development leading to increasingly ecological, resistant and inclusive cities that can contribute to fight against climate changes and resolution of urban imbalances [4].

Many cities have thus started to interconnect and, together with nearby smaller urban areas, create complex forms of *megalopolises*. People worldwide have moved to cities in search for job and advantages of urban culture, which led to establishment of large metropolitan areas with significant periurban zones.

The term *megalopolis* (Greek for large city, too large city) was used in modern time by Oswald Spengler in his book "The Decline of the West" (*Der Untergang des Abendlandes*, 1918), and subsequently by Lewis Mumford in his 1938 book "The

Culture of Cities", which described it as the *first stage in urban overdevelopment and social decline*. Later, it was used by Jean Gottmann in his studies and publications published in the 1950's and 1960's to describe the huge metropolitan area along the eastern seaboard of the US, and whose population in 1960 counted 37 million inhabitants [5].

Scientific use and application of the theory of metropolises is mostly founded on definitions and theoretical researches of Patrick Geddes, Mumford and Gottmann. Geddes is responsible for introduction of *conurbation* neologism in his 1915 book "Cities in Evolution" to define a polycentric urban agglomeration with the developed transport system connecting all areas in a single labor market [6]. Geddes had major influence on Mumford who anticipated the upcoming global cataclysm and wrote in "The Culture of Cities" [7]. Mumford saw the phases of megalopolises as a synonym for the decline in city development, although he left certain space for possible hope in the new beginning, overcoming of inertia and resistance to imminent disintegration processes [8].

Today's megalopolises are by default polycentric and, as such, they connect several differently built areas, covering the unbuilt areas as well, both inside the wider city area and between the individual elements of general megalopolis. European megalopolises are also the home for high percentage of the total population on the continent. These cities together make a connected line of settlements, and the best European example is the so-called "Blue Banana" or *European megalopolis,* from Liverpool to Milan, with around 110 million inhabitants.

Designers and planners of megalopolises are also faced with the challenge of location of complex urban forms of the new social and economic order of city networks, respecting the phenomenon of deregulation, capital accumulation, individual liberties and mobility [2]. Today, we probably witness the most intensive migrations in the history of mankind. In addition, the described intensive population growth in the world cities directly affects the rapid environment degradation, as well as the quality and quantity of renewable resources. The growth of production and consumption, aimed at meeting the demand of the increasing number of inhabitants, requires more resources, which inevitably leads to increasing ecological problems [9]. The consequence of population growth can thus be interpreted through interaction with other variables and transformations in technological sphere, economy, ecology, energy, social structure and other areas as well.

HYBRID MEGALOPOLIS

The comprehension of megalopolises, grown from trans-metropolitan clusters, and their current development requires the analysis of spatial connections and the manner of city connection [10]. Therefore, it is necessary to consider the so-called "space of flows" [11] or groups of connections that connect the locations through transport systems and business networks. The most complete analysis of these courses implies the consideration of place and course of the space [12].

Technology has changed the society and, subsequently, the city has changed as well. Today it lives parallel in real and virtual environment. By creating a hybrid space i.e. combining the physical, real and virtual space, urban areas gained an incentive for expanding its field of action. With a quicker growth of new technologies in the last decades of the twentieth century, the electronic communications have drastically expanded in global space. Innovations, particularly in the financial liberalization and electronic communications, incited the changes that cause radical merging of cities in city networks. This caused the connection between urban entities around the world. In this process, the entire planet is turning into a kind of matrix where all electronic and physical territories are inter-connected, and the limits between reality and virtual reality are hazy. This situation can be explained as global network which is "made up of multiple, complex processes with near-infinite levels of fractal detail and intensity, all built from an enormous number of constituent bits and bytes, a number which is growing exponentially every day" [13].

Radical changes in the sphere of technology created a complex urban geography, creating new challenges for the community, its economy, energy, ecology and culture, in urban areas. One can observe the increasingly complex functions and their differentiation between the cities, functions in the cities as part of the global network of cities [12]. In addition, a new term– global city, is being introduced [14].

Recently, new technologies striving to make the city expressively fluid, hybrid and complex are resulting in a phenomenon of new urbanization or the so-called hybrid geography. These technologies have reformed the space-time contours and changed the ontological and ecological limits, both on macro and on micro levels. In this sense, on macro level we can only discuss the global technological space which tends to deconstruct the existing spaces via electronic networks and through the process of deterritorialisation. On one hand, the rules of traditional planning insist on interpretation of urban space within urban territory, whilst, on the other hand, the urban approach, including virtual reality, implies exceptional mobility and mobility of information which radically change the comprehension of the city and city territory. Graham and Marvin deem that the difference between the traditional/real and virtual space is compatible and that these two spaces are actually mutually compatible [15].

Contemporary researchers are starting to observe the limits of physical space in a completely new manner. Namely, until recently, the inter-space was observed as unchangeable, inactive areas or as marginal, periphery space. But in a new perspective, such spaces are considered as growing, dynamic spaces. At the same time, with the income of new technologies in physical spaces of future cities and by generation of a new form of technological, social, economical, energy, ecology and cultural spaces and areas called virtual geography or cyber-geography [15], the limits between the real and virtual space, between humans and machines, become even more blurred. A hybrid space is slowly developed between them, as a part of our urban routine and practice.

In order for us to understand the relations between the physical, real urban space and the virtual space, it is necessary to consider the city as an urban matrix made of real and virtual courses. Edward Soja claims that the compressed spaces, such as the virtual city, do not really mind for distances any more [16]. The combination of spatial and electronic communications creates a mixture of different relations in time and space, which is more complex than the spatial elements of urban design. This requires a comprehensive conceptual approach which recognizes the impact of technology on physical space. Today we are faced with another kind of impact. By everyday use of electronic communications instead of time and space, the territory is actually increasing.

Kellerman deems that the connection and simultaneous growth of the real and the virtual space is particularly important, alike that of the space between them – hybrid space, reflecting the role of urban geography in production, spending, distribution, knowledge and experience [17]. In particular, the different correlations between the real and virtual space can be illustrated by mutual dependence of their action, parallel development of both spaces, even duplication of the phenomenon of appearance/disappearance of the place and activity in these two spaces [17] .

Graham and Marvin see the cyber-space as a metropolitan space, primarily as it developed from the traditional city [15]. Cyber-space enables the appearance of new forms of social aggregations that permit the individuals to meet and make new relationships. Several researchers such as Mitchell, Ostwald and Crang adopted these architectural metaphors to theoretically explain the cyber-space and its virtual environment. The permanent internet link makes the users feel like they are not "entering" the cyber-space. Subsequently, the difference between the physical-real and virtual space becomes blurred. The hybrid space starts where it is no longer necessary to depart the physical, real space in order to connect with other people, on different open geographic spaces that nurture this type of collaborative models.

Despite the anticipations of certain theoreticians that we are going to face the loss of place identity due to digital telecommunications providing the access to everything, at all places and at any moment, it is indeed impossible to imagine the disappearance of the spatial aspect of city. Paul Virilio poses the question of whether in the future city which loses its spatial aspect and which is atomized in electronic matrices, without strong physical connections, the digital interface can lead to the situation or environment deprived of horizon i.e. optical density [18]. Castells notes this dilemma underlining that we are increasingly living in an urban society without cities [19].

CONCLUSION

Today cities are completely different from the industrial one, endured new structural transformations, with more than half of the world population already lives in urban areas, and by the end of the century this percentage will significantly rise. This mass urbanization and quick expansion of cities and megalopolis regions worldwide represent the most important phenomena of our planet's transformation, where cities around globe are connecting into the networked cities. This connection in made both in the real and virtual platforms, and contributes to desolation of certain areas, along with updating and development.

From the aspect of regional planning in the context of development of information society applications, the suggested approach pertains to designing of hybrid spaces patterned. This hybrid urban model is a starting point for contemporary critical contemplation of significant social, spatial and metabolic urban transformations in the decades to come. However, by careful examination of the impact of these innovations incorporated in the modern city, it is becoming more obvious that the cities are faced with merging of physical and virtual spaces at several levels instead of mere urban dispersion, therefore hybrid megalopolises are our common future.

Acknowledgments

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REGIONAL LANDSCAPE PROPOSAL CONCEPT FOR PROGRAM GUIDELINES AND USAGE OF THE MUNICIPALITY OF ULCINJ IN REPUBLIC OF MONTENEGRO

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ABSTRACT

The municipality of Ulcinj is located in the extreme southern part of the Adriatic coast of Montenegro. The significance of the total area of the Municipality of Ulcinj, especially towards the development of the tourism industry to contact densely built urban areas of the city of Ulcinj it is necessary to pay attention and to guide the development of the municipality and quality to new areas of the tourism industry and new centers, to the extent that these spaces its capacity can support and in doing so does not disturb the natural, ecological, and hence social, political and economic trends.

Key words: Ulcinj, preservation, sustainable, landscape, tourism.

INTRODUCTION

We will briefly through the following text justify its richness and beauty that adorn it, but also the dangers that threatens to undermine the magnificence. The municipality of Ulcinj is located in the extreme southern part of the Adriatic coast of Montenegro. This area is located between 10° 0,9' i 22" East longitude and 41° 51' i 42° 0,4' North latitude and has 39 residential places with it in city center of Ulcinj. According to data taken from the General Urban plan from the year of 2008 in the municipality of Ulcinj there have lived 44390,00 residents of which 12900,00 suburban residents [1]. The significance of the total area of the Municipality of Ulcinj, especially towards the development of the tourism industry to contact densely built urban areas of the city of Ulcinj it is necessary to pay attention and to guide the development of the municipality and quality to new areas of the tourism industry and new centers, to the extent that these spaces its capacity can support and in doing so does not disturb the natural, ecological, and hence social, political and economic trends.

Geomorphic features indicate that a very large percentage of the terrain is below 100 m asl, approximately 65,90% of the municipality of Ulcinj which is otherwise very convenient. What is inter alia a negative dissected relief [1]. The geological composition of the area of Ulcinj minicipality is very complex. In the procedure it represents the middle Miocene and the middle and upper Eocene. There are a relatively small number of surface flows in spite of high rainfall, which is offset by underground streams. In municipality there are thousands of olive trees (over 80,000.00 trees only in Ulcinj city) along the coast, palm trees, oleanders, mimosas and wild and domestic pomegranates, figgs, oranges, mandarins, grapes and lemon trees. Most of the Ulcinj municipality regia by phytosociological origin remains unchanged but due to degradation of vegetation cover, by the flysch base with pronounced slopes and almost all sides of the limestone massifs are affected by erosion. Rare examples of flowers and decorative trees are cultivated there in the form of individual gardens and parks. Municipality of Ulcinj is extremely seismological active space. It Belongs to the ambience units of riparian zone and river valleys of lowlands.

MATERIALS AND METHODS

Literal material that is used for this paper is professional literature in the field of landscape ecology which deals with the interrelationships and hierarchical setting in the landscape.

Methods that is used in the analysis of the municipality of Ulcinj combines ascendant and descending layer-analysis approach in landscape [4]. It consists of the original boundary, separating regions of larger spatial units, according to the criteria of geomorphic and pedologic units and human activities through land uce, and lower hierarchical systems-functional landscape elements.

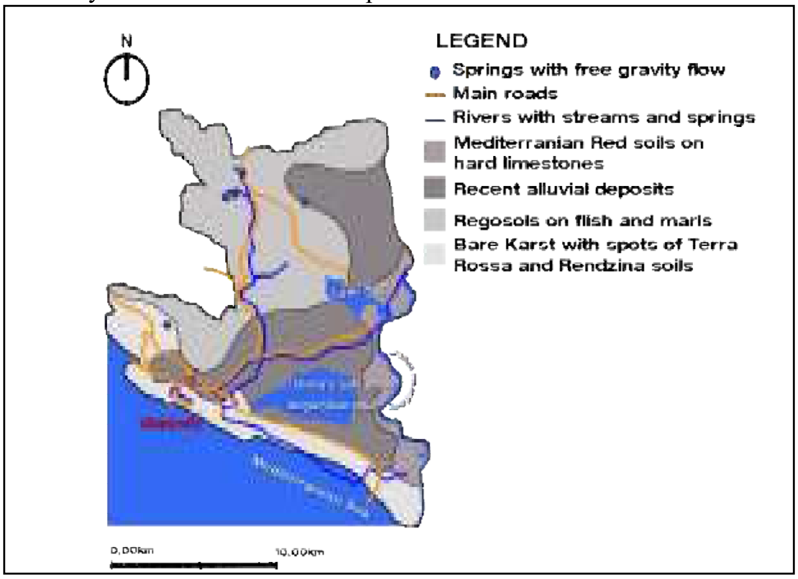

Figure 1. Pedological map of municipality of Ulcinj

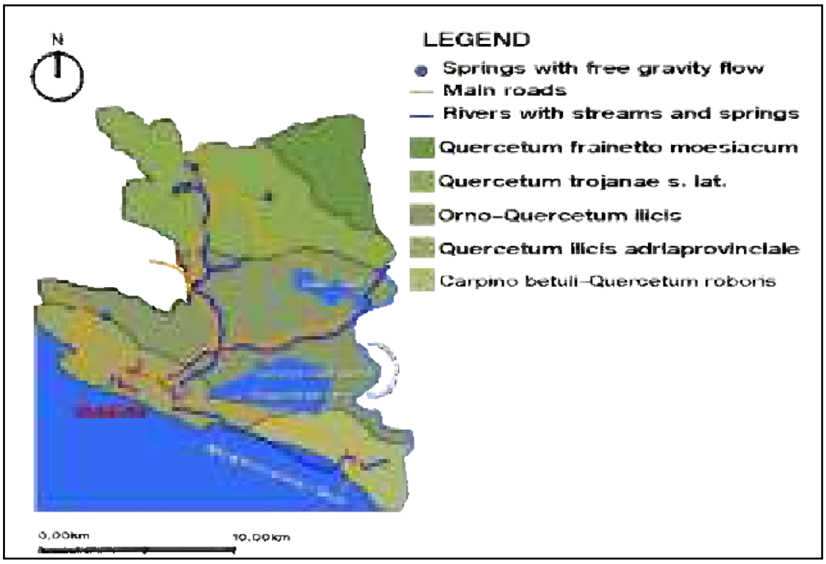

Figure 2. Map on natural potential vegetation of municipality of Ulcinj

DISCUSSION

After all the presentations of expert materials we can extract some of the following resources that are regional problems and manmade conditions and forms of Ulcinj municipality:

- Presence of some indigenous vegetation resulting through erosion processes;
- Negative tendencies construction building surfaces that result from uncontrolled called, "wild" and it works in the most sensitive areas;
- Unplanned and illegal cutting of forest vegetation;
- Absence of ecological zoning and hierarchy of the municipality and not crosslinking landscape elements into a single system;
- Insufficient of the existence of multidisciplinary planning documents and inconsistency with the regulations and laws in the area of sustainable development;
- Site conflicts in the capacity of the coastal zone with strict urban centers.

After all the presentations of expert materials we can extract some of the following resources that are regional potentials and manmade conditions and forms of Ulcinj municipality:

- Development and promotion of ecological, natural, social, economic, technical, cultural and political capacity through creation of closed local municipality system that is connected with its integral relation with the surrounding;
- Economic and geographical resources within the Municipality of Ulcinj are suitable for the development of economic activities are tourism, the use of the

sea, agriculture, citrus fruits, olives, vegetables, fodder, etc., industry and others;

- Planting and plant cultivation;
- Creating land reticular form field hedges and belts;
- Construction of residential buildings;
- Construction of the infrastructure of roads, water and sewer maintenance structure constant;
- Turistic development with educational, cultural, social development.

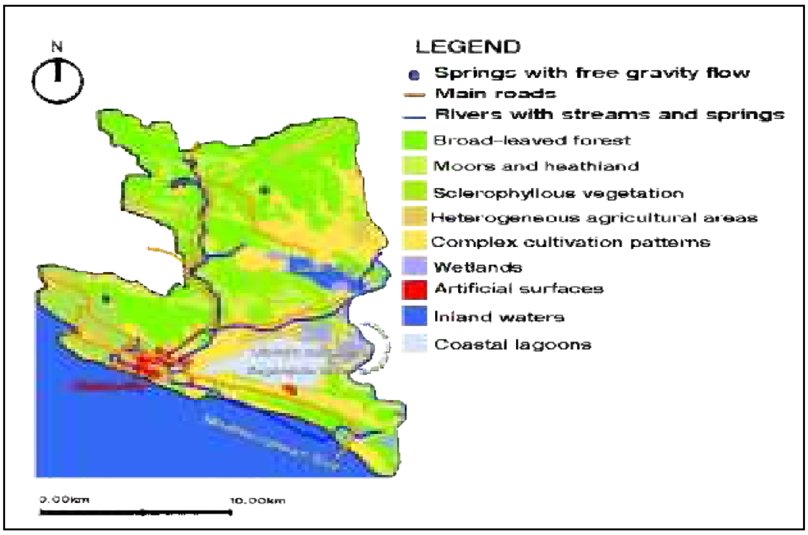

Figure 3. Map of CORINE land cover of municipality of Ulcinj

RESULTS

After the regional spatial problem and pottential guidelines we recommend main regional development program of Ulcinj Municipality through:

- Ecological and landscape zoning municipalities and networking in the international system of green areas (Natura 2002, Green Belt, EuroVelo network, etc.),
- Separation and protection of cultural and historical sites, areas, regions, morphological and geological formations and natural monuments of the Municipality of Ulcinj (parts of the village Kruce, Krute, Bratica, central part of the city of Ulcinj, resorts rigid, traditional way of working, and forms processing country, especially along rivers, strims, water flows and Old path of King Nikola);
- Creating and revival of greenways;
- The transformation of the villages is required to flow in the coridor direction without possibility of further expansion in the other direction;

- New construction is necessary to continue the existing ones, not overburdening the unbuilt area and leaving them as absolute and indispensable element of balance;
- Prohibition of construction of any nature on the coast, and the nearby environment;
- Limitation of the expansion of the land at the lowest possible level;
- Maintainice of the productive potential of land for different types of agricultural production, especially for so-called. "Healthy foods" and other agricultural products for which Ulcinj municipality has the greatest comparative advantage;
- The rational use of space for urbanization and control and limitation of intensive expansion of urban areas;
- Balance and rational exploitation of mineral resources (cement marl, etc.), with the application of measures of spatial and environmental protection;
- Ulcinj municipality should be developed as middle tourist center zone and at the same time organic agricultural development (revitalize olive plantation of 50,00 hectares with strict legal regulation of prohibition and the sale of old plantations of olives (with the encouragement of the development of smaller households), planted a tangerine plantation or eating olives 50,00 ha, activate the program for olive canning and packaging of tangerine, rebuild irrigation systems, restore windbreaks of cypress) [1];
- Raise of rural tourism, agro-tourism agriculturally Tourism (ECEAT - European Centre for Ecological and Agricultural Tourism-European Centre for Ecological and Agricultural Tourism);
- Take advantage of the impact of modern information technology, which will neutralize the many advantages of the villages. The emphasis should be on raising the value of local primary products, using traditional skills as Ulcinj's brand with its stamp;
- Protection and strict conservation of surface geological forms (for static fields and preserving image, beauty of landscapes);
- It is necessary to increase the educational-scientific, cultural, public, historical, technical (plant for desalination and rehabilitation, re-cultivation of Ulcinj saltworks, bioengineering erosion control along the coast and watercourses) content and capacity;
- Definition of scientific and research priorities in international cooperation of the municipality of Ulcinj, through appropriate projects and programs (ESPON, COST, UNESCO / HP, UNESCO / OECD, FPG, CEI, TEMPUS, INTERREG, etc.) [2]. Objects for scientific activities will be placed in the center of national importance, the center of special importance or in the centers of regional importance;
- Preservation of existing forest and associated vegetation [2];
- Preservation of natural habitat, natural sites and habitats through integrated environmental protection (for example Zagonjsko lake, Bojana river biotop, etc.);
- Preservation and forms of healing and prevention of wet river meadows and the prohibition of exploitation, usurpation (change in the composition of plant species);

- Monitoring, control of number and distribution of forest stands;
- Monitoring and networking of rural households on the map of tourist offer of Republic of Montenegro (ENRD network, etc.);
- Reconstruction of devastated stands with preventive and repressive measures of deforestation (mostly fertilizing cut) work in the traditional manner;
- Restoring mature stands;
- Strengthening cooperation with the local community;
- Raise ekoagricultural approach and cooperation with all stakeholders, strengthening local initiatives;
- Preservation of boundary forms of extensive agricultural areas (conservation network of dirt roads, control);
- Protection from exploitation and harvesting [2];
- Preservation of ground-vegetation;
- Sustainable use and exploitation of mineral resources;
- Sustainable prohibition of grazing cattle browse, pasture, acorn in the forest;
- Conservation of pasture borders;
- Prohibition of hunting and intimidation of wild animals;
- Establishment of feeding (fertilising, watering,) animal (game and wild game);
- Strict protection and strict conservation of surface geological shape;
- Preserving of coastal vegetation (prohibition of exploitation, collection, arson)
- Regulation and prohibition of illegal construction and restriction and prohibition of buildings in ecologicly fragile areas;
- Redistribution and greening of main traffic flows;
- Minimisation of waste, effectively prevent and control pollution and minimisation of environmental risks especially through good plan of greening;
- The protection and promotion of authentic cultural landscape and environment providing integrated protection of spatial units and special complexes and objects of cultural heritage features especially through protection of existing greenery and geomorfological forms (karst and limestone fields on the coast, alluvial river valleys, etc.) [3];

CONCLUSION

Regional programe guidelines for the improvement of the Ulcinj municipality landscape, the information for strategic policy planning, proposals and instructions for their location (spatial distribution) need to be directed on regional level. In a moment of globalization and vanishing small municipalities with its huge ecological pottentials and heritage, it need to resist. They changes the nature motivated by the satisfaction of human needs (resource), because people perceive nature in terms of effects (if nature provides benefits to a man because he wants to change it for his needs) and to eliminate the threat and danger. Man has changed the character of the landscape so that the trend continues dynamic balance is being influenced by the interaction of man and nature. The assumption is that if there is a weakening of the influence of man, (as has been observed in some parts of the landscape around the area) natural flows will be restored and act in the direction of the prevalence of the natural character of the landscape. If man continues to act, human effects will tend to further urbanization that will act in the direction of reshaping and destroying municipality landscape of cultivated and suburban landscape to industrialised agriculture touristic and urban area. That is why it needs to react as soon as possible but most of all is that it needs to transforme without possibility that new structures and contents expansions does not burden or endanger existing space and capital.

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GOOD MONITORING AS A PRECONDITION FOR HIGH DRINKING WATER QUALITY: CASE STUDY OF ZLOT WATER SUPPLY SOURCES (BOR, SERBIA)

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ABSTRACT

Water, as a natural renewable resource, is becoming increasingly important as a result of speedy development of science and technology, rapid population growth, and anticipated climate change impacts. In Serbia, some 70% of the population relies on groundwater for their drinking water supply. Among groundwater resources, karst aquifers are significant sources of water of the highest quality. Water supply sources in the catchment area of the Beljevina River, operated by the Bor Water Utility, are an example of well-thought-out monitoring of water quality and quantity, which is a major contributor to superior public water supply.

Key words: public water supply, monitoring, karst groundwater, quantity, quality, water supply system of Bor.

INTRODUCTION

Bor Municipality is situated in the easternmost part of Serbia and is the administrative center of the Bor District which, along with Bor Municipality, includes the municipalities of Majdanpek, Negotin and Kladovo. Bor Municipality occupies a land area of 856 km^2 and has a population of about 50,000 (some 38,000 residing in Bor and the remainder in 14 rural settlements). The overall development of this municipality relies heavily on the extraction of copper and other non-ferrous metals, ore processing, and production of blister copper, electrolytic copper and associated metals. However, ore extraction and processing have caused considerable soil degradation and environmental pollution (primarily of air and water). Once mining operations cease, decades of active remediation will be needed to restore the original state of the environment. (1)

In contrast, public water supply in Bor Municipality largely relies on karst groundwater which constitutes one of the cleanest water resources both in Serbia and worldwide. Given that raw water quality fails to comply solely with turbidity and microbiological requirements, only disinfection (or chlorination, to address microbiological non-compliance) is needed. The high water quality is certainly attributable to the fact that the karst spring watersheds are situated in inaccessible mountainous areas, where there is no industry or other anthropogenic impact, such that the water remains virtually pristine.

Surdup Spring, near the Village of Donja Bela Reka, was capped in 1949 but, as water demand increased, it was necessary to expand the water supply system. Another spring, Kriveljska Banjica, was capped in 1964, and then the Zlot system of water sources was commissioned in 1972, comprised of four springs (Gaura Mare, Gaura Mika, Rnić and Mejlanić), a pumping station, a pipeline, and a city reservoir called Topovske Šupe.

In the 1980's and 1990's, the capacity of the Zlot springs, which were the largest contributors to Bor's water supply, rapidly declined. This resulted in water shortages and water supply restrictions in dry summer months imposed on the City of Bor, its infrastructure and nearby villages. In order to provide sufficient quantities of water for the city and industry, construction of Phase 1 of the Bogovina Regional Water Scheme began in 1996. It was commissioned in 2002. (Group of authors, 2010)

Pre-existing water sources provide 250 l/s of water and Bogovina added 150 l/s, such that today Bor Municipality receives sufficient amounts of high-quality water.

Bor Municipality's public water supply comes from four sources. It should be noted that one of them, the Mrljiš source, is not operated by Bor Water Utility, but by Bogovina Co.; the utility purchases raw water from Bogovina to ensure a steady supply of high-quality water:

1. when the sources it operates experience turbidity, and
2. in dry periods, when the capacity of its sources declines.

One advantage of the Mrljiš source (where water is extracted by means of three wells) is that its discharge is steadier that that of the other capped springs and that turbidity is recorded only after extremely heavy rainfall. Even then, turbidity does not exceed 2.0 NTU. Another advantage of Mrljiš is that it is almost always microbiologically compliant. The names, locations and capacities of Bor Municipality's water supply sources are shown in Table 1.

Table 1. Names, locations, capacities and altitudes of sources that provide water supply to Bor Municipality

Source	Location	Capacity (l/sec)	Altitude (m a.s.l.)
Zlot	Beljevina springs, catchment area of the Beljevina River, 11 km southwest of Bor	110– 2,400	315 - 360
Zlot	Zlot spring, catchment area of the Zlot River, 1.5 km from the Village of Zlot	10 - 60	285 - 290
Krivelj	6 km north of Bor	0-100	386
Surdup	8 km east of Bor	60 -120	310
Mrljiš	Mrljiš Spring in the Village of Bogovina, 25 km southwest of Bor	150 - 240	230

WATER SUPPLY SOURCE IN THE CATCHMENT AREA OF THE BELJEVINA RIVER

There are several capped springs and one drilled well in the catchment area of the Beljevina River, 11 km southwest of Bor. This source provides water supply to the Village of Zlot and also delivers water to Bor. It is comprised of:

- Gaura Mika Spring, capacity 0-800 l/s
- Gaura Mare Spring, capacity 25-1250 l/s
- Rnić Spring, capacity 40-130 l/s
- Mejlanić Spring, capacity 45-200 l/s
- Well B4, capacity 30 l/s (up to 34 l/s when needed).

The capacity of this source fluctuates considerably, depending on precipitation, such that in dry summer months it does not provide sufficient amounts of water for the public water supply.

The raw water is not treated, except for disinfection by chlorine gas (or a water solution of chlorine) or a sodium hypochlorite (NaOCl) solution. Regardless of the chemical agent used for disinfection, it is important to note that the physical, physicochemical and chemical parameters of the raw water are such that only the turbidity parameter becomes elevated in rainy periods or after rapid snowmelt. Turbidity can then be as high as 25 NTU. The turbid water is yellowish (or acquires the color of mud). (Group of authors, 2010)

With regard to microbiological parameters, non-compliance is caused by the occurrence of coliforms and streptococci of fecal origin, and *Pseudomonas aeruginosa*.

Hydrogeological, hydrological and meteorological characteristics of spring drainage areas in the Beljevina River catchment

The Beljevina River rises from volcanic agglomerates and Upper Cretaceous breccias, and, flowing south, drains the southern slopes of Mt. Crni Vrh. When it enters Lower Cretaceous sediments (limestones of the Valanginian/Heuterivian stage - K_1^{1+2} and massive limestones of the Urgonian facies - K_1^{3+4}), it changes direction to the southwest and shortly after reverts to its original southerly course. It is there that it receives karst water from the studied springs. As soon as it leaves the karst terrain, it joins the Lazar River and together they form the Zlot River.

The discharge regimes of the karst springs and of the Beljevina River itself are largely conditional upon local precipitation. It should be noted that the discharge of the Beljevina River is monitored by a gauging station at Selište, where the regime is highly complex. It is primarily affected by geological and hydrogeological diversity of the river's catchment. In its source area and along its lower course, before it forms the Zlot River, the Beljevina drains volcanic agglomerates and breccias. However, the middle course drains karst, receiving water from Gaura Mike, Gaura Mare, Rnić and Mejlanić springs. Given that these springs have been capped to provide water supply to Zlot and Bor, the Beljevina only receives water from uncapped springs. As a result, the natural regime of this river has been significantly altered. (Group of authors, 2014)

Auto-correlation and cross-correlation analyses

The auto-correlation and cross-correlation analyses depicted in Fig. i 2 (Krešić and Stevanović, 2010) were used to assess the effect of precipitation on the water level regime of the Beljevina River (Fig. 1) at the Selište station. For the cross-correlation analysis, daily precipitation data were acquired from the nearest meteorological station, located on Mt. Crni Vrh (alt. 1037). The highest coefficient of correlation between precipitation and river stages of the Beljevina was found to be 0.25 for a one-day time step. Thereafter, the coefficient of cross-correlation declined. The secondary, less-pronounced peak occurred after 50 days (r = 0.06), reflecting a delayed effect of precipitation in the form of snow cover. The effect of precipitation on river stages after spring snowmelt is shown in Fig. 2. For example, a peak was recorded in February/March 2014, when there is generally minimal precipitation (or even no precipitation at all). The auto-correlogram showed that the watershed memory was long, up to 72 days (r = 0.2) (Ristic Vakanjac, 2015). This was largely a consequence of the highly-complex discharge regime of the Beljevina River.

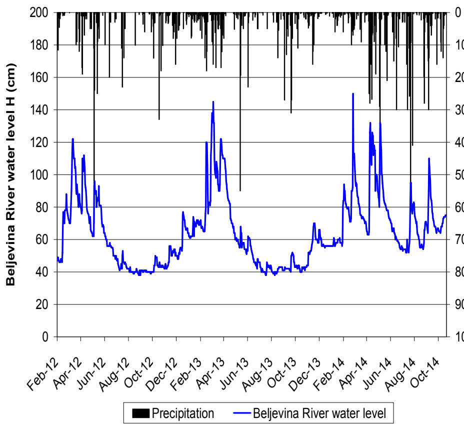

Figure 1. Beljevina River stages and precipitation regime

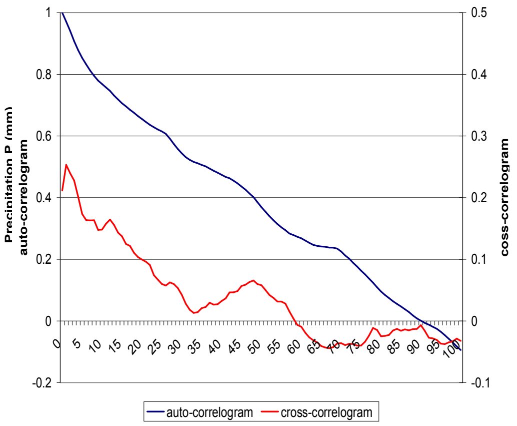

Figure 2. Auto-correlogram and cross-correlogram of Beljevina River stages at Selište

Information on the discharge regime and the amounts of water captured from each of the springs was unfortunately unavailable, such that analyses along the same principles as for the Beljevina River could not be undertaken. The water captured from the springs of Gaura Mare and Gaura Mika is delivered by means of a gravity pipeline to a primary reservoir at the Zlot Pumping Station. The water captured from the springs of Rnić and Mejlanić is also delivered by gravity, to a water reservoir at a secondary PS, from where it is pumped into the primary reservoir at the Zlot PS. Water is distributed in the direction of Bor from the primary reservoir.

As already stated, the karst aquifer regime is largely affected by local precipitation. Additionally, the precipitation regime affects the karst water quality parameters, such as turbidity (Fig. 3), nitrates, nitrites, bacteria... In this regard, auto-correlation and cross-correlation analyses were undertaken for turbidity recorded at the primary reservoir of the Zlot PS (Fig. 4).

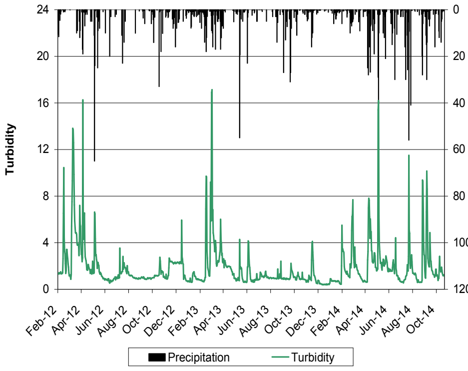

Figure 3. Turbidity of Zlot source and precipitation regime

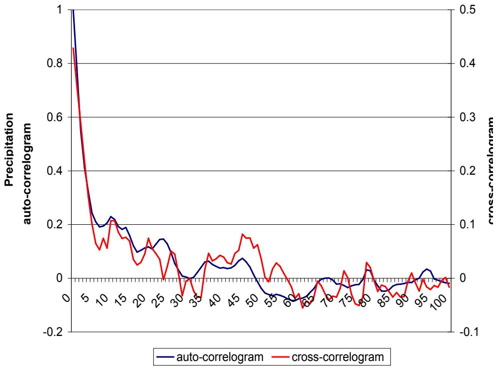

Figure 4. Auto-correlogram and cross-correlogram of Zlot source' turbidity

Similar to the river stage analysis as a function of precipitation, the present assessment clearly showed a match between turbidity peaks, which occasionally exceeded 16 NTU, and maximum daily precipitation (Fig. 3). In some cases (e.g. February/April 2012), there were rapid increases in turbidity even in the absence of precipitation. This was attributable to rapid melting of the pre-existing snow cover in the drainage areas of the capped springs. With regard to the auto-correlogram and cross-correlogram, these two functions exhibited a very good match, corroborated by a high coefficient of correlation after testing (r = 0.93). Both functions indicated a quick response of the watershed to precipitation, as spring water became turbid almost instantaneously. The memory of this system was short, up to 10 days, showing that after the cause (precipitation) ceased, turbidity quickly declined to acceptable levels for water distribution to end users. According to national drinking water standards, the upper limit for turbidity is 1 NTU. (National Drinkkig Water Standards, 42/98, 44/99)

Simulation of turbidity

In hydrology, multiple linear regression models (Krešić and Stevanović, 2010) are commonly used to simulate any dependent variable. In the present research, the idea was to simulate turbidity of the Zlot sources using known independent variables, such as precipitation, water levels and turbidity recorded at the given station on previous days. Keeping in mind the results of the auto-correlation and cross-correlation analyses, the following multiple linear regression equation was used:

$$TSD_i = a + b_1 \cdot TDS_{i-1} + b_2 \cdot P_{i-1} + b_3 \cdot P_{i-2} + b_4 \cdot P_{i-3} + b_5 \cdot P_{i-4} + b_6 \cdot H_{i-1}$$

where TSD_i and TSD_{i-1} are the turbidities of the Zlot source at times *i* and *i*-1, P_{i-1}, P_{i-2}, P_{i-3}, P_{i-4} are daily precipitation totals recorded by the Mt. Crni Vrh met station at times *i* -1, *i* -2, *i* -3 and *i*-4, and H_{i-1} is the river stage of the Beljevina at the Selište station at time *i*-1. The parameters a, b_1, b_2, b_3, b_4, b_5 and b_6 are dimensionless parameters of the above equation, to which the least squares method was applied. In this case study, they amounted to:

a	b_1	b_2	b_3	b_4	b_5	b_6
-0.63678	0.63380	0.07620	-0.00986	-0.00626	-0.00640	0.01841

Turbidity was estimated based on the above parameters and recorded data (e.g. precipitation, river stages and turbidity of the Zlot source). Figure 5 shows recorded turbidity levels and those that were estimated applying the above equation. The coefficient of correlation between the estimated and real turbidity levels of the Beljevina source was 0.83.

CONCLUSION

The above assessment of the effect of precipitation on the stages of the Beljevina River at the Selište gauging station, and on the water turbidity of the capped springs that constitute the Zlot water supply source, shows a very good correlation between precipitation and the considered variables. In order to predict turbidity in a timely manner, the primary requirement is to ensure good meteorological monitoring of the watershed. In the specific case, the Crni Vrh met station was in the immediate vicinity of the Beljevina watershed. However, significantly better and more reliable results would be ensured by locating a meteorological station in the karst part of the catchment area drained by the capped springs.

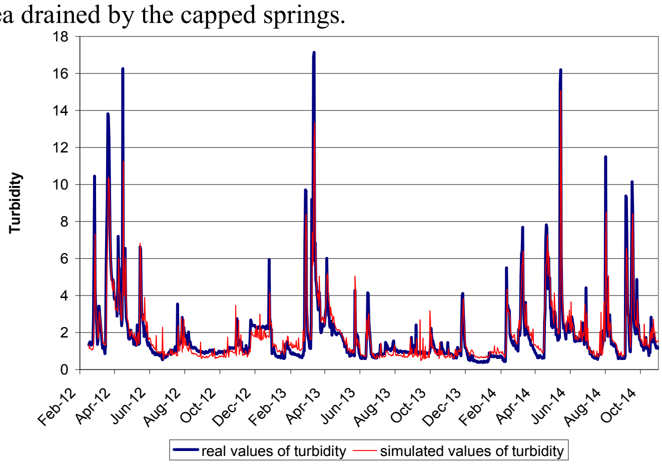

Figure 5. Real vs. simulated turbidity of Zlot water supply source

It should be noted, however, that none of the springs is monitored individually in both qualitative and quantitative terms, which was an aggravating circumstance. The discharge regimes of the four capped spring were all different; for example, Gaura Mika occasionally runs dry in the summer, while Mejlanić is an upward spring situated in the alluvium of the Beljevina River. These different regimes are certainly attributable to different altitudes, different sizes of groundwater conduits to the springs, and, consequently, different rates of precipitation propagation. As such, turbidity levels and similar parameters also differ and exceed maximum permissible concentrations after heavy rainfall.

In the case study, the simulation of the average turbidity levels of the capped springs yielded satisfactory results. However, had turbidity and discharge data been available on each individual spring, as well as a meteorological station representative of the area drained by the springs, simulation models could have been applied to each spring separately. In effect, the simulation model forecasts next-day turbidity, and if predictions exceed permissible levels, orders should be issued to intensify sampling and analysis of turbidity (or other problematic components), or even shut down the system if treatment will be unable to reduce turbidity to acceptable levels.

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POSSIBILITY OF ARSENIC REMOVAL BY FERRATE(VI) IN THE TREATMENT OF RAW DRINKING WATER

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ABSTRACT

The subject of this work is arsenic (As) removal from raw drinking water by electrochemically synthesized ferrate(VI) and by ferrate(VI) in combination with conventional coagulant ($AlCl_3$). The initial As concentration of 15,08 μM was removed with an efficiency of 99% by ferrate(VI) in two steps, whereas in combination with $AlCl_3$ removal efficiency was 95,62%. Artificial sample of raw drinking water (As=15,08 μM, permanganate index=10,11 mg/l) was treated in two steps by ferrate(VI). Arsenic removal was 71,79% and permanganate index decreased to 6,32 mg/l. $AlCl_3$ addition showed As removal in the presence of organic matter of 95,97% and reduction of permanganate index to 1,26 mg/l.

Key words: Arsenic, ferrate(VI), drinking water, humic substances, spectrophotometry.

INTRODUCTION

Hygienically safe drinking water supply is a basic requirement for a healthy population. In many parts of the world arsenic (As) is one of the most important contaminants of resources of raw drinking water for both surface and groundwater. A large number of adverse effects of As on living organisms is proven: appearances of cancerous diseases, neurological diseases, cardiovascular and respiratory system diseases [1]. According to UN Synthesis Report arsenic poisoning is the second major health risk which is linked to drinking water. In 2001 The World Health Organization estimated that about 130 million people are exposed to a concentration of 50 μg/l of arsenic in drinking water, so the European directive define the maximum allowable concentration of arsenic in drinking water of 10 μg/l [2,3]. In some countries such as Hungary, Serbia, Croatia, Greece, Italy and Spain it was found significantly elevated arsenic content in drinking water, which requires additional efforts in the treatment of raw water with the aim of achieving the maximum allowable concentration of 10 μg/l.

Groundwater in the territory of the Republic of Serbia are the basic resource of water, and in the Autonomous Province of Vojvodina water supply is exclusively oriented to groundwater. Most of these groundwater contains unacceptably high level of arsenic. According to the Regulation on hygienic quality of drinking water [4] maximum allowable concentration of arsenic in drinking water is 10 mg/l. More than 40% of the population of Autonomous Province of Vojvodina is supplied with water which contains a higher concentration of arsenic than it is allowed. In most cases, the concentration of arsenic in drinking water ranges from 50 to 100 μg/l, but there are also municipalities, such as Zrenjanin, where the concentration of arsenic in drinking water ranges from 150 to 250 μg/l. At the same time the content of natural organic matter in the raw water, expressed as the consumption of potassium permanganate, ranges from 20 to 150 μg/l, and in extreme cases up to 200 μg/l. The presence of organic matter in raw water additionally complicates As removal by the conventional methods of coagulation due to complex that As forms with organic matter. In the coagulation process also may be present the competition between natural organic matter and arsenic for free adsorption places on the formed hydroxide [5].

Most of the water supply systems in Vojvodina, except the water supply system in Subotica do not own the technology for arsenic removal from groundwater. Efficient removal of organic matter and arsenic from drinking water resources is still one of the greatest challenges in modern production of safe drinking water. A significant number of works based on the toxicity of arsenic and the techniques of arsenic removal from drinking water has been published in recent years [6-8]. Techniques for the removal of organic matter and arsenic from raw water are based on: oxidation, flocculation with microfiltration, adsorption, ion exchange. The results show that the efficiency of arsenic removal by these techniques is insufficient to meet the prescribed requirements. As(III) is more toxic and mobile than As(V), so it is highly desirable to oxidize As(III) species for enhancing the immobilization of arsenic. Therefore, many conventional arsenic removal procedures involve a pretreatment for As(III) oxidation, followed by the adsorption or coprecipitation of As(V) formed using adsorbents or coagulants, such as metal oxyhydroxides [9]. Until now, many oxidants or oxidant-generating systems have been tested for As(III) oxidation: oxygen and ozone, hydrogen peroxide, manganese oxides, UV/iron systems, and TiO_2/UV systems [10].

As an alternative or pre-treatment to conventional methods, the treatment of raw water by ferrate(VI) could be used, which at the same time oxidizes organic material, and convert As(III) to As(V), equation 1, and could be removed from the solution by formed $Fe(OH)_3$ as a slurry during flocculation and coagulation.

$$2HFeO_4^- + 3H_3AsO_3 \longrightarrow 2Fe^{3+} + 3HAsO_4^{2-} \quad (1)$$

The application of ferrate(VI) in the process of As(III) removal from raw drinking water is compatible with the conventional methods of water purification such as using chloride and sulfate salts of iron or aluminum, and they may supplement each other mutually. Recently, ferrate [Fe(VI), iron in +6 oxidation state] has gained great attention as an environmentally friendly oxidant and coagulant for water and wastewater treatment [11, 12]. Fe(VI) is a known powerful oxidant over the entire pH range; its redox potentials are 2,20 V and 0,72 V in acidic and basic media, respectively [13]. Oxidation efficiency of ferrate(VI) solution is increased by formation of atomic oxygen during water oxidation.

Ferrate(VI) solution is obtained by the electrochemical process of dissolving low carbon iron alloys in very alkaline solution. This process was developed within the project of technological development TR 19029 [14-16]. In addition to the relative simplicity and efficiency, the advantage of wastewater treatment by ferrate(VI) is the fact that it is very environmentally friendly process, because the only reagent is an alkali ferrate(VI) and the product of the reaction is $Fe(OH)_3$, which is a strong coagulation and flocculation agent, built on the site of use.

The advantage of wastewater treatment by ferrate(VI) in relation to the procedures mentioned before is the simultaneous oxidation of As(III) to As(V) as well as the organic material present in raw water. Simplicity of preparation of ferrate(VI) solution by electrolysis at the site of use and simplicity of application, due to direct adding of ferrate(VI) solution without prior preparation of water, make this process economically beneficial and environmentally favorable.

The aim of this paper is possibility of ferrate(VI) application in the process of As(III) removal from raw drinking water in the presence of natural organic matter, in the case of artificial water sample with addition of As(III) and humic substances.

EXPERIMENTAL

Artificial samples with As(III) concentration of 1130 mg/l (15,08 μM) and with added humic substances (consumption of K_2MnO_4 is 10,11 mg/l) were used in this experimental work. As(III) was in the form of As_2O_3, *p.a.* quality, a mixture of humic acids was used as humic substances and demineralized water was also used in the experiment. A 4% solution of $AlCl_3$ was used as an additional coagulant.

The Na_2FeO_4 solution, concentration of 3,5 g/l used for the treatment was synthesized electrochemically. The process of electrochemical synthesis of the alkaline solution of ferrate(VI) was carried out in a laboratory facility for electrochemical synthesis of ferrate(VI) composed of a two-part flow-through electrochemical cell and based on the transpassive anodic dissolution of iron alloys in a 10 M NaOH solution, in accordance with previous studies [13, 15]. The concentration of synthesized ferrate(VI) was controlled by the titrimetric chromite method at a temperature of 25 °C. Freshly synthesized ferrate(VI) was used for the treatment of the solution.

In the second set of experiments, treatment of samples with the same concentration of As(III) without humic substances was done in two steps. After the treatment by Na_2FeO_4 in the same ratio as in the previous experiment, filtration and pH correction to 5-6 an additional treatment was carried out. In the first step the samples were treated again by Na_2FeO_4 and in the second step the samples were treated by $AlCl_3$ in a molar ratio of 1 : 1 to Na_2FeO_4.

In the third set of experiments, treatment of samples with the same concentration of As(III) with the addition of humic substances was carried out according to the same procedure as in the second set of experiments.

The treated samples were stirred using Jar test, for 10 minutes at the speed of 240 rpm, and then at the speed of 120 rpm up to the color of ferrate(VI) disappearance. The pH value was adjusted to 5-6 using HCl [17]. The samples were filtered through a filter with the pore size of 0,20 µm. Analysis of the total amount of residual arsenic was determined by atomic adsorption spectrophotometry following the standard method for arsenic determination at MOL Institute, Stara Pazova.

The presence of organic matter regarding the changes in the concentration of added humic acid in the treated samples was monitored through the consumption of potassium permanganate.

RESULTS AND DISCUSSION

Results of As(III) removal from water samples with and without the presence of humic substances by ferrate(VI) are shown in Figures 1 and 2. Figure 1 shows the result of the treatment of water sample with As(III) concentration of 15,08 µM and without humic substances by ferrate(VI) in various molar ratios (As(III): Fe(VI)) 1 : 1,95; 1: 3,6; 1: 4,41; 1: 5,34; 1: 7,1. The results of additional treatments by ferrate(VI) and coagulant $AlCl_3$ are also shown in Figure 1.

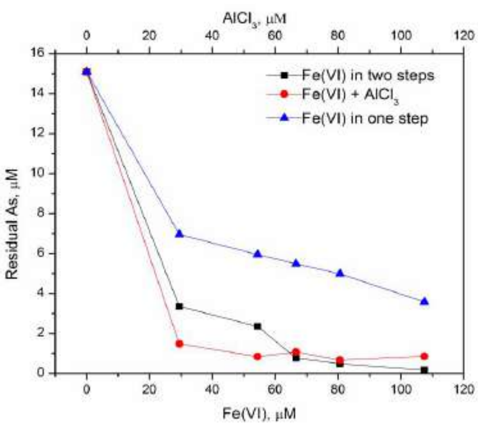

Figure 1. Removal of As(III) by Fe(VI), by Fe(VI) in two steps and by Fe(VI)/$AlCl_3$

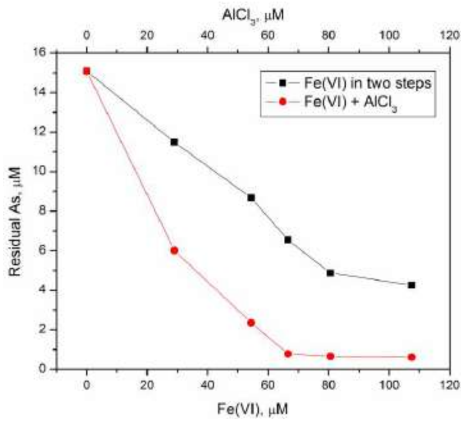

Figure 2. Removal of As(III) in the presence of humic substances by Fe(VI) and by Fe(VI)/$AlCl_3$

Treatment results show high efficiency in As removal by ferrate(VI), table 1, 76,33% in the first step of the treatment at a molar ratio (As (III): Fe(VI)) of 1 : 7,1 or 107,5 µM Fe(VI). Considering that As(III) is mobile and can not be removed from water by conventional flocculants, As(III) oxidizes to As(V) by ferrate(VI) due to the high oxidation potential of Fe(VI). Ferrous hydroxide, formed by reduction of ferrate(VI), as a powerful coagulant removes it from the solution. Due to the small amount of ferrate(VI), and therefore the small amount of formed ferrous hydroxide, in the first set of experiments the complete removal of As was not achieved.

By repeated treatment of the samples, with the same concentration of ferrate(VI), 99% of As is removed, whereas the addition of coagulant $AlCl_3$ removes 95,62% of As. In the second set of experiments it was shown that with the increase of added amount of ferrate(VI) it is possible to achieve complete As removal. It is necessary to add ferrate(VI) in two steps (each of the steps includes addition of Fe(VI), filtration, and pH adjustment to 5-6) due to the catalytic activity of ferrous hydroxide on ferrate(VI) decomposition which may decrease the efficiency of the added ferrate(VI). Slightly lower efficiency is obtained by the addition of a conventional coagulant $AlCl_3$ after the ferrate(VI) treatment, which shows that ferrous hydroxide is more effective coagulant, but also environmentally more favorable because, contrary to conventional aluminum- and chlorine- based coagulants, it produces no toxic by-products.

Table 1. As removal under different conditions by ferrate(VI)

Treatment	As removal, % (without humic substances)	As removal, % (with humic substances)
Fe(VI)	76,33	-
Fe(VI) in two steps	99,0	71,79
Fe(VI)/$AlCl_3$	95,62	95,97

Artificial raw drinking water sample contains, besides As (15,08 μM of As(III)), natural organic matter in the form of humic acid, whose concentration, expressed as the consumption of potassium permanganate, was 10,11 mg/l. Treatment by ferrate(VI) in two steps wherein the As removal was 71,79% and permanganate index decreased to 6,32 mg/l, Figure 3, shows that a large part of ferrate(VI) is spent on the oxidation and a large part of ferrous hydroxide on the absorption of organic material which reduced the overall efficiency of arsenic removal.

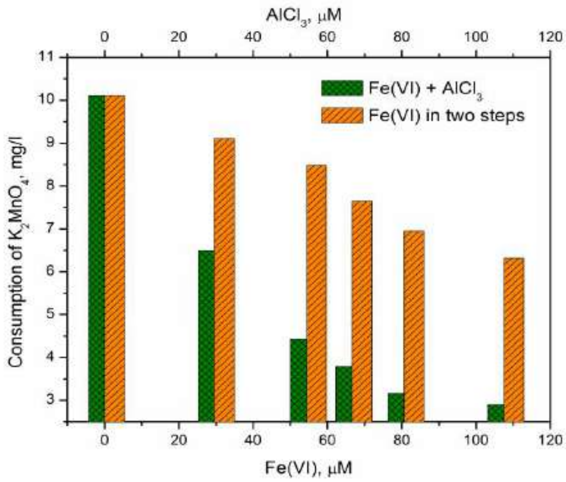

Figure 3. Change of permanganate index in the treatment of artificial water sample with the presence of As and natural organic matter

The addition of coagulant in the form of $AlCl_3$ shows far higher efficiency in As removal, 95,97% and higher reduction of permanganate index, 1,26 mg/l, because $AlCl_3$ absorb all the material oxidized by ferrate(VI). By applying larger amounts of ferrate(VI) a more efficient removal of As in the presence of natural organic matter could be reached which requires further optimization of the treatment process of raw drinking water by ferrate(VI).

CONCLUSION

The possibility of efficient removal of As(III) of 99% has been demonstrated by treatment of the artificial samples of drinking water with As(III) concentration of 15,08 µM by ferrate(VI). The treatment is carried out in two steps (Fe(VI), filtration, pH = 5-6) due to the catalytic activity of ferrous hydroxide, generated by ferrate(VI) reduction, on the decomposition of ferrate(VI). Taking into account that natural organic matter are also present in natural drinking water, the treatment of the artificial samples of water which contains As and humic acid by ferrate(VI) showed a lower efficiency at the same procedure and the amount of ferrate(VI). The addition of conventional coagulant, $AlCl_3$, after treatment by ferrate(VI) showed high removal efficiency of both, As and humic substances. Application of ferrate(VI) in the treatment of raw drinking water is possible and desirable, due to the high environmental performance of ferrate(VI) in comparison to aluminum- and chlorine- based coagulants. It has been shown that it is possible to use ferrate(VI) in both, the primary and the secondary treatment process of raw drinking water.

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THE QUALITY OF RIVER MLAVA IN POZAREVAC MUNICIPALITY

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ABSTRACT

Physical-chemical and microbiological analysis of water quality of the river Mlava, in the zone of the city Požarevac, was done in the period July-November, on five measuring points.

Physical-chemical analysis showed that the waters of river Mlava belong to III water class and at some measuring points even IV class, regardless the fact that officially these waters belong to II water class.

The results of microbiological analysis showed that total number of coliform bacteria in 100 ml was 24000, at all measuring points, in the period July-September which classify these waters into IV water class, except in October and November when this number was much lower and corresponded to II water class. The obtained results indicate dominant fecal contamination from households and agricultural farms.

Key words: Mlava, water quality, pollutants, waste waters, physical-chemical parameters, microbiological parameters.

INTRODUCTION

The river Mlava is one of the most important watercourses in eastern Serbia. In its lower reaches, which are analyzed in this paper, it flows through a wider territory of Pozarevac, including urban municipality Kostolac and the municipality of Malo Crniće, and flows into the Danube. Near Batuša settlements in the municipality of Malo Crniće, Mlava is divided into basic (eastern) river flow and Mlava sleeve (west flow), and near Drmno, in the municipality of Kostolac, reconnected. It is important to emphasize that between Mlava and Mlavskog sleeve there is no any settlement [1].

The total area of the analyzed part of river basin is 431 km^2. From this area, 259 km^2 is located in the municipality of Malo Crniće and includes 18 settlements, and 172 km2 (an area of fertile plain Stig) is located in the city of Požarevac and includes 8 settlements. In these settlements there are 5,706 households with approximately 20,000 inhabitants [1].

According to its location and local conditions, the river Mlava and Mlava sleeve, with its tributaries in the analyzed surface, belong to a lowland river in the typically agricultural region. The most developed economic sector is agriculture, while the larger industrial systems in this area do not exist. The rankings do not take into account the existence of open pit mines and thermal power plants, which are not subject to analysis in this paper.

In the basin of the river Mlava and Mlava sleeve, in the wider zone of Požarevac, there is a large number of diffused types of pollutants. The pollution occurs due to excessive, irrational use and improper treatment of chemicals for agriculture, rinsing and swelling of waters from livestock farms and "wild" landfills, septic tanks, waste waters from the existing infrastructure facilities along the roads and so on. There are no spotted types of pollutants and their impact on water quality is negligible.

On the whole analyzed territory, no settlement has any systematic disposal and treatment of wastewaters, even there are no parts of the sewerage network. Organized channeling and treatment of waste water does not exist. Wastewaters are mainly collected in septic tanks that represent the largest cause of pollution of surface and ground waters. In the basin of river Mlava and Mlava sleeve there are at least 6,000 septic tanks that are generally not constructed of waterproof material and not properly done technically, so waste fluids penetrating the wells from which drinking water is supplied by a large number of residents [1].

The manure rinse by rain has resulted in pollution of soil and surface and ground waters, especially with nutrients. Increased concentrations of nutrients that come from manure (especially nitrogen and phosphorus compounds), come into waterways causing excessive algae growth. As a result of this process, the water in these streams becomes polluted, smelly, useless for bathing and drinking. Therefore, due to lack of oxygen, there are no living organisms, such as crustaceans, fish or aquatic plants.

Also, the pesticides have an important role in the water pollution. Pesticides come into the water by water erosion from the soil and plants, by direct way through air-treatment, by improper spraying technology and dusting etc. In Serbia, and therefore in the analyzed area, there is no organized collection of discarded containers of pesticides, which can often be found in the beds of rivers and streams. The contribution of pollution from unlocalized diffused pollutants to overall pollution of water sources in the analyzed part of the catchment area of the river Mlava is near 100%.

MATERIALS AND METHODS

In order to determine the water quality of river Mlava, three measuring points were defined on the analyzed surface of 431 km^2, in the city of Požerevac, as presented in Figure 1. The measuring points are:

- MP1 - River Mlava before separating to the main stream and Mlava sleeve, between settlements Batuša and Kalište
- MP2 – Mlava sleeve before connecting to the main stream of Mlava, near settlement Bradarac
- MP3 - Mlava after connecting with Mlava sleeve, before settlements Drmno and Stari Kostolac

Water samples were measured in the period of July-November, once per month. The sample of sediment was measured only once, in September. The samples were analyzed by standard methods. All sampling, testing and interpretation of the results were performed in accordance with applicable laws and regulations of the Republic of Serbia [2-8].

Figure 1. The analyzed area of the river Mlava with presented measuring points

RESULTS AND DISCUSSION

Physical-chemical characteristics of river Mlava

21 physical-chemical parameters that characterize the water quality of the river Mlava were analyzed. Only key parameters are presented in Table 1.

The content of lead and zinc was lower than the MPC (maximal permitted concentration) in the analyzed samples. The content of iron was higher or very close to the MPC level of 0.3 mg/l. In all samples, the water was alkaline, the pH was around 8, but within the limits of MPC of 6.8-8.5. The concentration of suspended solids varied in the range of 89.4-21.8 mg/ll, which corresponded to I and II water classes, except in July when at all three measuring points was above 50 mg/l and belonged to the III water class. The content of ammonium and nitrate nitrogen was above the MDC level for II water class II waters and crossed the scope of the IV water class only at MP1. At other measuring points, the values of ammonium, nitrate and nitrite nitrogen were below MPC for II water class. The causes of intermittent transition from II to IV water class are great outpouring of different types of untreated waters, the presence of a large number of diffused pollutants and improper use of chemicals in agriculture. Based on the obtained results of dissolved O2, BOD5 and HOD, the samples belonged mainly to II and III water class. The test results of sediment presented in Table 2, are satisfactory.

In general, though the water of the river Mlava officially belong to the II water class, there are more parameters by which the water of the river Mlava belongs to the III and IV class, particularly at low watercourse levels.

Table 1. The results of physical-chemical tests of the river Mlava

Measuring point and time of sampling	Parameter, mg/l										
	pH	diss. O_2	NH_4^+	NO_2^-	NO_3^-	consum. $KMnO_4$	BOD_5	HOD	Fe	Zn	Pb
MM1											
07.07.	8.19	6.00	2.72	0.122	1.201	24.80	<3	20	1.25	<0.01	<0.01
10.08.	7.93	5.30	1.55	0.365	1.576	38.05	10.59	13	0.50	0.102	<0.01
07.09.	7.95	7.33	4.66	0.365	2.146	17.01	5.79	10	0.30	<0.01	<0.01
19.10.	7.82	8.85	2.33	0.060	2.443	10.34	<3	<10	0.30	0.052	<0.01
20.11.	8.09	7.77	3.18	0.182	2.538	10.99	3.98	10	0.25	0.033	<0.01
MM2											
07.07.	8.26	6.49	0.38	0.122	1.910	27.94	<3	17	1.75	0.026	<0.01
10.08.	8.03	7.01	0.097	0.015	1.635	10.40	<3	<10	0.25	<0.01	<0.01
07.09.	8.10	8.35	0.040	0.018	2.522	10.02	<3	<10	0.30	<0.01	<0.01
19.10.	8.19	10.60	0.389	0.030	3.175	9.03	<3	<10	0.30	<0.01	<0.01
20.11.	8.17	9.28	0.269	0.024	2.521	7.15	<3	<10	0.17	<0.01	<0.01
MM3											
07.07.	8.28	6.98	0.194	0.061	1.995	12.65	3.34	12	0.67	0.034	<0.01
10.08.	8.05	7.05	0.040	0.015	1.587	9.61	<3	<10	0.25	<0.01	<0.01
07.09.	8.16	7.95	<0.04	0.024	2.582	12.58	<3	<10	0.83	<0.01	<0.01
19.10.	8.25	9.80	0.039	0.018	1.759	8.78	<3	<10	0.30	0.044	<0.01
20.11.	8.13	9.20	0.276	0.020	2.550	7.65	<3	<10	0.75	<0.01	<0.01

Table 2. The results of sediment testing of the river Mlava

Element	Max limit in soil mg/kg soil (Sl.gl. RS 23/94)	Directive EU 86/278/EES from 12.06.1986.	MP1	MP2	MP3
Pb	<100	50-300	<0.9	<2.0	<0.9
Cd	<3	1-3	<0.2	<0.4	<0.2
Zn	<300	150-300	48.82	172.79	56.79
Ni	<50	30-75	4.72	20.99	8.84
Cu	<100	50-140	3.30	20.39	5.10
Fe			17641	33105	18531
Mn			659.30	1937.83	514.76
As	<25		0.143	0.484	0.257
Cr	<100		8.20	32.30	17.33

Microbiological characteristics of river Mlava

In addition to physico-chemical characteristics, important indicators of the water quality are microbiological characteristics. Legislation restricts primarily on pathogenic microorganisms and their direct or indirect detection, both in quantitative and qualitative terms. Fecal contamination is the most important parameter of water pollution. The number of coliform bacteria per 100ml of water is one of the most important microbiological parameters that affects the classification of water in a particular class.

As shown in Fig. 2, in July, a total number of coliform bacteria of 24000 CFU/100 ml was obtained at all three measuring points, which corresponds to IV class of water that cannot be used unless it is pretreated before. Identified bacteria species at these three measuring points were *E. coli* i *Klebsiella* sp. which suggests dominant fecal contamination of water from agriculture farms and households. In August, the obtained results and identified bacteria were the same as in July, except at MP2 and MP3 a total number of coliform bacteria was much lower, 3800 and 500 CFU/100 ml, respectively. These samples belonged to II class of water. In September, a total number of coliform bacteria of 24000 CFU/100 ml was obtained at all three measuring points. At MP1 and MP3, *E. coli* was identified, and at MP2 *Citrobacter* sp. which suggests fecal contamination of water. In October, the obtained results were much lower and belonged to II class of water. A total number of coliform bacteria at MP1, MP2 and MP3 was 880, 3800 and 3800 CFU/100 ml, respectively. This situation can be explained by the reduction of pollution caused by heavy rainfall at the time of sampling and the increase in water level, which significantly affects the level of water pollution. In November, a total number of coliform bacteria of 880 CFU/100 ml was obtained at all three measuring points, which corresponds to II class of water. Identified bacteria in October and November are *E. coli* and *Citrobacter* sp.

Based on the obtained results, it can be seen climate change (atmospheric precipitation) and discharge of sewage and agricultural and industrial water have a major impact on the water quality of the river Mlava.

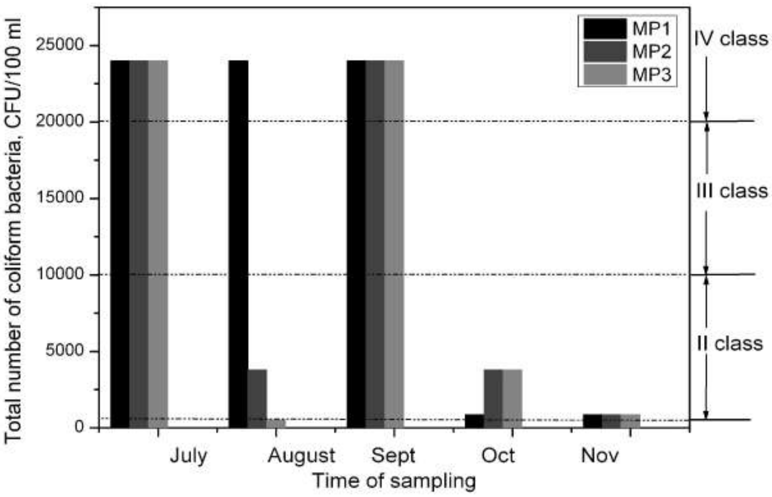

Figure 2. Microbiological characteristics presented as total number of coliform bacteria of river Mlava at three measuring points(MP) during the period from July to November

CONCLUSIONS

The river Mlava and Mlava sleeve with its coastline in a wider zone of Pozarevac represents partially and poorly regulated watercourse.

Going through the wider zone of Požarevac, river Mlava carries a large amount of mechanical and chemical materials, often dangerous and cancerous, and because of that the water quality of the river Mlava moves from II to III and IV water class.

The main factors that negatively affect the environment in the analyzed area, in the lower part of the basin of the river Mlava, are inadequate treatment of waste and wastewaters, uncontrolled use of chemicals in farming, and the lack of environmental monitoring system and underdeveloped ecological consciousness of the population.

Urbanization along the coast, proper waste management and construction of a wastewater treatment plant will improve the quality of these watercourses. All polluters of the river Mlava, Mlava sleeve and tributaries have a continuing obligation to discharge all their waste waters into the recipient, only as neutral ie. harmless.

Acknowledgments

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POLLUTION OF THE SAVA RIVER FROM ENTRANCE IN SERBIA TO CONFLUENCE IN THE DANUBE RIVER

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ABSTRACT

This paper analyzes results of two years testing the Sava River flow, from its entry into our country, to the confluence into the Danube. Four tested sites were considered: Jemena, Sremska Mitrovica, Šabac and Ostružnica. The aim of this study is to examine the level of pollution that Sava River brings entering in Serbia, as well as the impact of urban and industrial wastewater in Sremska Mitrovica, Šabac and Ostružnica on its quality. This paper presents only the physicochemical analysis.

Key words: urban and industrial wastewater, organic matter, heavy metals, phenols, nutrients.

INTRODUCTION

The Sava and the Danube rivers are of great importance for Belgrade. All wells for water supply of the city are located in the coastal areas, as well as water treatment plants in Bele Vode, and water intakes in Barič, Vinča and Makiš use water from the Sava and the Danube River. In the city area, both rivers come already loaded with waste water from upstream settlements and industry, and they receive significant quantities of wastewater in the city.

This paper describes the water quality of the Sava River from its entrance in Serbia to confluence in the Danube River. Testing was carried out on profiles of Jemena, Sremska Mitrovica, Šabac and Ostružnica. Great attention is paid to the Sava River due to the fact that it is an international river, but brings increasing pollution. The Sava River in Belgrade arrives burdened with wastewater of the upstream settlements and industries of the three countries, whether the waste water flowing directly into it or into its tributaries. This is especially important due to the fact that water supply of Belgrade completely relying on water from the river basin, abstracting from its alluvium - wells, or directly from the water stream - water factory Makiš. [1, 2, 3, 4]

QUALITY OF THE SAVA RIVER IN THE PREVIOUS PERIOD

The Sava River enters the territory of the Republic Serbia heavily polluted because it is the recipient of numerous municipal and industrial wastewaters from the Republic Slovenia, Croatia, Serbian Republic and Bosnia. After entering on the territory of Republic Serbia, the Sava River receives all urban waste water (municipal and industrial) from Šabac, Sremska Mitrovica, Obrenovac and Belgrade, and through the channel Galovica wastewater of the eastern part of Srem, without any previous treatment, because there is no central water purification in any of these settlements. Same case is with its tributaries, the Drina and the Kolubara River, so all that contribute to the worsening quality of the Sava River and creation of unfavorable conditions for the maintenance of biological organisms that contribute to self-purification of water.

Control of the quality of surface waters on the territory of Belgrade city is performed to assess the goodness of water streams, assess water pollution trends, assess the ability of self-purification and suitability for water supply of Belgrade, Obrenovac, Barič and Vinča, assess irrigation possibilities, as well as protect the health of citizens who can recreate themselves on these rivers. In order to obtain representative data on load of water with harmful and hazardous substances, or the vulnerability of ecosystems, it was necessary to develop a unique program of monitoring the quality of surface water that has been applied since January 1984. Testing was carried out by Republic Hydro-meteorological Institute under the Programme which was brought by the Assembly of Republic Serbia.

Data that wastewater of the municipal sewage discharging at over 31, and the industry at over 110 direct flows into Sava and Danube water streams and their tributaries show how Belgrade contributes to pollution of the Sava and Danube Rivers. According the Regulation on categorization of water streams and the Regulation on classification of waters, the Sava and the Danube Rivers and its tributaries are classified into second category streams, or in a class that can be used for recreation and drinking after purification.

We considered the period since 2000, when is concluded the worst deterioration in the overall water quality of the Sava River (in 2005), both in microbiology and physicochemical terms [5]. According to the results of field and laboratory tests in that period, only 19 (27.9%) of water samples for Sava River corresponded the waters suitable for public water supply, recreation, the food industry and fish ponds. Deviations from second class of river waters in physicochemical terms were not significant, with the exception of suspended solids. It can be said that the oxygen regime of balanced, though slightly less than the previous 2004, but in the warmer months and in the inner city area there is minimal disturbance, i.e. active and passive re-aeration fail to compensate the oxygen consumed in the decomposition of organic matter fully. The concentration of ammonia, nitrate and nitrite was constantly within the prescribed limits, indicating that the amount of protein in the wastewater discharged into the Sava relatively small and that their mineralization successfully carried out. The content of total organic carbon varies relatively little, from low to moderately high, and maximum values are registered in the profile "Kapetanija" (Port), and the situation is practically the same as in 2004. Increased concentrations of suspended solids were observed in 32 samples, mainly by the increasing of water level which is far more frequent than in the previous year. MAC exceeds were mainly within the boundaries of the third class and sporadically in the fourth class. There was no MAC exceeding among heavy and toxic metals. Some heavy metals, Cd, Hg, Ni and Pb, volatile phenols and anionic detergents (ABS) were consistently below or at the limit of detection for applied test method. Mineral oils are occasionally present, but the concentration is very low and constantly in the range of second class. Microbiological water quality of the Sava River was moderately deteriorated compared to 2004. [5]

This indicates that no action was taken on the construction of devices for the treatment of urban waste water in the upstream part of the basin. Considering the physiological groups of bacteria that perform decomposition of organic matter, there are not registered significant changes in water quality in comparison to the year 2004. Saprobiological tests indicating that there is no significant difference in the water quality of the Sava River in 2005 and 2004. Water generally corresponds to the second and the third class, as expected. In the river sediments are not registered concentrations of organic micro pollutants above effective value, and mineral oils, PCBs, organochlorine insecticides and herbicides are not detected. The content of heavy metals (Zn and Cr) was above the "effective value", while Pb, Cd, Cu, As and Hg were within the limits prescribed by the Regulations [3]. The situation is a little more favorable than in 2004. [5]

Globally, the water quality of the Sava River, according to certain microbiological and physico-chemical parameters, is significantly worsened in the year 2005. This was one of the worst years in the last decade. As in the previous year, the number of inhabitants and the influx of sanitary and industrial wastewater did not significantly changed; the deterioration of the situation can be explained by the frequent and heavy rains that have led to intense rinsing impurities from the coast. [6]

International Sava River Basin Commission - ISRBC since 2000 examines the quality of the Sava River in the profiles of Jemena, Sremska Mitrovica, Šabac and Ostružnica. These studies for the first five years noted the greatest deterioration of the overall water quality of the Sava River in 2005, both in microbiology and in physicochemical terms.

Report of the International Sava River Basin Commission - ISRBC from 2010 for the previous period, shows the water quality of the river Sava in the sections: Jamena-border profile, where the water is III class; Sremska Mitrovica, where the water is II / III class; Šabac where the water is II / class III; and Ostružnica where the water is III class. It is noted that even during sampling are observed changes in organoleptic properties of water. Water color on profile Ostružnica in two tests matched the water class III, while the existing visible floating waste materials in one study were out of category. From entering into our country to the confluence, from Jamena to Ostružnica, oxygen saturation of water occasionally was on the II class level and occasionally beyond class. The content of suspended solids was increased (class III) on some samples of all tested sites, while on Jemena, in one sample, content of suspended matter was outside the class. At all profiles was recorded increased metal content as dangerous and harmful substances. Concentration of iron was at the level of III and IV or out of each class. Manganese and copper were outside of each class. On the Šabac profile is observed elevated concentrations of Pb, level of III and IV class, and on the profile Ostružnica is observed increased concentration of zinc, on the level of III and IV classes, and nickel out of each class. On the profile Jamena and Šabac in a single case was recorded increased value of phenol index, level of III and IV classes, while on the profile of Sremska Mitrovica, in one case, was registered increased concentration of surface anion matter at the level of III and IV class. [7]

Saprobiological testing of water on these profiles indicates moderate organic matter pollution of water streams. It is noted domination of organisms that are indicators of alpha and beta mesotrophic zone. Siliceous algae dominate throughout the year, but the number of phytoplankton is small. Obtained values of the index of saprobity, in all periods of testing, indicate the II class of water quality. [7]

Belgrade's contribution to the pollution of the Sava River, and the Danube River, the test results

According to an International Sava River Basin Commission - ISRBC from 2010, the results show that wastewater of the municipal sewage system discharged at over 31, and of the industry at over 110 direct flows into these water streams and their tributaries.

According to the Regulation on Classification and Categorization of Water, and the Rulebook on Hazardous Substances in Water, the Sava River is, from entering in our country to its confluence into the Danube River, II class water stream, while testing of the Agency for Environmental Protection of RS in the same year, in all these profiles, show that it deviates from the prescribed categories. [1,2,3,6,7]

MATERIALS AND METHODS

This paper analyzes the results of the Sava River for 2011 and 2012, on profiles of Jemena, Sremska Mitrovica, Šabac and Ostružnica. The results of physicochemical testing by Agency for Environmental Protection of the Ministry of Energy and Environmental Protection RS were discussed, whose laboratory is accredited for this type of testing. The paper presents the results of physicochemical testing given as minimum, maximum and mean values of two-year examination. These investigations Agency performs during regular monitoring of surface water quality, according to the Plan of RS, in its laboratory that is accredited for this type of testing [6,7].

RESULTS AND DISCUSSION

Table 1 shows the minimum, maximum and mean values of two-year testing of the Sava River, from its entry into Serbia to the confluence into the Danube River. [6, 7]
From the test results, it can be clearly observed increased pollution of the Sava River at the moment of its entry into Serbia. The concentration of oxygen, as the most important parameter for evaluating the quality of streams or detecting the presence of organic pollution, and thus municipal wastewater, is quite high. At the entrance to Serbia at Jemena, the oxygen content is high; the average value is 9,52mgO_2 / dm^3, which indicates that the water contains enough oxygen for the oxidation of organic impurities, while the mean oxygen saturation ranges from a minimum of 78 to a maximum of 92%.
On the test locations after Jemena, in Sremska Mitrovica, Šabac and Ostružnica, dissolved oxygen gradually increasing, so at Ostružnica reaches a value of 9.83 mgO_2 /

dm^3, and oxygen saturation increases for 5%. The level of organic pollution at the entrance to Serbia is relatively high, ranging from 1.8 to a maximum 4.3 mgO_2 / dm^3, while the average value of organic matter is 2.45 mgO_2 / dm^3 and BOD_5 is 1,66 mgO_2 / dm^3, which means that for a period of five days is microbiologically degraded about 68% of organic matter. Further, down the the Sava River, near Sremska Mitrovica and Šabac, mean values of organic matter are lower, and in Ostružnica we noticed increased content of organic matter, 2.57 mgO_2 / dm^3. [8, 9]

BOD_5 decreases at Sremska Mitrovica, and in Šabac and Ostružnica increases on 1.81 mgO_2 / dm^3. This indicates an increase in the presence of biochemicaly harder degradable organic matter, which reduces the self-purification of water streams and is unfavorable from the aspect of purification of the water. Exactly this is confirmed by the content of total organic carbon as the best parameter for assessing the organic load of water, which ranges from 1.8 to 7.3 mg O_2 / dm^3, which indicates the presence of complex organic compounds. These are mainly pesticides, polychlorinated biphenyls.

Nitrate concentration is relatively low, far below the MAC. The mean value is 0.67 mg / dm^3. Ammonia concentration is 0.027 mg / dm^3, which is above the MAC values for class II of water stream. Along the Save River stream this concentration increases, and at Sremska Mitrovica and Šabac is almost twice higher, and in Ostružnica three and a half times higher. Phosphate concentration is significantly higher at the entrance to our country than on other test sites. The maximum concentration of total phosphorus in Jemena is 0,132 mg / dm^3, and slowly decreases to Ostružnica, where its value is 0,047 mg / dm^3. This indicates a high concentration of nutrients at the entrance of the Sava River in our country and on the presence of organic pollution it brings into the Republic of Serbia [10]. In the Sava River, at the entrance to our country, the concentration of nitrate, ammonia, phosphate, and the content of suspended solids and turbidity were significantly increased in comparison to other test sites to its confluence in the Danube River. In the Sava River at Jemena were identified toxic compounds phenols with a mean concentration of twice higher value than MAC. However, on test locations along the Sava River to Belgrade, where it flows into the Danube, their concentration increases, and at Ostružnica its mean concentration reaches ten times higher value than MAC, 0.010 mg / dm^3, while the maximum concentration on this test point is 0.012 mg / dm^3.

High concentrations of phosphorus and nitrogen compounds impairs the quality of the Sava River and this tendency is becoming more pronounced over time, as it continues with the practice of pouring untreated municipal and industrial city wastewater along its course. This affects tendency of deterioration the Sava River quality and all that more pronounced eutrophication processes in it.

Tests have shown high concentrations of heavy metals. Lead, cadmium, arsenic and mercury are increased up to ten times than MAC. In Ostružnica mean value for lead is 1.13 mg / dm^3, and maximum value for cadmium is even 3,81 mg / dm^3, which are far above the MAC values. The concentration of chromium and arsenic goes up to fifty or a hundred times above the maximum allowable concentration.

Table 1. Characteristics of the Sava River in Serbia

No.	Tested parameters	MAC II class water	THE SAVA RIVER Jamena Min	max	midi	Srem. Mitrovica Min	max	midi	Šabac min	max	midi	Ostružnica min	max	midi
1.	Flow (m^3/s)					179	2155	827						
2.	Turbidity (NTU)		3	44,4	11	3	26	9,2	2,19	19,7	8,53	1,68	18,2	9,19
3.	pH		7,9	8,3		7,5	8,3		7,9	8,2		7,6	8,3	
4.	EC (s/sm)		415	550	481	387	547	428	383	517	421	333	439	403
5.	Suspended solids (mg/dm^3)	40	2	51	10	2	15	5,3	1,0	15	6,42	1,0	13	5,82
6.	TDS (mg/dm^3)		211	338	285	177	328	249	204	323	245	217	292	260
7.	COD from $KMnO_4$ (mgO_2/dm^3)	/	1,8	4,3	2,45	1,3	3,5	2,12	1,7	3,0	2,39	1,8	3,6	2,57
8.	BOD_5 (mgO_2/dm^3)	5	1,0	2,4	1,66	0,5	2,6	1,49	1,0	2,1	1,36	1,1	2,7	1,81
9.	Total organic carbon (mg/dm^3)		1,8	4,3	2,45	1,7	7,3	3,29	1,8	6,2	2,98	1,9	5,7	3,69
10	Dissolved oxygen (mgO_2/dm^3)	6	6,9	12,8	9,52	9,0	13,8	8,75	7,7	12,7	10,1	7,1	12,9	9,83
11	Oxygen saturation (%)	/	78	110	92	83	116	99	87	101	94	84	109	97
12	Ammonia (mgN/dm^3)	0,1	0,02	0,16	0,027	0,01	0,1	0,047	0,01	0,08	0,044	0,03	0,14	0,083
13	Nitrates (mgN/dm^3)	10,0	0,2	1,1	0,67	0,5	0,9	0,62	0,3	1,0	0,65	0,1	1,	0,41
14	Total organic nitrogen (mgN/dm^3)		0,2	1,8	0,785	0,2	1,3	0,554	0,1	1,9	0,53	0,1	1,36	0,77
15	Total nitrogen (mgN/dm^3)		1,0	2,2	1,54	0,8	2,10	1,17	0,7	2,1	1,27	0,3	1,93	1,37
16	Orto phosphates (mgP/dm^3)	/	<0,05	0,102	0,05	<0,005	0,064	0,031	<0,005	0,084	0,033	0,009	0,049	0,023
17	Total phosphate (mgP/dm^3)		0,031	0,710	0,132	0,037	0,131	0,054	0,036	0,135	0,059	0,02	0,091	0,047
18	Anion active substances (mg/dm^3)	0,05	<0,01			< 0,01			< 0,01	0,01	0,01	< 0,01	0,01	0,0
19	Phenols (mg/dm^3)	0,001	<0,01	0,006	0,002	<0,01	0,015	0,010	<0,01	0,014	0,013	<0,0	0,012	0,010
20	Pb	0,05	<0,5	0,5	0,5	<0,5			<0,5	0,6	0,6	<0,5	1,8	1,13
21	Cd	0,005	<0,02	0,05	0,034	<0,02	0,08	0,052	<0,02	0,04	0,04	0,03	3,81	0,50
22	Cu	0,1	1,9	16 ,1	5,15	1,3	20,8	5,4	1,2	17,4	5,31	3,4	17,4	10,40
23	Zn	0,2	2,3	39,4	15,35	4,7	22,5	12,71	2,7	26,8	10,81	4,2	26,3	10,52
24	Cr	0,1	0,5	4,9	1,3	<0,5	0,8	0,625	<0,5	1,0	0,73	<0,5	1,3	0,8
25	As	0,05	0,6	2,0	1,05	0,6	1,6	0,875	0,7	1,6	0,97	1,0	2,5	1,82
26	BOD5/COD (%)	/	55	56	68	38	74	70	59	70	57	61	75	70

CONCLUSION

As stated above, we can conclude that the quality of the Sava River from entering our country to the confluence into the Danube River worsens in terms of the content of organic matter, nutrients, phenol and other harmful substances due to spillage of municipal and industrial wastewater from surrounding settlements.

Reducing of biochemically degradable organic matter downstream from Belgrade indicates that in the Belgrade area into Danube entering dangerous and toxic organic substances that are harder microbiologically degraded, which reduces the value of BOD_5, and reduced self-purification processes in the system.

High concentrations of phosphorus and nitrogen compounds impairs the quality of the Sava and this trend will become more pronounced over time, as it continues to practice of pouring untreated municipal and industrial wastewater of cities along its course. Hence, we can expect the rapid deterioration of the quality of the Sava River and more pronounced eutrophication process. Tests have shown high concentrations of heavy metals. Lead, cadmium and mercury are increased up to ten times than MAC, whereas the concentrations of chromium and arsenic increases even fifty or a hundred times above the maximum allowable concentration.

This research and testing physical-chemical characteristics of the water of the Sava River, indicate the need for treatment of municipal and industrial wastewater, as well as the need to take measures for prevention possibility of the occurrence of an accident.

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APPLICATION OF THE FILTER-ANTRACIT® FOR DRINKING WATER PURIFICATION

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ABSTRACT

Anthracite from coal mine „Vrska Cuka" Avramica represents a energy raw material with high level of carbonization. Anthracite, as a natural and inactive adsorbent, has the significant adsorption ability. In recent years, is dedicated a lot of attention in the invetsigations of its efficiency as an adsorbent for purification of drinking water as well as oily wastewater.

This paper presents an overview of the results of research in order to show the possibility of production of filter-anthracite for purufucation and tretament of drinking water.

Keywords: anthracite, Vrska Cuka, purification, drinking water, ecology.

INTRODUCTION

Anthracite mine "Vrska Cuka" Avramica is located in Eastern Serbia around 10 km South East from City of Zajecar. Anthracite is semi metallic in colour with a middle grey in reflection, has a high luster, depending on metamorphosis it can remind on graphite. It is happen to appear very fragile so it is hard to find bigger pieces. Scratch mark is also black. Shale is irregular with sharp edges. Anthracite generates in two varieties as amorphous and crystallite. Crystallite variety is used for the production of filter-antracit®.

USE OF ANTHRACITE AS FILTER-ANTRACIT® FOR DRINKING WATER PURIFICAION

Filter-antracit® is manufactured from anthracite produced in RA "Vrska Cuka" Avramica. It has high carbonisation level and it is also beneficiated in wet separation facility and physical-mechanical methods and also in thermal processing.

This product is used for drinking water purification originated from rivers, lakes and wells.

Previous investigations of anthracite for the purification of drinking water

First testing and use of anthracite as Filter-antracit® in drinking water purification started as joint project between Trayal-Krusevac and RA "Vrska Cuka" in 1994. Results showed that it is possible to replace active carbon with Filter-antracit®. According to test results the best product must have characteristics as shown in table below:

- Ash content less than 6%
- Fixed carbon 85-90%
- Density 700-730 kg/m³,
- Total Moisture 5-9%
- Acid solubility starting from 0,5 %,

Filter-antracit® made by "Trayal" Krusevac has been used in few drinking water facilities in Serbia, with good results.

Also Trayal in 1997 sent two samples for adsorption testing. Jovisic (1997) was investigated adsorption properties of activated carbons produced from anthracite from RA „Vrska Cuka" Avramica [1]. In the paper are presents the results of the testing adsorption of phenol from the Danube water and the adsorption of natural organic matter from groundwater of northern Banat.

For these studies, two samples are taken with size class of 2 and 4 mm.

Table 1. Characteristics of anthracite as activated carbon

Activated Carbon (anthracite)	Ash (%)	Moisture (%)	Iodine number (mg/g)
Particle size 2 mm	9,00	19,80	725
Particle size 4 mm	9,70	20,75	670

Activated carbon made from anthracite in the size classes 2 mm and 4 mm respectively have high ash and moisture content and low Iodine number.

Investigations of the adsorption characteristics of activated carbons in static conditions showed that anthracite have the higher capacity for the adsorption of phenol. Adsorption capacity of activated carbons from RA "Vrska Cuka" Avramica tested on water originated from Danube and underground waters are slightly lower.

From the table 1, it can be seen that ash content more than 9 % in the analyzed sample, and for such tests ash content of the sample should not be higher more than 5 %. According to the quality of raw materials, the results of investigation of the adsorption characteristics of anthracite can be considered satisfactory.

In 2002, RA „Vrska Cuka" Avramica together with the Institute for general and physical chemistry began research on the application of anthracite in the technology of water treatment [2, 3].

From samples of anthracite from RA „Vrška Čuka" Avramica obtained four filtration agents, such as: KP, SP, KT and ST.

Table 2 shows physical chemistry data of products made for anthracite for filtration originated from RA Vrska Cuka Avramica produced in Institute of General and Physical Chemistry and Trayal Krusevac respectively.

Table 2. Physical and chemistry characteristics of anthracite for filtration

Name	Volume mass g/cm³	Bulk Density kg/m³	Ash (%)	Sorption CCl_4 (%)
KP	1,40	743	5,86	2,72
SP	1,42	753	7,32	2,89
KT	1,39	679	4,86	3,28
ST	1,41	685	5,08	3,82
KM	1,40	734	6,06	2,15
SN	1,39	711	8,07	3,38

Table 2 shows the most important characteristic sorption capacity (percent of residue organic substance left on anthracite grain) is higher on samples for Institute than samples from Trayal for 10 to 40 percent

With better processing in wet separation of coal, ash content can be decreased and that will increase adsorption capacity.

Sizing is very important in use of anthracite as filtration agent.

The variety of applications anthracite as filtration agents, special attention should be paid to getting the various granulations and their better classifying to obtain a granulation with a uniform grain size.

Grouping anthracite grains by size helps to compact layers without any caverns, fluid used for filtration can pass through those caverns without contact with filtration layers and that decrease filtration efficiency. Grouping particles by size is only way to avoid creation of caverns and to increase contact between fluid and filtration agent.

Besides that, in the regeneration, rinsing by water in opposite direction will permanently damage filtration layers. Common size are in the range between 0.6-1.2 mm, 0.8-1.6 mm, 1.2-1.5 mm, 1.4-2.5mm, 2.5-5.0mm, and 5.0-10.0 mm. Grouping particles in those ranges is not a problem, it is easy accomplished by set of sieves with predefined sizes.

Expert declaration of healthy usage

Anthracite sample (filter-antracit®) has been sent to Institute of Public Health of Serbia Dr. Milan Jovanovic-Batut to Centre for Microbiology for drinking water purification testing. Testing results are in Report 6283/po u.896 dated from May 14, 2002.

Test were focused coal characteristics (volatility and heavy metals), solubility (lab simulation of timely contact between water and contact), change in water characteristic after contact with anthracite and migration dynamism for TOC, PAH, benzopyrene after 24, 48 and 72 hours. According to results it can be said that extraction of organic and inorganic components with destiled and ionised water is equal and relatively small. After water treatment with anthracite there was no significant migration any of tested components, or all parameters were compliant with recurements stated in Rulebook on hygienic quality of drinking water (Sl. SRJ br 42/98). Polyaromatic hydrocarbons and benzopyrene extraction is minimal and under detection level. Report states: "it can be concluded that use of anthracite treated as stated above cannot harm users considering that in simulation real parameters were used.

Anthracite sample is tested again for healthy usage in Institute of Public Health of Serbia Dr. Milan Jovanovic-Batut in Centre for Hygiene and Human Ecology and report has been published on April 04, 2014 under number 178.

According to the results of lab testing and expert opinion it is said that from aspects of tested parameters sample is compliant to Law (Sl.gl.RS 92/2011) and applicable norms issued in Rulebook (Sl L SFRJ 26/83, 61/84 and 18/91)

CONCLUSION

Anthracite mine „Vrska Cuka“ is one out of eight anthracite mines with a good coal quality. Coal usage is various, from drinking water and sewage purification, graphite cathodes, graphite, silicon carbide graphite etc. By products from coal separation are used in smelters, brick factories, for heating etc.

Anthracite mine „Vrska Cuka“ produces high quality coal (anthracite) using room and Pillar mining method. Raw coal contains between 30 and 35 percent of ash and can be used for heating. Mine has brand new wet separation for coal processing. After beneficiation in wet separation the best quality products are with ash content between 2 and 6 percent. That product can be used in production for active carbons, materials used in adsorption and purification of drinking water oily waters, and sewage. This facility is environmental complaint, water used for washing is in closed circle, after used in Separation it is flowing to the sumps and from sumps directly to washing again.

Washing facility is processing coal with ash less than six percent, and this by product is used for producing drinking water purification. For production of anthracite it is necessary to construct facility equipped with mill, drying facility and set of sieves for granulation.

Construction of beneficiation facility mine will be capable to produce A grade product used in various types of water purification, and by products should be sold as thermal coal to cement plants, heating plants, smelters and brick factories. Installation of new production line will increase productivity up to 95 percent.

As it is stated above it possible to produce Filter-antracit® because there is wet separation in place capable to remove ash from raw coal as low as two percent. The lower ash content in Filter-antracit® increases its sorption plus if combined with set of sieves sizing is improved and leads to much better quality of product.

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WATER QUALITY ASSESSMENT BASED ON MACROINVERTEBRATES – SMALL HILLY STREAMS IN THE CARPATHIAN-BALKAN REGION OF EASTERN SERBIA

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ABSTRACT

In this paper the status assessment of small hilly streams in the Carpathian-Balkan region (Eastern Serbia) is given based on aquatic macroinvertebrates. The research was conducted in April, June, and September 2013 at nine sampling sites on seven streams. During the investigation 85 macroinvertebrate taxa from 11 taxa groups were recorded. Diptera (32.06 %) and Ephemeroptera (28.47 %) were dominant groups. Following indices were used for the status assessment: total number of taxa, Saprobic Index, Diversity index H', BMWP and ASPT, number of sensitive taxa and EPT. The results indicate low degree of organic pollution in analyzed streams.

Key words: Macroinvertebrates, Water Quality, Streams, Eastern Serbia.

INTRODUCTION

Macroinvertebrates are an important component of stream and river systems and have an effect on structure and function of freshwater ecosystems (1). For the assessment of aquatic ecosystems status, benthic macroinvertebrates are the most frequently used biological indicators (2). Macroinvertebrates are found in all aquatic habitats and are (noted as) more sensitive to changes in water quality in comparison to other Biological Quality Elements (BQE). They are less mobile, have relatively long periods of development in the aquatic environment and they are easily collected (3). Thus, macroinvertebrate communities should reveal harmful changes that have occurred in the aquatic environment during any stage of their development (4). Due to their sensitivity Ephemeroptera, Plecoptera and Trichoptera are the most commonly used taxa as bioindicators among macroinvertebrates, and their indices are appropriate for evaluation of the streams ecological status (5, 6).

Study area is situated in Eastern Serbia (the Carpathian-Balkan region), towards the border of the Wallachian-Pontic basin. Rivers Bigar, Jagnjilo, Valja Saka, Tisnica, Crna Reka, Valja Streži, and Vrkaluca belong to the Danube River Basin (catchments of rivers Mlava and Pek) and are located in the hilly-mountain part of Eastern Serbia. Larger settlements in the region are Žagubica, Bor and Majdanpek. Broad-leaved forests and transitional woodland/shrub surround the investigated rivers which lie on limestone. Neighboring agricultural land is scattered as small agricultural lots, according to the CORINE Land Cover Database for Serbia (7). The biggest permanent stream is the Jagnjilo River. Valja Saka stream springs below Čoće at 860 m a.s.l. (8) and joins the Bigar River to form the Jagnjilo River, which further flows to the north. The Lipa River confluence into the Jagnjilo River and forms the Veliki Pek River in Jasikovo village (8). The Crna Reka River is a small watercourse that often dries out. It is a right tributary of the Tisnica River, which originates at Kučajske Mountain, flows to the north near the eastern slope of Beljanica Mountain. The Tisnica River is a right tributary of the Mlava River (8). The Mlava River rises from Žagubičko spring after which it immediately receives the Tisnica.

The aim of this study is to determine the water quality in small hilly streams in the Carpathian-Balkan region (Eastern Serbia) based on the macroinvertebrate community as the main biological component.

MATERIAL AND METHODS

Samples were collected during April, June, and September 2013 from the nine localities on rivers in the study area: Bigar (lower stretch), Valja streži, Jagnjilo at two sampling sites (Jagnjilo upper stretch and Jagnjilo lower stretch), Tisnica at two sampling sites (Tisnica lower stretch and Tisnica upstream of the Crna Reka confluence), Crna Reka (lower stretch), Vrkaluca and Valja Saka (Figure 1).

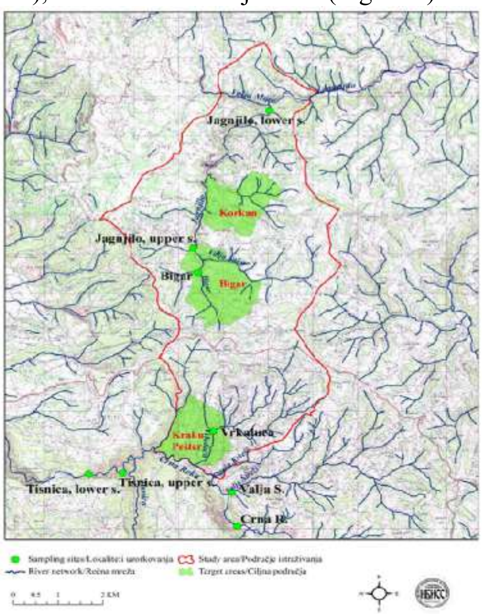

Figure 1. Aquatic macroinvertebrates sampling locations

RESULTS AND DISCUSSION

In total 85 macroinvertebrate taxa from 11 taxa groups were recorded within the study area. The qualitative composition of macroinvertebrate assemblages is presented in Table 1.

Table 1. List of identified taxa of aquatic macroinvertebrate assemblages

Turbellaria
Dugesia gonocephala (Dugès, 1830)
Dugesia sp.*

Oligochaeta
Enchytraeidae
Eiseniella tetraedra (Savigny, 1826)
Henlea ventriculosa (d'Udekem, 1854)
Limnodrilus hoffmeisteri Claparede, 1862
Mesenchytraeus sp.
Nais bretscheri Michaelsen, 1899 *
Nais elinguis Muller, 1774 *
Nais sp.
Stylodrilus heringianus Claparède, 1862
Rhyacodrilus falciformis Bretscher, 1901

Gastropoda
Bythinia tentaculata (Linnaeus, 1758)

Bivalvia
Pisidium sp.

Crustacea
Gammarus balcanicus Schäferna, 1922
Austropotamobius torrentium (Schrank, 1803)

Odonata
Cordulegaster boltoni (Donovan, 1807)

Ephemeroptera
Ephemera sp.
Baetis alpinus (Pictet, 1843)
Baetis rhodani Pictet, 1843
Baetis vernus Curtis, 1834
Baetis sp.
Ephemera danica Müller, 1764
Ecdyonurus helveticus Eaton, 1885
Ecdyonurus sp.
Liponeura sp.

Trichoptera
Allogamus auricollis (Pictet, 1834)*
Ceraclea sp.
Oecismus monedula (Hagen, 1859)
Glosossoma boltoni Curtis, 1834
Halesus digitatus (Schrank, 1781)
Hydropsyche fulvipes (Curtis, 1834)
Hydropsyche pellucidula (Curtis, 1834)
Hydropsyche sp.
Hydroptila sp.
Leptoceridae
Limnephilus sp.
Polycentropus flavomaculatus (Pictet, 1834)
Philopotamus montanus (Donovan, 1813)
Potamophylax cingulatus (Stephens, 1837)
Sericostoma sp.
Rhyacophila fasciata Hagen, 1859
Rhyacophila obliterata McLachlan, 1863
Rhyacophila tristis Pictet, 1834
Rhyacophila sp.
Silo nigricornis (Pictet, 1834)
Drusus monticola McLachlan, 1876

Coleoptera
Agabus arcticus (Paykull, 1798)*
Ryolus sp.
Normandia nitens (Müller, 1817)
Dryops gracilis (Karsch, 1881)
Elmis sp.
Oulimnius troglodytes (Gyllenhal, 1827)
Limnius volckmari (Panzer, 1793)
Halipus confinis Stephens, 1828*
Hydraena gracilis Germar, 1824
Elodes marginata (Fabricius, 1798)
Elmis aenea (Müller, 1806)
Colymbete ssp.

Diptera
Tipula sp.
Tabanus sp.

Heptageniidae
Epeorus sylvicola (Pictet, 1865)
Ephemerella mucronata (Bengtsson, 1909)
Ephemerella ignita (Poda, 1761)
Ephemerella sp.
Rhytrogena sp.
Rhytrogena semicolorata group
Paraleptophlaebia submarginata (Stephens 1835)

Plecoptera
Brachyptera risi (Morton, 1896)
Leuctra sp.
Isoperla grammatica (Poda, 1761)
Nemoura cinerea (Retzius, 1783)
Nemoura sp.
Perla bipunctata Pictet, 1833
Perla sp.
Protonemura montana Kimmins, 1941

Psychoda cinerea Banks, 1894
Antocha sp.
Atherix ibis (Fabricius, 1789)
Clinocera sp.
Eleophila sp.
Ibisia marginata (Fabricius, 1781)
Gnophomyia sp.
Hexatoma sp.
Oxycera pardalina Meigen, 1822
Ceratopogonidae
Simulidae
Chironomidae
Pericoma sp.
Tonnoiriella pulchra (Eaton, 1893)

Megaloptera
Sialis lutaria (Linnaeus, 1758)

The number of recorded taxa per locality varied between 16 (Tisnica, upstream of the Crna reka confluence) and 37 (Valja Streži). A considerable taxa richness was recorded for locality Vrkaluca (27 taxa), Bigar (24) followed by Jagnjilo lower stretch (22) and Crna reka lower stretch (20), while a smaller number of species was recorded for the rest of the sampling sites. Analysis of the macroinvertebrates fauna indicated that, the main components of the community in relation to relative abundance were Diptera (32.06 %) and Ephemeroptera (28.47 %).

According to the ecological classification of the taxa, 18.73% of the identified species belong to the xenosaprobic and oligosaprobic group (14). Species that are tolerant to moderate organic loading (beta-mesosaprobic) were represented by 15%, while only 3.28% of the taxa could be characterized as alpha-mesosaprobic. No species adapted to high organic loading (polysaprobic) were recorded.

The majority of recorded species (46.82%) were typical for rhithral. A lower proportion of the taxa belong to those of the potamal type (14.32%) and only 7.53% to crenal type, according to Moog (14) and AQEM (13).

In regard to flow preference, the recorded community was dominated by rheophilous taxa (27.37%) and indifferent taxa (27.33%). Rheobionts and rheo-limnophilous taxa were represented with 15.48% and 10.21%, respectively. A low number of species (<0.2%) were characterized as limnophilous and limno-rheophilous, while 19.35% of the taxa could not be classified in regard to current preference.

Lithophylous taxa that prefer coarse gravel, stones and boulders (grain size > 2 cm) were dominant, representing 25.20% of the macroinvertebrate assemblages. The phytophylous taxa had also a significant presence of 19.42%, as well as the species that prefer fine-to-medium-sized gravel (pelal, psammal and argilal) – 18.37%. A smaller number of taxa (0.92%) prefer particulate organic matter such as woody debris, while for the remaining taxa there is not enough data on microhabitat preference (13).

The values of SI indices varied per sampling location from 1.28 to 1.65, indicating high status (I class) for all investigated streams (Table 2). BMWP Scores for rivers in the Study area ranged from 59 to 142. The highest ASPT score was recorded for the stream Vrkaluca (7.23) − corresponding to high status (I class), low ASPT value means low level of organic pollution and good to high ecological status; on the contrary, high value of ASPT means higher level of organic pollution and moderate to bad ecological status. ASPT Scores from other investigated streams have been slightly lower, indicating good water quality (II class) (15) (Table 2).

Table 2. Assessment of ecological status based on macroinvertebrate metrics. SI - Saprobic Index (Zelinka & Marvan 1961), H' - Shannon Diversity Index; Sites: 1 – Bigar, 2 – Valja Streži, 3 – Tisnica lower stretch, 4 – Tisnica- upstream of the confluence with Crna reka, 5 – Jagnjilo-lower stretch, 6 – Jagnjilo-upper stretch, 7 – Crna reka-lower stretch, 8 – Vrkaluca, 9 – Valja Saka

Metric/Sites	1	2	3	4	5	6	7	8	9
SI	1.65 (I)	1.30 (I)	1.47 (I)	1.45 (I)	1.28 (I)	1.42 (I)	1.52 (I)	1.31 (I)	1.39 (I)
BMWP	112 (I)	142 (I)	82 (IV)	59 (III)	87 (IV)	116 (I)	105 (I)	123 (I)	80 (IV)
ASPT	6.59 (II)	6.76 (II)	6.31 (II)	5.90 (II)	6.21 (II)	6.44 (II)	7 (II)	7.23 (I)	6.15 (II)
H'	0.78 (IV)	0.86 (IV)	0.85 (IV)	0.81 (IV)	0.82 (IV)	0.87 (IV)	0.89 (IV)	0.91 (IV)	0.35 (V)
EPT	14 (III)	25 (I)	11 (III)	8 (IV)	11 (III)	16 (II)	12 (III)	17 (II)	9 (IV)
Sensitive taxa	6 (I)	11 (I)	5 (II)	6 (I)	6 (I)	10 (I)	8 (I)	12 (I)	1 (V)

The values of EPT Index are shown in Table 2. The higher values of EPT index are associated with non-impacted or slightly impacted streams, while decline of index indicates increasing of environmental stress. The number of EPT taxa per locality varied in range from 8 to 25. The EPT index is a useful tool for status assessment in rivers with hard bottom substrates. The index clearly reflects the quality of the aquatic environment (16).

Status assessment according to the number of sensitive taxa revealed good status (I class) for most localities except Tisnica, lower stretch (II class) and Valja Saka (V class).

Values of diversity index H' (11) ranged from 0.35 to 0.91, indicating bad status (IV class) for most localities and poor status (V class) for locality Valja Saka. The overall status of rivers in the study area could be assessed as high to good. Parameters that are based on number of taxa (BMWP score, EPT and diversity index) indicate moderate and poor status, but mostly due to unfavorable hydrological conditions at the time of the sampling - high water level and current in the Spring sampling period and extremely low water level and drought during other investigated periods of the year.

Based on used community indices, the general conclusion is that the degree of organic pollution of streams from this study is low. This is also confirmed by the taxa richness - characteristic number of species for small streams of hilly-mountainous regions of ecoregion 5 and 6 (17) and community structure - appearance of taxa characteristic for small streams of hilly-mountainous regions of ecoregion 5 and 6 (17). Evenness of the community is high, more precisely, there is absence of the phenomenon that one, or only a few species, overtake absolute domination within the community.

Our study proved that the use of selected macroinvertebrates and their communities in ecological status assessment of determined river types is an effective approach for estimating and monitoring aquatic ecosystem health.

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ALLOCHTHONOUS MACROINVERTEBRATE SPECIES OF THE SERBIAN STRETCHOF THE TISA RIVER

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ABSTRACT

The aim of this paper is to provide the list of allochthonous macroinvertebrate species of the Serbian stretch of the Tisa River. Material was collected during 2010 and 2013 at four sampling sites. In total, eight allochthonous macroinvertebrate species were registered. The most abundant species was *Dreissena polymorpha*. Comparing to previous investigation, six new allochthonous species were identified, denoting that the Tisa River is upon significant influence of aquatic invasions.

Key words: Allochthonous species, the Tisa River, Serbia.

INTRODUCTION

The Tisa River is the largest tributary of the Danube in Serbia. It comes from Hungary and enters Serbia south from the city of Szeged. In its 160 kilometres long stretch through Serbia, the Tisa River has the typical characteristics of a lowland river. In this sector, it receives the Begej River and smaller tributaries through the Danube-Tisza-Danube Canal System (HS DTD, 1). Near the village of Slankamen it reaches the Danube at 1215 river kilometer.

Previously published results concerning allochthonous macroinvertebrates of Serbian part of the Tisa River (1, 2) presented only a brief overview on alien macroinvertebrates and for that reason this paper is a starting point for further investigation in this area of interest.

MATERIAL AND METHODS

The survey of allochthonous macroinvertebrate species resulted from long-term investigations from four sampling sites at the Tisa River (Table 1). The material was collected in September 2010 and July 2013. The samples were collected with benthological hand nets, mesh size 500 μm. Samples were collected from all available habitats represented with more than 5% of total habitats area on the sampling stretch (multi-habitat sampling procedure).

The analyses comprised the calculation of selected metrics by using ASTERICS software (3) – the number of allochthonous taxa, percentage participation of the allochthonous taxa in the community, saprobic preference, functional feeding group relations and microhabitat preference.

Table 1. Sampling sites along the Tisa River and the year of sampling.

Site	2010	2013	River km	Latitude, N	Longitude, E	Altitude
Kanjiža		•	148.0	46°04'04,3"	20°04'08,4"	78.9
Ada	•	•	102.8	45°47'36,2"	20°08'49,3"	148
Novi Bečej	•	•	72.0	45°35'18,3"	20°08'01,3"	90.7
Titel	•	•	9.7	45°11'41,1"	20°18'39,3"	90.2

RESULTS AND DISCUSSION

During the investigation, eight allochthonous macroinvertebrate species belonging to three different groups were recorded, as presented in Table 2.

The overall quantity of the allochthonous species per sampling period was 222 species in 2010 and 111 species in 2013, which represents 17.20% and 14.25% of the total number of macroivertebrate species, respectively. The locality with the least number of allochthonous species was Titel (only one species), while the greatest allochthonous species diversity has been recorded at the locality Novi Bečej (four species). The most abundant allochthonous species was *Dreissena polymorpha* with 25.56% of the total macroinvertebrate community.

Table 2. The list of recorded allochthonous macroinvertebrate species

Taxon name	TaxaGroup
Branchiura sowerbyi Beddard, 1892	Oligochaeta
Chelicorophium curvispinum (G. O. Sars, 1895)	Amphipoda
Dikerogammarus haemobaphes (Eichwald, 1841)	Amphipoda
Dikerogammarus villosus (Sowinsky, 1894)	Amphipoda
Limnomysis benedeni Czerniavsky, 1882	Amphipoda
Corbicula fluminea (O. F. Müller, 1774)	Mollusca
Dreissena polymorpha (Pallas, 1771)	Mollusca
Sinanodonta woodiana (Lea, 1834)	Mollusca

The majority of recorded allochthonous taxa are typical representatives of potamal (63.75%), adapted to soft bottom sediment which is in concordance with the type of the river. Regarding the functional structure of the aquatic ecosystem, the majority of detected allochthonous taxa belong to active filter feeders (50%), while other feeding types were much less represented. Also, the saprobic preference of recorded allochthonous taxa is presented at Table 3, which shows the domination of β-mesosaprobic taxa.

Table 3. The percentage of species preferring the particular saprobic conditions

Saprobic preference	%
xeno	0
oligo	10
β-meso	53.75
α-meso	22.50
poly	1.25
no data available	12.50

Comparing to previous investigation (2), six new allochthonous species were identified, denoting that the Tisa River is upon significant influence of aquatic invasions. Earlier identified allochthonous species of the Tisa have had much higher abundance according to presented study and the only species that has not been detected in investigated period was snail *Physella acuta*.

Filtration as dominant feeding type and toleration to organic and nutrient pollution could be underlined as a feature that largely contribute to the invasiveness of detected allochthonous taxa, which was already proven for certain species (4, 5).

Three allochthonous species (*C. fluminea*, *S. woodiana* and *D. polymorpha*) found in the Tisa River are already pointed as potentially invasive for the watercourses of Serbia due to high potential to spread, high potential for establishment in new environment and high potential to cause ecological and negative socio-economic impacts (6).

Although it is very hard to determine the degree of impact of the allochthonous organisms on the native fauna certain activities are needed to be done in order to prevent further invasions and to limit the spread of already detected alien species. Definition of effective national legislation and continual National monitoring programs are the most urgent issues concerning Strategy on alien species. Activities aiming the rising of public awareness in regard to bioinvasion of aquatic ecosystems should be also one of the priorities, since some of the invasive taxa reached recipient areas by the deliberate releasing.

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THE SPECIFICS OF RISK ASSESSMENT FOR SMALL AND MEDIUM-SIZED ENTERPRISES

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ABSTRACT

The health and safety policy in Small and Medium-sized Enterprises (SMEs) demands a different approuch from that of big company. There are many differences between SMEs and their larger counterparts, and this must be taken into account when assessing risks in SMEs. The aim of this paper is analyzing he characteristics of SMEs, current economic changes and their impact on developing the health and safety policy of the company and risk assessment. Also, we will describe the importance of labor inspection service, as an important external partners in supporting small and medium-sized enterprise with risk assessment.

Key words: small and medium-sized enterprise, characteristics, risk assessment, labor inspection service.

INTRODUCTION

The health and safety policy in Small and Medium-sized Enterprises (SMEs) demands a different approuch from that of big company. There are many differences between SMEs and their larger counterparts, and this must be taken into account when assessing risks in SMEs. This paper focuses on three main issues.

Firstly, the characteristics of SMEs. These characteristics influence the way SMEs manage risks in the workplace and how they carry out their risk assessment.

Secondly, the impact of current economic changes and the priorities in this specific context. Changes create new challenges for SMEs and hence new challenges for risk assessment. Risk assessment requires know-how and expirience. SMEs don’t always have these competencies within their own company. Many of them have to seek external partners to help develop the health and safety policy of the company in general, and risk assessment in particular.

Thirdly, the labor inspection services should be an important external partner in helping SMEs with risk assessment, where should be guided by the principle “less sanctions but more support”

SPECIFIC CARACTERISTICS OF SMEs1

Benefits

The way SMEs approach the topic of risk assessment is strongly influenced by the structure and strengths of the particular SMEs, but there are some characteristics that are applicable to most of SMEs, as follows[5]:

Informal social dialogue – In most SMEs, social dialogue is conducted in a very informal way. In most of them there are no formal consultation bodies or procedures. The social dialogue in SMEs is a continuos, informal interaction between employer and employees and also among employees. Many SMEs don't have, and don't need, formal consultation bodies or procedures to identify problems or pinpoint risks. The problem and the solution are discussed at the working area (offices, shop floor, construction site, etc.)

Employer works with employees – An important advantage for most SMEs is the fact that the employer works alongside the employees. This means they can see risks in the workplace and operation first hand, and will be more likely to take measures to reduce or eliminate risk. These measures can include important inovative changes or simply small changes with great effectivness for the safety of workers and employer. With this kind of operation, risk assessment is a continuous, informal process.

Flexibility – Flexibility is the key for SMEs. Employer and employees are often required to multi-task in a constantly changing envinronment. They are highly adaptable. This also means that workers have a good knowledge of how their company works, and most of workplace risks. This flexibility among staff affects the way the risk assessment is carried out.

Fast decision-making process – Another advantage of SMEs is the fast decision-making process. In biger companies when one wants to introduce changes, it's usually necessary to consult several hierarchies of menagers. In SMEs with a flat hierarchy, the employee can go directly to the right person and make a proposal. This saves both time and energy.

Family atmosphere – Employees work for the company, but are also ready to be mutually supportive and to help each other if necessary. The willingness to support colleagues creates a very special atmosphere in the company between workers and employer and between employees. This make easier for employees to correct one another, and to educate one other on risk assessment.

Easy communication – The traditional informal communication and the direct and personal relationships at all levels of an SME facilitate rapid adaptation of change and better prevention of risks. These positive elements create a sound basis for carrying out a risk assessment which is adapted to the needs of the company.

Shortcomings

On the other hand, SMEs also have some shortcomings when it comes to risk assessment. Typical problems that need to bi solved in SMEs include[5]:

Low degree of delegation – The employer is responsible for all the various tasks,from human resources management to accounting and the production process. The Health and Safety policy of the company is just one among many responsibilities. While employer remains responsible for every aspects of the company's activity, he needs to be supported by other employees in the risk assessment area.

Lack of long-term strategic vision – Another shortcoming in SMEs is that they don't have a strategic vision.Problems tend to be solved as and when they occur. They are not dealt with in advance. Because of this approach, it is difficult to teach employers how to be proactive about Health and Safety and risk assessment. In some cases, employers only take action after an accident. It is never too late to do risk assessment, but it should be done proactively.
Less formal risk assessment – Employers in SMEs tend to carry out the assessment and any preventive measures in practice, without formal documentation. Each time they have to start from scratch once more. A more formal risk assessment, using specific practical tools, would be much more productive for them in the long term. Many SMEs need improvement in this regard.

CHANGES IN BUSINESS ENVIRONMENT AND PRIORITIES

Economic changes, new economic challenges

Changes in business environment influence the work of SMEs, and therefore risk assessment.These include[5]:

- a more complex society (globalisation, structural change, rapid technological development, etc.)
- more complex business operations
- shorter lifespan of technologies
- customer-oriented production
- need for company networks
- new products and operations
- new technologies / innovation
- increase in outsourcing.

When we say that the changes in the business environment affect the risk assessment does not mean the scope and methodology of risk assessment but the loss of priority, because SMEs focused on solving the problems that these changes are made, and which have significant impact on the business result. Of course, this statement applies to our business environment.

Risk assessment in the workplace and work environment perceive the work organization, work processes, equipment of labor, raw materials used in technology and work processes, tools and equipment for personal protection and safety, as well as other factors that may cause risk of injuries, damage to health or illness of the employee.

The risk assessment includes[8]:

- general information about the employer,
- a description of technology and business processes, description of tools and their grouping and description of the resources and personal protective equipment at work,
- analysis of the work organization,
- identifying and determining the risks and hazards in the workplace and working environment

- determining the means and measures to eliminate, reduce or prevent risk
- conclusion.

State authorities, the Ministry of Labour and Social Policy (the Commitee of Occupational Safety and Health at Work and the Labour Inspectorate) have to take these strengths and shortcomings into account when dealing and cooperating with SMEs in the field of safety and health. The real challenge for SMEs is the correct and effective application of all existing legislation. The Commitee of Occupational Safety and Health at Work and the Labour Inspectorate have to act as partners to SMEs to achieve those objectives.

Legal framework and instruments available to SMEs in the risk assessment

At the state level security issues and occupational health deals with the Ministry of Labour, Employment and Social Policy, and within it, the Committee of Occupational Safety and Health at Work – OSH Committee and the Labour Inspectorate (previously mentioned). In accordance to the Law on Safety and Health, OSH Committee performs state administration with the aim to improve and develop safety and health at work and reduce occupational injuries, occupational diseases and diseases related to work.
According to Article 60. of Law, this OSH Committee performs the following tasks [7]:

- preparation of regulations concerning occupational safety and health, as well as reviews for their implementation;
- prepares technical basis for the development of the national development program of safety and health at work and monitors its exercise;
- provides technical assistance in the areas of health and safety at work;
- preparation of methodology for conducting examinations and tests in the field of safety and health at work;
- explores and encourages development in the area of humanization of labor
- organizes preparation and professional examinations to conduct safety and health (OSH person and responsible person)
- supervises the legality of legal persons and entrepreneurs, as well as responsible persons with the license and the preparation of solutions for the issuance and revocation of licenses;
- collects and analyzes data on injuries, occupational diseases and illnesses related to work and issues that affect the health of employees;
- organizes professional conferences, educates employees, employers, persons OHS, inspectors and others;
- to the application as international, (EU) legislation in the area of safety and health at work;
- encourage training and development culture occupational safety and health at work.

Inspection in the field of OHS's, according to the law on health and safety at work, is done by the ministry of labor (Labour Inspectorate) through the labor inspector. The labor inspector has the right and obligation to control the implementation of measures for safety and health at work, and in particular hygiene and working conditions, production, distribution, use and maintenance of assets, resources and equipment for personal protection and safety, dangerous substances used in the work, and to[7]:

- control of general and individual acts, records and other documents:
- take statements from responsible and interested parties;
- employers, employees, and representatives of their union gives explanations and advices in the field of OHS;
- take samples for analysis, expertise, etc..;
- order measurements performed by another professional organization when the employer itself or through a particular professional organization performs measurements in the relevant fields, and measurement results provide a basis for it;
- report to the employer and the employee or representative of employees on the inspection and supervision of the established condition.

The next important state institution that participates in the affairs of the OHS's is Occupational Health Service. For the performance of health at work the employer engage occupational health services, which performs the following tasks[7]:

- participates in the identification and assessment of risks in the workplace and work environment when creating document on risk assessment;
- carries out preliminary and periodic medical examinations at workplaces with high risk and issue reports of medical examinations in accordance with the regulations on OSH-in;
- provides staff training in first aid;
- evaluates and identifies specific health skills that must be met by an employee to perform certain tasks at work or at risk for handling certain work equipment;
- advises the employer in the selection and testing of new assets, hazardous materials and resources nopreme for occupational safety, the health aspect;
- advises the employer in selecting appropriate job to another medical fitness of the employee;
- participates in the analysis ardu injuries, occupational diseases and diseases related to work;
- cooperates directly with the person of health and safety at work.

Safety and health jobs at work may be performed by a person who has passed the examination in accordance with the law. The employer may designate one or more of its employees, the state exam, or to hire a legal entity that holds a license (hereinafter referred to as the person of health and safety at work). Person for safety and health at work has a key role in the performance of safety and health at work in any company, even in the SMP, and these activities are[7]:

- participation in drafting legislation on risk assessment;
- control counseling employers in the planning, selection, use and maintenance of work equipment, hazardous materials and resources for occupational safety;
- participation in equipping and regulation of the workplace in order to ensure safe and healthy working conditions;

- the organization of preventive and periodic examination of the working conditions;
- the organization of preventive and periodic testing of work equipment;
- daily monitoring and control of implementation of OSH measures;
- preparation and training in safe and healthy work;
- preparation of guidelines for safe and healthy work and control of their applications;
- monitoring related to injuries and at work and occupational diseases;
- prohibition of workplace guides and resources for the work, in case of imminent danger to life and health of employees.

The existing legal framework is comprehensive and includes a number of laws, rules, regulations and directives. Also, there are certain standards in this area. We will mention some of them:

- Law on Safety and Health at Work;
- EU Council Directive 89/391;
- EU Council Directive 92/57/EEC of compliance with the minimum requirements for health and afety in the interim and mobile construction sites;
- Law on Labour;
- Regulations on the procedure for the assessment of risks in the workplace and working environment;
- Guidelines for the risk assessment of the EU, ISBN 92-827-4278-4 out in 1996.;
- Standard SRPS ISO 14001/2005 Environment Management System;
- Standard SRPS OHSAS 18001 / 2008 Occpational Health and Safety Management System, etc.

Priorities

SMEs need practical and effective instruments

The existing legislative framework for risk assessment at state level is adequate. The focus should now be on the implementation of this legislation at regional, local and company level.

Although the risk assessment is a legal obligation, many companies did not do the risk assessment act. The state could provide financial support for companies that commit to it, either through a tax relief or through funds (eg fund from fines for violating the Law on Safety and Health at Work).

In addition, companies should not be automatically held responsible for everything that goes wrong, which very often gives a negative image of entrepreneurs and entrepreneurship.

Strengthening the culture of prevention

All parties should work towards a culture of prevention. This must be based on a partnership between all the players involved and must be accompanied by substantial efforts in information provision and training and in enhancing awareness[5].

State agencies (Department of OHS), professional associations, chambers of commerce need to work on promotion of risk assessment and risk prevention, as well as to encourage the exchange of best practices between companies in the same industries and between regions.

The need for a partnership

The Health and Safety policy, the risk assessment and prevention in general have to be based on a strong partnership between all players involved. There is no need for new institutions, but rather for better networking and cooperation between the relevant actors, and between sectors at all levels. We have to bundle different forces towards strong collaboration, with only one target: a better Risk Assessment in SMEs, a better health and safety environment for employer and employees.

The role of labour inspection services

The work of inspection services should be an important external factor for small and medium enterprises. They need the support of labor inspectors to better comply with regulations, especially through education, and then, when necessary, through punitive measures. Proper and effective implementation of the legislation is very important, both from the social, and economic perspective. It is expected that the labor inspection service is a modern, contemporary and professional authority. It has to be run by highly professional staff members. The establishment of a management system for OHS ensuring that the same policy and strategy are implemented, would be particularly welcome.

CONCLUSION

Risk assessment in the workplace is a central issue for all employers. However, in our country, employers are still not aware of the importance of the topic for their workforce. Another reason for lack of consideration for this area is the existence of too many legal obligations (many of OHS regulations) which, combined with a poorly designed forms and documents you need to fill in, are not helping employers in small and medium-sized enterprises to carry out their obligations. Therefore, we urgently need a strong support to facilitate the understanding of laws and regulations by small employers, and therefore its better implementation in the workplace.

Last but not least, a strong partnership between small and medium-sized enterprises and the Labour Iinspection Services and OSH Committee is necessary. They should provide more help for SMEs in developing the health and safety policy of the company in general, and risk assessment in particular. They should be guided by the principle of "less sanctions but more support". When sanctions are applied, they should be aimed at those companies which, after having been warned, still neglect health and safety or refuse to carry out a risk assessment.This is the key message of this paper.

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HABITATS CONSERVATION IN CASE LAW OF COURT OF EUROPEAN UNION

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ABSTRACT

The EU is committed to the protection of biodiversity and in that sense over the last 25 years a vast network of 26.000 protected areas has been built up and a broad range of environmental legislation has been put in place. However, many challenges persist and these must be tackled together in a structured way. One of these is a question of environmental assessment with regard to protection of habitats. In tackling this question of great importance is case law of EU Court of Justice related to crucial articles of Habitats Directive.

Key words: biodiversity, Habitats Directive, environmental assessment, Court of Justice.

The cornerstones of Europe's legislation on nature conservation are Council Directive 79/409/EEC of 2 April 1979 on the conservation of wild birds and Council Directive 92/43/EEC of 21 May 1992 on the conservation of natural habitats and of wild fauna and flora (hereinafter "the Habitats Directive"). These Directives represent the most ambitious and large scale initiative ever undertaken to conserve our natural heritage across the European Union. This Directive adopted in 1992 as the main aim has the promotion of the maintenance of biodiversity, taking account of economic, social, cultural and regional requirements. While the Directive makes a contribution to the general objective of sustainable development; it ensures the conservation of a wide range of rare, threatened or endemic species, including around 450 animals and 500 plants. Some 200 rare and characteristic habitat types are also targeted for conservation in their own right. The Directive provides for a ban on the downgrading of breeding and resting places for certain strictly protected animal species. Exceptions to the strict protection rules can be granted under very specific conditions.

In case of dispute or diverging views, it rests with the EU Court of Justice to provide definitive interpretation of a Directive. Strictly speaking, the case-law is not a source of law. However, through its case-law, the Court of Justice has identified and established fundamental principles, such as the primacy of Community law over national law or the liability of Member States for breach of Community law. With regard to the nature and biodiversity cases, the development of the Court's case-law contributed to clarifying the obligations of Member States under the Habitats Directive and strengthening the rights of the European citizens. Even if most Court rulings primarily concern failures of individual Member States to fulfil their obligations or specific national situations, all EC and national authorities are bound by the general interpretation of the Court. In other words, the rulings of the Court are legally binding and both EC and national authorities are obliged to follow them.

Regarding Habitats Directive, precisely obligation of assessment of plans and projects and compensatory measures set in Article 6 and 7, Court delivered several rulings. Article 6(3) of the Habitats Directive establishes a procedure intended to ensure, by means of a preliminary examination, that a plan or project which is not directly connected with or necessary to the management of the site concerned but likely to have a significant effect on it is authorised only to the extent that it will not adversely affect the integrity of that site, while Article 6(2) of the Habitats Directive establishes an obligation of general protection consisting in avoiding deterioration and disturbances which could have significant effects in the light of the Directive's objectives, and cannot be applicable concomitantly with Article 6(3). The 10th recital in the preamble to the Habitats Directive states that an appropriate assessment must be made of any plan or programme likely to have a significant effect on the conservation objectives of a site which has been designated or is designated in future. That recital finds expression in Article 6(3), which provides inter alia that a plan or project likely to have a significant effect on the site concerned cannot be authorised without a prior assessment of its effects. The Habitats Directive does not define the terms plan and project. By contrast, Council Directive 85/337/EEC of 27 June 1985 on the assessment of the effects of certain public and private projects on the environment, the sixth recital in the preamble to which states that development consent for projects which are likely to have significant effects on the environment should be granted only after prior assessment of the likely significant environmental effects of these projects has been carried out, defines project as follows in Article 1(2): - the execution of construction works or of other installations or schemes, - other interventions in the natural surroundings and landscape including those involving the extraction of mineral resources. Such a definition of project is relevant to defining the concept of plan or project as provided for in the Habitats Directive, which, seeks, as does Directive 85/337, to prevent activities which are likely to damage the environment from being authorised without prior assessment of their impact on the environment. The fact that the activity has been carried on periodically for several years on the site concerned and that a licence has to be obtained for it every year, each new issuance of which requires an assessment both of the possibility of carrying on that activity and of the site where it may be carried on, does not in itself constitute an obstacle to considering it, at the time of each application, as a distinct plan or project within the meaning of the Habitats Directive (C-127/02 – "Waddenvereniging and Vogelbeschermingsvereniging"). The Directive does not distinguish between measures taken outside or inside a protected site. Therefore the definition of 'project' in national legislation which refers to acts carried out outside a protected site cannot be narrower than that which concerns projects carried out within a protected site (C-98/03, Commission v. Germany) The first sentence of Article 6(3) of the Habitats Directive must be interpreted as meaning that any plan or project not directly connected with or necessary to the management of the site is to be subject to an appropriate assessment of its implications for the site in view of the site's conservation objectives if it cannot be excluded, on the basis of objective information, that it will have a significant effect on that site, either individually or in combination with other plans or projects. The requirement for an appropriate assessment of the implications of a plan or project is thus conditional on its being likely to have a significant effect on the site. Therefore, the triggering of the environmental protection mechanism provided for in Article 6(3) of the Habitats Directive does not presume - as is, moreover, clear from the guidelines for interpreting that Article drawn up by the Commission, entitled "Managing Natura 2000 Sites: The provisions of Article 6 of the Habitats Directive (92/43/EEC)" - that the plan or project considered definitely has significant effects on the site concerned but follows from the mere probability that such an effect attaches to that plan or project. As regards Article 2(1) of Directive 85/337, the text of which, essentially similar to Article 6(3) of the Habitats Directive, provides that Member States shall adopt all measures necessary to ensure that, before consent is given, projects likely to have significant effects on the environment ... are made subject to an assessment with regard to their effects, the Court has held that these are projects which are likely to have significant effects on the environment. It follows that the first sentence of Article 6(3) of the Habitats Directive subordinates the requirement for an appropriate assessment of the implications of a plan or project to the condition that there be a probability or a risk that the latter will have significant effects on the site concerned. In the light, in particular, of the precautionary principle, which is one of the foundations of the high level of protection pursued by Community policy on the environment, in accordance with the first subparagraph of Article 174(2) EC, and by reference to which the Habitats Directive must be interpreted, such a risk exists if it cannot be excluded on the basis of objective information that the plan or project will have significant effects on the site concerned. Such an interpretation of the condition to which the assessment of the implications of a plan or project for a specific site is subject, which implies that in case of doubt as to the absence of significant effects such an assessment must be carried out, makes it possible to ensure effectively that plans or projects which adversely affect the integrity of the site concerned are not authorised, and thereby contributes to achieving, in accordance with the third recital in the preamble16 to the Habitats Directive and Article 2(1) thereof, its main aim, namely, ensuring biodiversity through the conservation of natural habitats and of wild fauna and flora. Pursuant to the first sentence of Article 6(3) of the Habitats Directive, where a plan or project not directly connected with or necessary to the management of a site is likely to undermine the site's conservation objectives, it must be considered likely to have a significant effect on that site. The assessment of that risk must be made in the light inter alia of the characteristics and specific environmental conditions of the site concerned by such a plan or project. As is clear from the first sentence of Article 6(3) of the Habitats Directive in conjunction with the 10th recital in its preamble (see above), the significant nature of the effect on a site of a plan or project not directly connected with or necessary to the management of the site is linked to the site's conservation objectives. So, where such a plan or project has an effect on that site but is not likely to undermine its conservation objectives, it cannot be considered likely to have a significant effect on the site concerned. Conversely, where such a plan or project is likely to undermine the conservation objectives of the site concerned, it must necessarily be considered likely to have a significant effect on the site. In assessing the potential effects of a plan or project, their significance must be established in the light, inter alia, of the characteristics and specific environmental conditions of the site concerned by that plan or project. Under Article 6(3) of the Habitats Directive, an appropriate assessment of the implications for the site concerned of the plan or project implies that, prior to its approval, all the aspects of the plan or project which can, by themselves or in combination with other plans or projects, affect the site's conservation objectives must be identified in the light of the best scientific knowledge in the field (C-127/02 – "Waddenvereniging and Vogelbeschermingsvereniging").

The condition, to which the assessment of the implications of a plan or a project on a particular site is subject, which requires such an assessment to be carried out where there are doubts as to the existence of significant effects, does not permit that assessment to be avoided in respect of certain categories of projects, on the basis of criteria which do not adequately ensure that those projects will not have a significant effect on the protected sites: "Projects consisting of acts affecting nature and the countryside other than changes of form or use of surface areas or changes to the level of the water table connected to the surface soil stratum" - the fact that that national legislation requires verification, that serious environmental damage which may be prevented by current technology is in fact prevented, and that damage which cannot be prevented by current technology is reduced to the minimum, cannot be sufficient to ensure compliance with the duty laid down in Article 6(3). The duty of verification laid down by the national legislation is not, in any event, capable of ensuring that a project relating to such an installation does not adversely affect the integrity of the protected site. In particular, the duty to verify whether serious environmental damage, which cannot be prevented by current technology, is reduced to the minimum, does not ensure that such a project will not give rise to such damage. "Projects relating to installations or to use of water, on account of the fact that they are not subject to authorisation" - the fact that it concerns the use of small quantities of water does not in itself preclude the possibility that some of those uses are likely to have a significant effect on a protected site. Even assuming that such uses of water are not likely to have a significant effect on the status of a body of water, it does not follow that they are not likely to have a significant effect on neighbouring protected sites. System when the authorisation of "installations causing emissions" is refused only where they appear likely to affect a protected site situated in the area of impact particularly of those installations, installations whose emissions affect a protected site situated outside such an area may be authorised without taking account of the effects of those emissions on such a site. That the system, so far as it covers emissions within an area of impact, as defined in technical circulars in accordance with general criteria on installations, do not appear to be capable of ensuring compliance with Article 6(3) and (4). In the absence of established scientific criteria which would a priori rule out emissions affecting a protected site situated outside the area of impact of the installation concerned having a significant effect on that site, the system put in place by national law in the field in question is not, in any event, capable of ensuring that the projects or plans relating to installations causing emissions which affect protected sites situated outside their area of impact do not adversely affect the integrity of those sites, within the meaning of Article 6(3) (C-98/03, Commission v. Germany).

With regard to the concept of appropriate assessment within the meaning of Article 6(3) of the Habitats Directive, it must be pointed out that the provision does not define any particular method for carrying out such an assessment. None the less, according to the wording of that provision, an appropriate assessment of the implications for the site concerned of the plan or project must precede its approval and take into account the cumulative effects which result from the combination of that plan or project with other plans or projects in view of the site's conservation objectives. Such an assessment therefore implies that all the aspects of the plan or project which can, either individually or in combination with other plans or projects, affect those objectives must be identified in the light of the best scientific knowledge in the field. Those objectives may, as is clear from Articles 3 and 4 of the Habitats Directive, in particular Article 4(4), be established on the basis, inter alia, of the importance of the sites for the maintenance or restoration at a favourable conservation status of a natural habitat type in Annex I to that Directive or a species in Annex II thereto and for the coherence of Natura 2000, and of the threats of degradation or destruction to which they are exposed. With regard to the conditions under which an activity may be authorised, it lies with the competent national authorities, in the light of the conclusions of the assessment of the implications of a plan or project for the site concerned, to approve the plan or project only after having made sure that it will not adversely affect the integrity of that site. It is therefore apparent that a plan or project may be granted authorisation only on the condition that the competent national authorities are convinced that it will not adversely affect the integrity of the site concerned. So, where doubt remains as to the absence of adverse effects on the integrity of the site linked to the plan or project being considered, the competent authority will have to refuse authorisation. The authorisation criterion laid down in the second sentence of Article 6(3) of the Habitats Directive integrates the precautionary principle and makes it possible effectively to prevent adverse effects on the integrity of protected sites as the result 38 of the plans or projects being considered. A less stringent authorisation criterion than that in question could not as effectively ensure the fulfilment of the objective of site protection intended under that provision. Where a national court is called on to ascertain the lawfulness of an authorisation for a plan or project within the meaning of Article 6(3) of the Habitats Directive, it can determine whether the limits on the discretion of the competent national authorities set by that provision have been complied with, even though it has not been transposed into the legal order of the Member State concerned despite the expiry of the time-limit laid down for that purpose. The obligation of a Member State to take all the measures necessary to achieve the result prescribed by a directive is a binding obligation imposed by the third paragraph of Article 249 EC and by the Directive itself. That duty to take all appropriate measures, whether general or particular, is binding on all the authorities of Member States including, for matters within their jurisdiction, the courts. With regard to the right of an individual to rely on a directive and of the national court to take it into consideration, it would be incompatible with the binding effect attributed to a directive by Article 249 EC to exclude, in principle, the possibility that the obligation which it imposes may be relied on by those concerned. In particular, where the Community authorities have, by Directive, imposed on Member States the obligation to pursue a particular course of conduct, the effectiveness of such an act would be weakened if individuals were prevented from relying on it before their national courts, and if the latter were prevented from taking it into consideration as an element of Community law in order to rule whether the national legislature, in exercising the choice open to it as to the form and methods for implementation, has kept within the limits of its discretion set by the Directive. That also applies to ascertaining whether, failing transposition into national law of the relevant provision of the Directive concerned, the national authority which has adopted the contested measure has kept within the limits of its discretion set by that provision. More particularly, regarding the limits of discretion set by Article 6(3) of the Habitats Directive, it follows from that provision that the competent national authorities, taking account of the conclusions of the appropriate assessment of a plan or project for the site concerned in the light of the site's conservation objectives, are to authorise such an activity only if they have made certain that it will not adversely affect the integrity of that site, that being the case if there remains no reasonable scientific doubt as to the absence of such effects. Such a condition would therefore not be observed were the national authorities to authorise that activity in the face of uncertainty as to the absence of adverse effects for the site concerned. It follows that Article 6(3) of the Habitats Directive may be taken into account by the national court in determining whether a national authority which has granted an authorisation relating to a plan or project has kept within the limits of the discretion set by the provision in question (C-127/02– "Waddenvereniging and Vogelbeschermingsvereniging").

According to the Court's settled case-law, the principle that projects likely to have significant effects on the environment must be subjected to an environmental assessment does not apply where the application for authorisation for a project was formally lodged before the expiry of the time-limit for transposition of a directive (see, with respect to Council Directive 85/337/EEC of 27 June 1985 on the assessment of the effects of certain public and private projects on the environment (OJ 1985 L 175, p. 40), Case C-431/92 Commission v Germany [1995] ECR I-2189, paragraphs 29 and 32, and Case C-81/96 Gedeputeerde Staten van Noord-Holland [1998] ECR I-3923, paragraph 23).

The text of Article 7 of the Habitats Directive expressly states that Article 6(2) to (4) of that Directive apply, in substitution for the first sentence of Article 4(4) of the Birds Directive, to the areas classified under Article 4(1) or (2) of the latter Directive. It follows that, on a literal interpretation of that passage of Article 7 of the Habitats Directive, only areas classified as special protection areas fall under the influence of Article 6(2) to (4) of that Directive. The fact that the protection regime under the first sentence of Article 4(4) of the Birds Directive applies to areas that have not been classified as special protection areas but should have been so classified does not in itself imply that the protection regime referred to in Article 6(2) to (4) of the Habitats Directive replaces the first regime referred to in relation to those areas (C-374/98, Commission v. France - "Basses Corbières"). Since Article 7 of the Habitats Directive on habitats provides that the obligations which arise, among others, under Article 6(2) of that Directive are to replace those arising under the first sentence of Article 4(4) on birds in respect of SPAs, the legal status of protection of those areas must also guarantee the avoidance therein of the deterioration of natural habitats and the habitats of species as well as significant disturbance of the species for which those areas have been designated. (C-415/01, Commission v. Belgium) As far as land classified as an SPA is concerned, Article 7 of the Habitats Directive provides that the obligations arising under the first sentence of Article 4(4) of the Birds Directive are replaced, inter alia, by the obligations arising under Article 6(2) of the Habitats Directive as from the date of implementation of the Habitats Directive or the date of classification under the Birds Directive, where the latter date is later. Article 6(2) of the Habitats Directive, like the first sentence of Article 4(4) of the Birds Directive, requires Member States to take appropriate steps to avoid, inter alia, deterioration of habitats in the SPAs classified pursuant to Article 4(1) (C-117/00, Commission v. Ireland – "Owenduff-Nephin Beg Complex"). It can be seen from Article 6(3) of the Habitats Directive, read in conjunction with Article 7, that any plan or project not directly connected with or necessary to the management of a SPA classified under Article 4 of the Birds Directive but likely to have a significant effect thereon, either individually or in combination with other plans or projects, is to be subject to appropriate assessment of its implications for the SPA in view of the SPA's conservation objectives. In the light of the conclusions of the assessment of the implications for the SPA, the competent national authorities are to agree to the plan or project only after having ascertained that it will not adversely affect the integrity of the SPA concerned and, if appropriate, after having obtained the opinion of the general public (C-209/02, Commission v. Austria – „Wörschacher Moos").

The assessments under the Habitats directive are required where a project or plan may give rise to significant effects upon a Natura 2000 site. It is the responsibility of the competent authority in each Member State to make the key decisions within these assessments. The diversity of habitats, species, projects and plans that exist within the European Union and the variations between national regulations require the approach to the Article 6 assessments to be robust and yet flexible. A wide range of perspectives exists throughout the EU on the importance or value of sites and projects. For these reasons, the decisions made through the application of the methodology should attempt to be as transparent and objective as possible and at the same time should reflect the value judgments inherent in any environmental assessment.

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CONSERVATION AND LAND PLANNING

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ABSTRACT

The main resource of any territory is land, the land should be planned, directing and maintained in the best possible extent. Land gives us hope for a better future, allows us the basic necessities of life, and in the modern world, the proper use of land allows us great material profit. To take maximum potential of a certain area, it is necessary to take a lot of effort, and also a lot of time spent on analysis of the current situation. Then planning a future state and is constantly monitoring the market which is lately a very important factor.

Key words: land, planning, environmental, conversation.

INTRODUCTION

The land is hope.

Each area has some potential, and provides different ways land can be used. There are a number of factors that can make a difference planning of land from site to site, some of them are: whether the area is urban or rural, a different type of landscape, whether there are streams, hills, mountains or plains, whether the infrastructure associated with the environment, land slope, soil quality... Everything should be carefully analyzed, that our own analysis indicates in which direction we need to plan land.

Definition- Land use planning is a procedure that ensures the improvement of the land, the need to harmonize national, regional and local level, in order to progress in the economic, environmental and social dimensions.

Goal- Land use planning is based on achieving an efficient and productive use of land, which must be economically justified.

To be effective, it is necessary to link the various land uses, where a certain territory with minimal investment had greater benefit. Conflicts are inevitable in such situations, because there are many conflicting influences, but it is necessary to make sustainable use of land, which would satisfy the present needs of the population, also to protect resources for future generations.

The value of land decreases from the center to the periphery, and comes to a marginal decline in revenue. The formation of building land occurs transformation of agricultural and other land, in accordance with the law of supply, demand and competition in the real estate market. [1]

ROLE AND IMPORTANCE OF LAND PLANNING

The importance of planning is reflected in several aspects. The starting point of planning is the analysis of the current situation and the current situation is the result of the past. The actual space usage may be contrary to the adopted planning solutions, for identification of targets by the planning team does not have to match the objectives of the owner (user) of land [2]. Conclusions on the optimal, desirable or possible intentions comes a comparative analysis of the present application and the actual use of space. In this way, planning identify the causes that led to problems in land use and focus on improving in the future. Then, the planning involves public and thus allows more regular decision-making.

Public involvement has several advantages: the locals know best the space and all its advantages and disadvantages, when the local population is involved in the process to better respect the decision of the plan, joint planning to bring common goals and thus appear less conflicts of interest, etc.. However, when the participation of a large number of participants in the preparation of the spatial plan requires that all stakeholders are aware of the importance of the task, as well as being behind the planning and implementation of the following [3].

When planning its use, land can be considered as:

Resurs- or as a source of raw material or as a resource for themselves, in each case observation event is economic. However, population increase and their upgrowth needs are created pressure to the earth. Therefore, from the aspect of planning necessary to understand the country as a resource restriction.

As ecosystem- Where the ecosystem necessary to understand such as complex and dynamic system in which any change in one element affects more or less the in other elements. This kind land observing, mainly applies when there are large problems, and rarely preventative.

As a landscape- landscape is regarded as a public good, but the aesthetic experience of the landscape is private.

FORMS OF OWNERSHIP

Land by type of ownership may be privately or publicly owned. The inevitability of the appearance of conflict between public and private interests.

-*Private property*
-*Public property*

In order to resolve disputes in mutual gain, Country can regulate disagreements and weaknesses with good policy.

Private ownership

The land is privately owned, is used on the basis of objectives that form the land owner. The objectives of the owner can be changed, sometimes the owner haso no target. The main factors that affect how the owner will individually decide how to use land are:
- objective that he wants to achieve,
- value that he wants to be held,
- background factors: social factors, from of the environment, how the environment benefits the country with those who are dominant forms use cleansing in our cultural. The main objective is the benefit. What can be material or not material.

Social causes are the need to satisfy basic needs, in terms of security, recreation, that the tradition from previous generation [4].

The goals are changing, the market dictates how owner will treat their land, there are also land owners who do not have a goal, they simply have land and do not invest it. Those owners who do not invest in their land, they have no future development plans in order to improve their environment. Benefit which is not material in the sense that the owner simply has a plot that keeps the sake of tradition, or inherited, so the owner does not want to sell it, or improve, as he material profit is not the main aim, already enjoy in their possession and creating a stable income every year.

The big change in Serbia was made with full agricultural employment, when we devide agricutrural depresses to the maximum size of 10ha., to all the population living in the countryside. So all individual owners made a dertimitation about land use. Many have not even used, but have left it. It is very important that the owner is present or not. Owners who are not present, their land will be devastated. The attitude towards the environment is very important, it tends to underestimate the true potential environment, very often we are limited to the use of certain agricutrural, because we do not know the true potential of the land that we own. They do not know what its true value, and all the new knowledge, it is very important to be familiar with new trends.

The age structure is quite significant, how often owners change the purpose of land use, of course, younger people will indulge in more risk and more change the purpose of land. Culture is the one who may also depend on decisions [5].

Public ownership

In the case where the state owns dominant political than economic factors. The optimal way to use it is to find a compromise between the economic and political criteria with abandoned leeway to adapt in the future [2b].

The process of increasing privatization has forced the state to through a complex system of policies and mechanisms exerts its influence. One of the main reasons is that the private and the public interest generally do not coincide. States usually act through:

1. Land Policy on where the state focuses on the proper use of land, preventing the re-appropriation, encouraged to take maximum advantage of the space and the like. Different policies are used in different countries.
2. Stimulating Policy on the more economic. The emergence of this policy is caused by pressure on agricultural lands, which led the state to intervene in various ways: pricing, tax policy... [6]

URBAN AND RURAL ISSUES

Urban problems

Problems are inevitable in towns, cities represent a very complex and dynamic social, economic, political, cultural and environmental systems, and it's very complicated to manage them. Modern cities are faced with problems: overpopulation, building outdated infrastructure, inadequate housing, undeveloped land ...

Municipalities face a very complex problem when it comes to planning the use of urban areas. The main instrument is the spatial plan adopted and adopted by the Municipal Assembly. Disregard for the law and planning solutions lead to urban chaos, illegal construction and the emergence of many conflicts and problems, which later corrections through rehabilitation plans, very expensive.

According to the spatial plan of the Republic of Serbia in 2010, the problems that occur in urban eligible regions are:

- unresolved property issues, unregulated cadastre, conflicting criteria and standards of recording categories of land make it difficult to land use planning.
- inadequate land policy, which in our country rarely advance preparation of land for construction.
- building land as one of the key resources, especially cities capitalize putting into operation and the creation of a new social product. In Serbia, the low share of revenue from construction land in the formation of budget revenues in most local communities.
- urban problem is also a lack of infrastructure and infrastructure systems. In cities with high growth is difficult to build infrastructure with the same intensity. While cities with lower development and maintenance capabilities they have a problem and lagging infrastructure.

Because of the lack of regulation in real space unplanned use of land accelerates and, with the financial capacity and the appropriation as the only limit. [7]

Rural problems

The Regional Plan of the Republic of Serbia in 2010, according to the fact that in Serbia, rural areas account for about 85% of Serbia's territory, are inhabited by approximately 55% of the Serbian population. The main problems of rural areas are depopulation, lack of equipment technical and social infrastructure, etc.

Agricultural land is threatened by the expansion of settlements, the work of large mining-energy-industrial basin, construction of industrial, labor and other areas and an increase in so-called "greenfield" investments, continuing the negative trend of loss of agricultural land. Erosion, siltation, loss of nutrients, chemical pollution from bio sources, mechanical compaction, floods, loss of fertility, inadequate waste disposal and others, are just some of the current problems.

The expansion of cities in relation to the city center led to the capture of significant areas for housing, which in some areas caused the imbalance in the planned redistribution of land use and urban functions.

CONCLUSION

Land use planning has exceptional importance for each country. The planning of land use planning at the national, regional and local level. In the planning of land involved everyone from politicians, planners and to the local population, who owns private land. It is important to avoid conflicts that arise when planning land use, they are inevitable companions planning. It is necessary to adequately coordinate land use, in order on the one hand the state-region-municipalities, and on the other side of the population, which had a greater mutual benefit.

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MODELS FOR CALCULATION OF MACHINE OUTPUT AND PRODUCTION COSTS

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ABSTRACT

This issue is being studied in the state master studies at some universities, but with the intensive development of private entrepreneurial companies, it should be taught on studies of technical, economic and management faculties. This paper, in summary form, sets out the ways of research and formation of mathematical models to solve some problems in the organization of production.

Key words: productivity, costs, organization, production.

INTRODUCTION

Productivity of work is an indicator of production in the production facility, which should be maximized, because it involves utilization of machinery, labor, energy, or affects to indicators of production costs, ergonomics and safety of operation. Selected work organization, machines and devices for achieving the shift-or-hour production capacity, or the effect of the selected variant of process, may be such that requires a direct contact between people (workers, miners) to manage with them. Thereby is determined the number of workers executors in a production system. Can be selected variants of machines and equipment with which is managed from the dispatch center or wherein is present full automation. Depending on the mode control of the machines and other equipment depends labor productivity and ergonomics and safety of workers.

CALCULATION OF MACHINE OUTPUT AND PRODUCTION COSTS

The annual capacity of mine or manufacturing facility

Annual capacity of a mine depends on the need for this product, mining and geological conditions of deposit occurrence, and optimal economic opportunities. In the technological production chain, production capacity of individual machines or their sum, must correspond to the desired annual capacity of the mine. Thus, in the technological chain in any process will find: one machine of adequate capacity, and in other process, several of them, so the sum of their capacity satisfies the annual capacity of the mine or manufacturing facility. The required maximum and minimum (annual, daily, shift, time) production capacity of manufacturing facility and individual machines in the technological chain, is calculated according to formulae:

Annual$A_{god} = \frac{R}{Tk}$, daily: $Ad = A_{god}/305$, (t/dan)

shift: $Asm = Ad/n_s$, ili technical time: $Ah = Asm/Tef_1$, (t/h) and production capacity of machine (one machine in the chain $K_s = A_{sm}/Tef_2$ (t/h); or for more machines $Ks = Asm/Nj$ (t/h)).

Where are:

R - for mines, ore reserves in deposit (t);

Tk - Time of repayment of investments, and for mine, the duration of concession;

A_{god} - annual production of the mine or annual demand for certain products, t / year; Ad -required daily production to realize annual, given the number of working days in a year (if it does not work on Saturdays and Sundays and public holidays, the number of days, 305 days);

Asm -Shift-production (Ad/3), if during the day is working (n_s=3) three shifts per 8 hours.

Ah - time production capacity of the machines and people, t / h;

Tef - effective working time per shift, depending on the organization of work (h);

Ks -Industrial production capacity of individual machine or equipment,

Nj - The number of production machines at work which the sum of capacity satisfies the required capacity.

With larger production capacity, if it is economically justified, faster it will reach recovery of funds invested, so the rest of concession period of use, or operation of the company, will be very profitable. Thus defined minimum annual, daily, and hourly shift-production in mines, besides of physical and mechanical characteristics of rocks (and is dependent on the organization of work), is used to choose the type and capacity of equipment for work in the mine and for performing all calculations of economic and technical indicators Uij, of selected technical solutions in the sub-systems of the production system, as well as for the selection of optimal construction of production system that minimizes or maximizes them. Work productivity of workers and machinery in the production facility is expressed by the following indicators:

$Psm = Asm/Nr$, (t/rad/sm), ili $P\sim = A\sim/Nr$, (t/~as/rad)

Where are:

Nr - the number of workers in the production facility or subsystem of company

A_{sm}, $A_{\sim as}$ -designed or realized hourly or shift-production facility (t, pcs, m^3)

P_{sm}, $P\sim$ - Shifts or Hourly labor productivity of employed workers or machines

Productivity (capacity) of the machine and production costs

The capacity of a production machinery or equipment selected for work in a variant of the technical solutions of subsystems of production can be considered as: theoretical, technical and manufacturing (industrial).

Theoretical capacity

Theoretical capacity (productivity) of a mining machinery or equipment in the variant selected of technical solution into production subsystem is given, usually, in the brochures manufacturers of equipment and machines and refers to the the effects of the machine based on the geometry of the working body, speed of operation and the effective operation time in one cycle. It is expressed in the quantity forms of the possibility of realization of production task Qx(m^3, t),which depends on the machine design (power, dimensions, speed of movement, etc.), in units of time of effective work in one cycle Tc

$$Kt = Qx/Tc \quad (m^3/h;\ t/h;\ t,\ km/h)$$

Where are:

Kt - Theoretical productivity (capacity of machines or equipment), (m^3/h, t/h, tkm/h,pcs/h)

Qx - quantitative unit for expression of theoretical productivity, (m', t, tkm, kom.);

Tc - effective operating time of machine from the start to the first interruption of work. (min,ili h).

For example: The theoretical capacity of the excavator loading the material or digging and loading of materials, depends on the volume of buckets Vk (m^3), coefficient of buckets charge p and the cycle time of filling, lifting, turning, dump in the truck and returning to the loading position, which depends on the skills of the operator, if the process is not automated:

$$Kt = (p/k_r).Vk.\rho/Tc\ ;\ (t/h)$$

Where is:

p - coefficient of filling of buckets; it depends on the size of the material and is less than one for solid rocks that are broken in pieces of larger mean diameter d_{avg} mm';

k_r- friability coefficient of rocks that are loaded, (p/k_r)= b-coefficient of dredging,

Vk - Bucket volume, or crib of some type of machine m^3;

ρ - volumetric mass of rocks t/m^3,

Tc - Cycle time (min) consists of individual times which are determined by chronometric recording $Tc = (t_p+ t_0+t_i+ t_v)$, (sec, or reduced to h).It is a stochastic variable and depends on the skills of the operator: t_p- charging time of buckets, t_o- time for turning the dredger, t_i- time of dump of buckets, t_v- time of return of buckets into the loading position. Therefore, the production capacity of these and other machines are given ranging from-to, or in charts. To work in concrete terms mean values of all time should be determined on the basis of the chronometric recording. This is why some researchers call this productivity the technical capacity of the dredger. In a similar way are in brochures, and other equipment given capacities, performance or speed of work,(m/min or for example - number of cycles per hour) . On the basis of these is determined productivity of machine, based on the number of people which is serving it is expressed also productivity of labor per worker.

Technical capacity

Technical capacity (productivity) of selected machinery or equipment relates to the productivity of machine in real conditions in one shift. It differs from the theoretical capacity, because it must be taken into account: time of for the arrival of workers, inspection and putting machine into operation, etc., time to stop the machine and shift of workers t_s, time of 30 min for lunch and physiological needs t_o and other times during the work for which shall be delays for switching machine to a new location Σt_l, replacement, addition of working elements $\Sigma t_{z,,}$or break of workers if the work requires high efforts Σt_e. These are the times of planned downtime $Tpz= (t_d+t_s+t_o + \Sigma t_l + \Sigma t_z +\Sigma t_e)$These times are obtained by hronometric recording, but among them is a time of break Σt_e, which can be determined by calculation based on the knowledge of ergonomics at work on the relationship estimated between man and machine. If the energy of workers who works with a machine larger than i = 16,75 kJ/min, then the employee has a need to take a break during operation (cease and rest). The participation of rest periods in the time available to work during shifts Trs, can be determined by ergonomic measurements of energetic demand of workers at work with the machine, p (kJ/min) (It does not take much to deviate from ergonomically acceptable burden). The participation of rest in the available time work during shifts Trs is expressed (in the literature of ergonomics) in form:

$D = (p/i - 1).100\%$, pa je $\Sigma t_e = Trs.D.100$

Where are:

Trs- available working time per shift to work with the machine, $Trs = Tsm - (t_d + t_z + t_o)$

Tsm - planned work time in an eight-hour shift at work is 8h or 640 min

Tef_l- effective working time for workers and machines with good organization $Tef_l = Tsm - Tpz$

Technical capacity, productivity of machine is less than the theoretical capacity. It is determined for a longer period of work of machine in real time of effective work in shifts, because it is calculated in relation to the Tef which is longer than the duration of a single cycle of continuous operation and is obtained by the formula:

$Km = Kt.Tef_1$, (m/h; t/h; tkm/h) or for previous example: $Km= (n_1Kt.b.Vk\ \rho)$;

$n_l = Tef_l/Tc$ - the number of cycles that can be completed in uptime.

Industrial (manufacturing) capacity

Industrial (shift) capacity, production ability some selected variants of machines and equipment in the production subsystem. It depends on time Tnpz,- of the unplanned outages due to poor work organization, (waiting on material, energy, insurance of workplace, etc.). This all occurs within the time available for work during the shift, that is further reduced by not scheduled downtimes, which brings, $Tef_2 = Tsm - Tpz - Tnpz$. Shifts capacity (productivity of variants of technical solutions in the sub-system with considering poor organization of the work) is given by the relation:

$Ks = Km.\ Tef_2$ or for previous example $Ks = n_2\ Kt.b.\ Vk\ .\rho$;

Where are:

n_2-the number of cycles that can be completed in a poor work organization $n_2 = Tef_2/Tc$,
Kt - theoretical capacity, productivity of machine,
$Vk.\rho$ - bucket capacity or crib expressed in tons.

Number of machine units

Number of units of machinery and equipment for work Nj, in variant of technical solution of the production subsystem, can be determined based on required shift effect (capacity) of machines, if in plant expects also unplanned downtime, according to the formula;

$Nj = Asm/Ks$, (kom);

Time needed of active (effective) work of machines and people in hours h, During the eight-hour working time per shift (h), Ter, when it is known the required shift effect t/Asm and possible effect of machines and people on the site Ks, t/ shift (in subsystem) is obtained on the basis of simple proportion:

$Ter = Tsm.Km/Asm$ (h).

This time, depending on organization of work, should be less than planned duration of working time per shift, to cycle of work could complete during the planned working time per shifts, and leave time for inspection and maintenance of machinery and replacement of workers. Time of effective work of machines and people is important to achieve high work productivity and capacity of machines.

The costs of production

The cost of production of material goods for work of some machinery and people who are serving it are the basis for estimation of the cost of product units (din/t; din/pcs). Cost of the produced mineral raw materials or processed ore, quite simplified, can be expressed by the formula:

The cost of operation of the machine

The price-hour engagement of any machine is determined by theoretical formula:$C_{rm} = (Tm + Te + Tr + Ta + To)$ din/h

Where are:

Crm - costs for one hour of work of machine in operation (din/h)

Tm - cost of consumables for operation of the machine per hour (lubricants, water, grease, etc.) are obtained by multiplying each normatives of consumption (kg/h) with costings (din/ kg) and hour is reduced to one hour of work.Σdin/h

Te - costs of energy (consumption of diesel fuel or electrical energy to full power),din/h;

Tr - labor costs are taken into gross amount according to the collective agreement (din/h);

Ta -- fixed costs of annual depreciation and annuities, maintenance of observed machine and other reduced to hour of machine work, respectively, Ta = EnK/n_s Tef_s 304(rd/god). (din/h). Ta = EnK/3648, (din/h).

EnK - costs of capital, (din/year) are reduced to the hour of machine work. Costs of amortization and repayment of machinery depend on their price, and the way of repayment.

To - cost of maintenance of machinery (din/h)

For example: The function of costs of loading and transport of ore from excavation sites can be combined with taking into account of technical hour capacity of the equipment in use t/h; tkm/h; m/h and labor costs of machine in the order of their expression per hour of machine work, in din/t; din/tkm; din/m as follows:

$C_{ut\text{-}od} = C_{rm}/Kt$ din/t

The total cost of loading and removal $C_{ut\text{-}od}$ consist of costs for materials, energy, work and capital assets which include: depreciation, maintenance, insurance and payment of annuity, reduced to hours of work. Each of these costs is determined individually. To calculate the costs (din/t) or (din/m^3) costs are taken of all consumed materials, energy and hours of work, according to actual structure of machine operators and other auxiliary labor force. For costs resources is taken the actual cost of depreciation, while for maintenance activities shall be taken into account the sum of all maintenance costs, depending on the age of the machine. Cost of annuities can be large, depending on the conditions under which the equipment was purchased and interest calculation method. The general form of reducing costs per unit of output for the given example can be written in the form of a complex formula:

$$C_{ut-od} = \frac{a+\frac{q}{T}}{\frac{bV_k \cdot \rho}{t_u+t_v+t_i+t_m}} = \frac{a+\frac{q}{T}}{\frac{bV_k \cdot \rho}{t_u+t_v+t_i+t_m}}; \text{(din/tkm)}$$

Where are:

T - the total number of hours of effective work per year, or if we consider costs per shift; Tef

Vk - Bucket volume or crib of loading transportation means,

L- transportation length from excavation to unloading place m', or km'

w - driving speed m/h,

ρ - volumetric mass of ore, t/m^3

t_u, t_v, t_i, t_m, - times of : loading, driving, unloading, maneuvers, expressed in hours.

In the formula driving time can be replaced by relationship of double distance of driving and driving speed, because driving means drive across the road once full and once empty, with almost the same speed. If transport distance L is seen as a variable, with others constant, then the costs can be obtained for the same transport means as a function of distance of transport and expressed by derived dimension (din/t.km).

a - fixed costs of annual depreciation and annuities, maintenance and other reduced to one hour of machine operation, or, a = EnK/8760, din/h. or for double shift work: Ta = EnK/n_s Tef_s 304(rd/god). (din/h).

Ta = EnK/3648, (din/h).

q=(Tm + Te + Tr) consumption of materials, energy and norm for working hours for the price of work, (din/year).

CONCLUSION

By reviewing the costs of loading and transportation of ore for different loading and transport machines, of different dimensions, price, consumption and driving speed, using method of variants it is possible to choose a variant (asset) with the lowest costs and for it to determine the load capacity and transport. Dividing the capacity of the mine with machine capacity per hour, the required number of units is obtained, which may not be optimal from another aspect of mining production.

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PREVENTING CONTAMINATION IN DISASTERS - FROM THEORY TO THE PRACTICE IN SERBIA

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ABSTRACT

Environmental protection in different disasters is an important issue in global world. Hence, there is an urgent need for creation of preparedness culture which is the main implication of this study. Authors present the current state in the Republic of Serbia regarding prevention of contamination into soil and water caused by disasters - a field in which the examined country still doesn't have sufficient knowledge about the level of risks and the ways of management. Weak institutional capacities and lack of relevant policies couldn't be excuses for wasting the money of tax payers. Therefore, in the near future Serbian public stakeholders have to establish a new policy regarding disasters which threaten sustainable development of Serbian society in general, and the problem of contamination and consequences environment and human well-being in particular.

Key words: disaster, contamination, stakeholder, funding, environmental security.

INTRODUCTION

Scientist and wider global community in last few decades proved that disasters pose numerous risks to society by threatening human life, destroying personal resources and, in late modernity, creating toxic and hazardous environments where humans are exposed to dangerous chemicals, radiation, infectious disease and other biotechnological threats [1]. Hence, environmental security become unavoidable part of national security and this issue affects the creation of prevention policies on different hierarchical level - from global to local.

Numerous hazmat releases occurred during almost every disaster: from the worst hurricane "Katrina" in the United States of America (USA) to various earthquakes (Fukushima Daiichi nuclear power plant), floods all over the world and the European Union (EU), and in the area of West Balkan countries in particular. Extreme weather events in Europe caused series of releases of toxic and hazardous chemicals that as occurred were both directly and indirectly associated with the massive physical damage to built and modified environments. West Balkan countries did not successfully learn a lesson from Romanian Baia Mare cyanide spill, Red sludge spill in Hungary, etc. The recent example could be found in the floods which happened a year ago. Continuous, heavy rainfall, commencing on 13 May 2014, caused extensive flooding in Serbia, Bosnia and Herzegovina (BiH), and Croatia. Croatia was affected by the floods to a lesser extent than Serbia or Bosnia, but the most critical area was in its Southern part, Slavonia. Despite long previous history of floods, and well-known probabilities of other existing environmental risks, Serbia, Croatia and Bosnia and Herzegovina still face a lack of capacity, as well as awareness, and so many times mentioned responsibility to prevent the loss of life and suffering of humans in disaster.

Disasters cause spills which could be extremely danger not only at the site where accident has occurred. This risk goes beyond geography, it also includes historically developed industrial production systems, industrial waste facilities, etc. Contamination could severely impact biophysical environment of territory and it could pose serious risks to health and social well-being of residents. Contamination is present in all environmental components and could be fast spread from one component to another (from soil to water, etc.).

Soil is essential environmental component and its health is a priority task for global world. In many countries soil management is a priority task for all stakeholders [13]. Management of contaminated sites is a tiered process starting with a preliminary survey searching for sites that are likely to be contaminated, followed by doing site investigations where the actual extent of contamination is, defining its environmental impacts, and finally implementing remedial and after care measures [9]. The public welfare concern over the hazards of soil contamination has led to some legislative action aimed at controlling and preventing contamination. The implementation of such activities in Serbia are still far from objectives, and they are evaluated as insufficient in numerous official reports and scientific researches, due to many objective and subjective reasons. Currently the remediation process of contaminated sites is mainly sporadic, and it is proved in the articles of recent award for excellence in investigative journalism to the journalist Adama Santovac and Nova Television about the lack of capacity in Serbian government to cope with consequences of failure tailings in closed mine "Stolice" near the Krupanj caused by the floods in 2014.

The Joint UNEP/OCHA Environment Unit (JEU) provided an environmental expert to assess risks from flooded industrial zones as well as a flood management expert to identify flood mitigation measures in Serbia in 2014 [3]. UNEP carried out a series of field visits to priority environmental sites of concern, including the collapsed Kostajnik antimony tailing dam abandoned from 1991 and many other contaminated sites. Failure of the Stolice mine tailing dam in Krupanj is one of the major environmental concerns from the extremely heavy rainfall that flooded South-Western Serbia in mid-May 2014 and still are in mid May 2015.

Serbia's environmental problems remain formidable as well as for other countries which are usually recognized with specific political regime in the past (socialist, communist), and especially facing numerous economic troubles caused by global economic crises and other various factors. This process is constantly followed by the obstacles how to provide needed financial means. The Republic of Serbia presented that it needs international financial help in the area of environmental protection in the approximation of strategy and it would be useful to consider in advance cost and financial management aspects of remediation activities [4]. Furthermore, after catastrophic floods in 2014 Serbia was forced to seek international help and took numerous loans for the purpose of mitigation of horrible consequences which will significantly affect future sustainable development.

The lack of ability to prevent contamination effectively in disaster is a specific issue of current study. The main objectives of this paper are to analyze the example from practice of one among many environmental risks caused by floods. The investigation is substantiated by the fact that despite all the efforts in emergency management stakeholders missed to prevent contamination in disasters. The hypothesis of this article is that Serbia has enough orphan sites [7]. In practice, it has to enforce more responsible behavior in prevention of contamination and mitigation of consequences with clear and well established policy regarding environmental protection and management.

PREVENTING CONTAMINATION CAUSED BY DISASTER - KNOW WHO IS YOUR ENEMY!

The exploration of resources has accelerated in the period of industrialization of the former Socialist Federal Republic of Yugoslavia (SFR Yugoslavia or SFRY) and its trace could be found in all the countries originated after its dissolution. The problems of air and water quality in the major industrial centers, the decline in agricultural land and the reduction in soil fertility are all still major concerns. Mining and chemical industry additionally jeopardizes environment, especially in the process of privatization, and remains a source of significant environmental pollution, mainly owing to inadequate capacity and poorly enforced environmental standards. This fact is presented in public by the statement of Serbian Prime Minister Vucic when he mentioned that even Serbian Security-Information Agency (SIA) in its report about the flood risk in 2014 expresses the worry about "ecological disasters" due to abandoned industrial facilities, mostly chemical factory in Sabac. It could be an important step to move forward especially having in mind that environment has already become an important task for the Intelligence Community in the global world [10].

There are a lot of scientific articles in which researchers, experts and other interested parties present various analyses of scope and success of Serbian planned remediation activities – ongoing and some of the future challenges, but it looks that still there are a great gap between academic community and policy makers. Soil management in Serbia is accomplished by planning sustainable use and conservation of soil quality and diversity in accordance with environmental protection requirements and measures established by the various laws and sub-laws. Even though Serbia made a lot of progress, it is far from satisfactory levels regarding soil protection. In the Serbian environmental protection agency (SEPA) report it is stated that 375 contaminated sites have been detected in the Republic of Serbia, mainly as a result of industrial processes, mining activities, inadequate waste management and accidents, etc. Serbia has achieved small progress in the management of contaminated sites: remediation was done on 5.7% of identified and confirmed sites; detailed research is completed on 0,5% sites. Since the identification of sites preliminary research has been done in 93.8% of sites [11]. Surprising facts are presented in the part devoted to the issue of management: contaminated sites in 2013 were 422. Industrial commercials sites make 36.30% of this figure, since industrial contaminated location is noted in 222 sites. Except few paragraphs there are not much information about the management of contaminated sited and soil remediation processes. This fact is not encouraging, especially having in mind the exposure level to different kind of disasters in Serbia [12]. The question that arises is what could we expect in the future and how will we prevent probable contamination in disasters and avoid spending of financial resources for remediation purposes. We have to be sure that decision makers would make the most appropriate choice among contaminated sites and would not accept the conversion of private contaminated sites into orphan sites [7], and therefore force citizens to pay for some irresponsible behaviour which is not institutionally prevented. Government activities should encourage and force enterprises to increased preventive measures if they handle toxic substances. If the last ones expect to bear cleanup costs for future contamination, they may generate less waste and use more permanent treatment and disposal than they would in the absence of liability. The private debt nowhere in the world could be treated as a public debt, and therefore has to be clear that state actors will act following the established legal framework and force anyone to pay for caused environmental damage. In numerous laws "polluter pays principle" is clearly defined, as well as the criminal acts against environment. Serbia should not become a country from Garret Hardin's article titled "Tragedy of Common" [2]. Furhtermore, at the same time it expects to become a part of the European Union.

ARE WE REALLY IN RISKY AREA AND DO WE CONSIDER THAT FACT IN OUR RESPONSE PLANS?

In the last decade a lot of articles have been published with the objective to explain how to manage consequences from natural disasters presenting the theories about crises and emergency management and so far. It starts to be a question of prestige in Serbian academic community to attract the attention of wider public and almost it became a question of "academic fashion". Despite all there is a question what are we doing in practice and how to response timely and adequately on perils. This question which is still seeking for answer is: Who should conduct response efforts in disasters and be responsible? The answer stayed hidden, hardly even recognizing common theories, and followed with explanation of numerous subjective and objective obstacles. Despite clear legal responsibilities, in practice everything remains hidden "behind the wall". Some events left experts speechless, or even they spoke about destiny and real causes remain unclear. Often officials from the emergence sector insist on facts that from 2009 almost none of the local municipalities don't have a specific emergency response plan, without even thinking on why they don't have such, and what the reason local communities not to do that is.

Lead by the all facts mentioned above, the authors want to present in front of the academic and wider public the data obtained from two kind of important reports from the world about Serbian capabilities to cope with existed perils. The first one is the World Risk Report presenting an index only related to natural hazards and it is obtained and calculated by combining the four components of exposure, susceptibility, the lack of coping capacities and the lack of adaptive capacities. Table 1 show that Serbia has a high probability of being affected by natural disasters in 2012. It holds the second place in the selected set of the neighbour countries with high values for both factors of exposure and vulnerability. Serbia is at the 66th position out of 173 countries that are included in the World Risk Index overview [15].

Table 1. World Risk Index 2012, and World Risk Index 2014 for Serbia

Country	Year	Rank	Vulnerability	Exposure	World Risk Index
Serbia	2012	66	42.52%	18.05%	7.67%
	2014	76	38.30%	18.05%	6.91%

Sources: *World Risk Report 2012 and World Risk Report 2014[15, 17]*

The closer explanation of the methodology about calculating the World Risk Index is that it is the result of the product of Exposure and Vulnerability (the two contributed factors). From the data presented in Table 1 is clear that Serbia, despite improving its position, is still on inadequate place regarding the value of the World Risk Index [14-17].

Another report is based on the data obtain from InfoRM report (Table 2). The overall InfoRM (index for risk management) identifies countries at risk from humanitarian crises and disasters that could overwhelm national response capacity. InfoRM is a global, open-source risk assessment and it can support decisions about prevention, preparedness and response [3].

Table 2. Serbian risk profiles

	Value	Rank
InfoRM	3.69	87
Hazard	3.22	76
Vulnerability	3.57	84
Coping capacity	4.37	115

Source: *InfoRM 2015 [3]*

There are numerous considerations about the future prevention of contamination during and after disasters in Serbia. Polluting mine accidents and widespread environmental contamination associated with historic industrial pollution in Serbia has triggered the improvement of related environmental legislation and of the environmental assessment and management methods for pollution prevention. Therefore, there is a need to review and evaluate some of the decision support methods that have been developed and applied to environmental contamination during disaster. For instance, after Hurricane Katrina numerous research were performed to follow up what is going in months and years after it on the territory which was devastated. The U.S. Environmental Protection Agency cleaned up or removed contaminated topsoil across the city [5]. The same action also was performed after Fukushima Daiichi nuclear power plant in Japan after horrible earthquake followed by tsunami.

In Serbia stakeholders have to be more active regarding this issue. In numerous researches the health risk from contaminated sites is proved but actions are missed. It is the final time that policy makers among all accept their responsibility to enforce the implementation of approved environmental regulation. Long-term contamination sometimes stayed for years in a recovered area affected by a toxic spill. For example pollution from the spill of Aznalcollar mine (Spain) was monitored by analysing polluted soils in 1998, 1999, 2004 and 2013. In 2013, fifteen years after the spill, some spots remain a major source of pollution from which pollutants are scattered through the solid and liquid phases of runoff water requiring action to immobilize pollutants and encourage the restoration of vegetation on these soils [6].

At the end, the most significant obstacles in funding need to be overcome by the political will of the government, despite all unfavourable economic and social conditions, because these environmental risks could significantly affect the health of the population and make further actions more expensive.

CONCLUSION

There is no need to invent something new, there are methodologies which are proved to be useful, and the country should follow experience from the practice of other countries. Policy makers have to be responsible for their acts or missing the adequate actions. The results of the paper confirmed that if the approach of emergency management is changed in practice, Serbia will avoid being the object of numerous scientific and institutional reports presenting Serbian insufficient capacity to cope with different perils. Government has to work on increasing the level of knowledge and skills of stakeholders, recognize and amend inadequate institutional activities, improve and implement the legal environmental framework into practice, especially general policy regarding environmental justice in the Republic in Serbia. Kostajnik has to be treated as Belgrade and any other town in Serbia. Serbian government is responsible to provide security in every part of Serbia, in any area, with no differences in case of a terrorist act or "an irresponsible person" jeopardizing health and life of people, and environmental status in generally. The bond between the few considerations in this study lies in the aspiration of the authors to emphasize the importance of urgent implementation of effective methodological methods and the need policy makers to change the responsibility approaches in emergencies as a whole, and specifically those concerning environment and its components – a question not only of having a good public will and relevant legislation, but also putting it into action and building capacities in a number of fields and processes in society and business for achievement of sustainable development.

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SERBIAN WATER MANAGEMENT AND EUROPEAN INTEGRATION

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ABSTRACT

Preserving and providing the required quantities of good quality water is the first major activity of a group country.This follows from the recognition that the use of water and use a basic prerequisite for life, economic activity and development. [1] .Waterworks facilities and systems are most sensitive infrastructures , of which depends on the security of people and property and that creates conditions for the development of all other systems and environmental protection.

Key words: development of water resources, water management structures, systems.

INTRODUCTION

Development of water management is closely linked to the development of economy and society, both from the aspect of quantity and quality of water. Given the spatial and temporal mismatch between the need for water and available water needs are extremely high investment funds. The investment funds will create conditions for better quality of life and development of economic sectors.

TASKS IN WATER AREA

Besides the great importance of water resources development have not been paid special attention. Characteristics of water resources indicate finding new directions especially in the context of the reform of our system and of European integration processes. The reform of our system of long-term objectives in the field of water are:

- ensuring good ecological status of waters,
- providing water for the needs of the population and the economy,
- ensuring the safety of water users,
- achievement of the minimum cost,
- harmonization of water management with the development of the economy,
- rational energy and water use,
- ensuring the security of redundant flood and inland water.

The transition process and strategic water management Serbia is in direct correlation with the European integration process.

VISION WATER RESOURCES

The vision of water management in the context of European integration is based on the low economic development and performance in relation to the target environment. They should consist of:

- intensification of investment in the rehabilitation, modernization and construction of physical infrastructure, water management,
- activities to develop the structure of water services (quality and quantity),
- improvement of standardization of water management in the construction and maintenance of water facilities,
- development of a system of sustainable development and protection of water systems,
- improvement of continuing education the manager and the entrepreneur to use water and providing water services.
- activities on the establishment of new development and research activities in all sectors and areas of water management and activate the regional policy in the field of water.

In the integration process of Serbia, which indirectly affects the process of integration of water management is also important to build a modern market structure. The influence of modern market structure is twofold, through stabilizing and increasing demand for water and water management services and reduce stability in the provision of inputs to provide quality offers for the operation of water facilities and systems.

The economy of the Republic is in the transition process which directly influences the activity of the water management given the nature of the infrastructure and operation of the system. Changes made in the fiscal system directly influenced the amount of funds and manner of securing funds for the operation of water management. These changes have resulted in the first unfavorable, as a consequence of the decrease in the share of water management of public expenditures in favor of social and other benefits. Reducing funds to public expenditure in favor of social and other benefits. Reducing funds to public expenditure prevented the construction, reconstruction and maintenance of water facilities of general interest to a pre-determined schedule or norms and standards. Second, the amount of fees for water use, water protection and material extracted from watercourses is administratively determined without considering the real costs, their height, which is lower in comparison to the same category of environment (Croatia, Hungary, etc.).

A third adverse effect disable the acquisition of assets of public companies in the water sector that, by applying the tax system to perform charging fees for drainage, irrigation and water facilities, as this has been done to reform the fiscal system.

Reform of the infrastructure has just started so that the current investment is mainly concentrated on the rehabilitation of existing facilities and systems. System of strengthening the infrastructure will be reflected in an increase in quality of supply and to meet the demands of population and economy.

The water management taking into account these reforms and solving problems of structural adjustments or restructuring required and can be included the following elements:

- strengthening of the central water management and uniform water management strategy,
- establish derivative market mechanisms that will in the public sector to emulate the effects of the market (strengthening the offer, prices, taxes, public expenditure)
- decentralization of control functions or systemic distribution of resources at several levels (the importance and size of water use and water services)
- debureaucratization or closer to customers by expanding choice of services for the development of strategic change.

BASIC PRINCIPLES

Time management

The cost-effectiveness through new management styles and organizational forms. Manager profile should match the placid, pragmatic and business figure who is proactive, creative, focused on the task and focused on the result and who is friendly to the public.

The principles of management are:

- continuous observation results, the measurement of capacity, capacity utilization monitoring and evaluation;
- focus on cost reductions;
- request to reduce the scope of work and influence of the state administration;
- focusing on key responsibilities and tasks of the highest priority;
- openness to the private sector as well as practice in the application of methods that ensure more competitive and cheaper services;
- risk management that is result-oriented, avoiding bureaucratic system in which there is no risk;
- • consistency in the orientation towards the user and the public;
- • acceptance of users and the public as an accomplice in management.

Management

An assessment of the results and efficiency on the basis of the elements of the entire system at a certain level, and the individual functions or in part,

- directing the activity directions of the score, or the quality of water, quality of water use or provide services and not on the assessment of costs,
- weight-differentiation in systems where the manager of a higher level in the system does not need to take action at lower levels, unless they are disturbed standards,
- using the right information in the right place and create a level and scope of information that will present the bits of data.

The process of determining the source of the funds depends on the structure and volume of construction works and measures taken on the one hand, and on the other of the load profile or budget; with a view to strengthening and increasing the quality of water use, protection against.

External supply

Means the supply of goods and services from the private sector, since it achieved savings. Some studies show permanent savings of about 20%.

Treaty PERFORMANCE / results

Certain powers of public administration transferred to public agencies due to:

- faster and better response to the demands of the population and users,
- the benefits of information technologies and systems to increase efficiency,
- innovations which supports lower levels of insight with the more specific factors influence the tangible cost-effective results.

Decentralization of personnel system

Implies flexibility in managing human resources on elements such as the system of classification of jobs, mobility, workplace and hiring procedures.

The process management are integration processes in the EU, which are in addition to those in the financial, customs, traffic, transport and other spheres manifested in water management.

Integration

Is contained in the Water Framework Directive and it is featured as a basis for water management, and includes:

- integration of environmental protection as a combination of qualitative and quantitative economic objectives in protecting highly valuable aquatic ecosystems and ensuring a general "good" water status,
- integration of all water resources in the river basin as the links between surface water and groundwater,
- integration all use water features in water and values into a common policy framework that contains a combination of water quality in the environment and their use in the economy, water testing and impact on health,
- integration or uniformity legislave of water into a common system,
- integration of different analyzes and expertise to cause impacts and pressures on water resources and finding solutions to achieve the objectives of the Directive in a cost-effective and efficient manner,
- integration of all functions and phases of the environmental aspects related to the planning of participatory river basin and flood control,
- integration of all measures in the river basin management plan which includes rates, economic and financial measures in a joint approach to management of this river basin,
- integration of the public in decision-making in the process of passage of river basin management plan,
- integration of different levels in the public sector to make decisions relevant to water resources and water status,
- integration member countries in water management in river basins that cover the territory of several countries.

CONCLUSION

Basis of integration processes in the Republic of Serbia to views of the water as a natural resource that is both food, raw materials, instruments of labor, energy, living space and much more. Water is a prerequisite for the survival of the natural environment and the entire human community as well as the development and quality of the functioning of society.

Historically, investment in the water sector in our country was different, that in the last 25 years have reduced what caused negative changes to the state of water and infrastructure facility.Primary strategic goal Water Master Plan is defined by the Water Act [3], as well as maintenance and development of water regime which ensures the best and most appropriate technical, economic and environmental solutions for uniform water management, flood protection, water, water protection and water use [4].

Water Management of Serbia should develop solving a following issues relating to:

- adoption of water management strategies,
- rapid and massive technological standardization of all water management keeping in mind the requirements of the European directives on water,
- homogenizing the legal and institutional foundation of the entire water management system with national and European regulations,
- the revitalization of existing and construction of new water supply system for what they estimated the necessary funds. These funds will provide sufficient water for drinking and increase the level of population connected to public systems to the construction of the regional water supply system,
- construction, reconstruction and efficient operation of the plant for waste water treatment with the implementation of control measures emissions from bulk and other sources of pollution in order to improve water quality in streams,
- construction,rehabilitation and reconstruction to ensure the quality of irrigation water,
- construction and revitalization of the drainage system in order to eliminate the risk of excess water on the land,
- upgrade, reconstruction and revitalization of the Danube-Tisa-Danube,
- construction and reconstruction of facilities for defense and protection against flooding,
- construction and taking measures for the facts antyerosive and torrential water.

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ANALYSIS OF PUBLIC OPINION TOWARDS THE RECENTLY PROCLAIMED NATURE PARK "RUSANDA"-VOJVODINA, SERBIA

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ABSTRACT

The Nature Park "Rusanda" is known for its bird fauna and specific salt water lake. In order to successfully manage the protected area, the positive attitude of the local public is of vital importance. For this reason, a questionnaire was compiled and survey conducted among pupils of the local elementary school and local adult inhabitants. Survey results confirm a positive attitude towards the NP for most of the respondents. Further education of the public is necessary, especially in the field of agricultural practices which potentially have the strongest negative effect on the surrounding protected area.

Key words: Nature Park, Rusanda, public opinion.

INTRODUCTION

The Nature Park (NP) "Rusanda" is located in the Autonomous Province of Vojvodina, between towns Melenci and Kumane (geographical coordinates: N 45º30'37" - 45º35'23"; E 20º12'54" -20º19'10"). This area was oficially protected on 3rd July, 2014, and placed under the administration of the Special Spa Hospital for Rehabilitation "Rusanda". The total surface of the NP is 1159 ha. The local climate belongs to the moderate continental zone with semi-arid characteristics. The significant hydrological phenomenon is Rusanda lake, the only salt lake in Serbia with a salinity between 40-60‰ [1]. Saline soil is specific for this area. Various vegetation communities are present (water plankton, marsh, therophyte, steppe) as well as a number of endemic plants [2]. The biodiversity of wildlife is rich, especially the bird fauna, 201 bird species have been recorded [3]. This was the main reason for protecting Rusanda and it has an IBA (Important Bird Area) status [4]. Since the NP is surrounded by urban areas, in order to sustain the quality of this protected environment, it is of vital importance that local inhabitants have a positive attitude towards this Nature Park. In this respect an opinion survey was conducted among the inhabitants of Melenci.

MATERIALS AND METHODS

With the aim of investigating the local people's attitude towards NP "Rusanda" an opinion survey was conducted among seventh and eighth grade pupils from Elementary school "Dr Boško Vrebalov" in Melenci and among local inhabitants and staff in the Special Hospital for Rehabilitation "Rusanda", on 14th May, 2014. This survey consisted of a questionnaire, a modified version of the one which was made for Banjička forest in Belgrade [5].

The questionnaire in this survey consisted of structured and combination of structured-unstructured questions [6]. The total number of pupils in the seventh grade who completed the questionnaire was 24 (11 boys and 13 girls), who were between 13 and 14 years old. There were also 45 pupils from the eighth grade (27 boys and 18 girls) who participated in the survey, between 14 and 16 years of age. The total number of local inhabitants of Melenci and staff in the Special Hospital for Rehabilitation "Rusanda" who participated in the survey was 20, 5 males and 15 females. Among the respondents were those of different age groups, level of education and occupation. The youngest respondent was 23 and the oldest was 72. Respondents were with various occupations: physiotherapists, waiters, hygienists, policeman, professor of religion and biology professor. One person finished elementary school, 11 finished secondary school and 6 had higher education.

RESULTS AND DISCUSSION

Planning and implementation of environmental policy requires the support of local citizens, thus it is necessary to conduct a public opinion survey [7]. The results of our opinion survey are shown in Table 1. followed by the results of structured-unstructured questions.

Table 1. Survey results for pupils, local inhabitants and staff in the Special Spa Hospital

Structured questions with ordinal numbers as they appear in the questionnaire	Pupils in seventh grade Results in percentages (%) No. of respondents (24)		Pupils in eighth grade Results in percentages (%) No. of respondents (45)		Inhabitants and staff Results in percentages (%) No. of respondents (20)	
	Yes	No	Yes	No	Yes	No
6. Do you consider yourself a nature lover	70.83	29.17	93.33	6.67	70.83	29.17
7. Do you strive to keep the environment clean	100.00	0.00	91.11	8.89	100.00	0.00
8. Do you know that Rusanda lake and the park of spa complex are important habitats for birds	100.00	0.00	97.78	2.22	100.00	0.00
12. Do you agree that Rusanda lake and the park of spa complex need to be protected under law	100.00	0.00	100.00	0.00	100.00	0.00
14. Do you think that hunting should be forbidden in this area	87.5	12.5	95.56	4.44	87.5	1.,5
15. Does agriculture with chemical utilisation have a negative impact on wildlife and water quality of Rusanda lake	87.5	8.33	88.89	11.11	87.5	8.33

According to the results from Table 1., it is evident that the majority of pupils have a positive attitude towards the environment, Rusanda and its surrounding. However, a relatively high percentage of pupils are not well informed about the potential negative impact of agricultural practices on the environment, as shown in question 15.
Furthermore, the inhabitants of Melenci and staff in the Hospital "Rusanda" are aware of the importance of Rusanda lake and the park of spa complex, as seen in Table 1., questions 8 and 12. Nevertheless, a relatively high percentage of respondents are not well informed about the negative impact of hunting on the biodiversity of this area and the threat which agricultural practices have on the wildlife and water quality of Rusanda lake, as shown in questions 14 and 15.

By analyzing the answers to structured-unstructured questions, ordinal numbers corresponding to those in the questionnaire (**A.** seventh grade pupils, **B.** eighth grade pupils, **C.** local inhabitanst and staff from the Special Hospital), the results are as follows:

Question No. 10: Do you know some bird species that can be seen in the spa park and on Rusanda lake? If you do, please write down up to five species.
A. From the total number of pupils who participated in the survey, 62.5% are familiar with local birds, however 33.33% are not familiar with species living in this area. Some of the bird species that pupils mentioned are: Short-eared owl, heron, swan, sparrow, lapwing, crow, jackdaw, pigeon, magpie, kestrel, grey kestrel, stork, swallow, peregrine falcon.
B. As regards the knowledge of some bird species that can be seen on Rusanda lake and in the park, 28.89% of pupils are familiar with some species. On the other hand, a high percentage of eighth grade pupils (64.44%) are not familiar with species inhabiting this area. The mentioned species are: Owl, swan, sparrow, pigeon, wild duck, heron, gull, swallow, stork, woodpecker.
C. The majority of local inhabitants and staff from the Special Hospital, 85%, know various bird species, while only 15% is not familiar with local birds. The species that are mentioned: Short-eared owl, swan, sparrow, crane, stork, crow, jackdaw, woodpecker, pheasant, swallow, duck, goose.

Question No. 13: Would the local community have benefits from protecting Rusanda lake and the spa park? If your answer is positive specify some of the benefits.
A. Half of the pupils (50%) consider that the protection of this area would bring a number of benefits to the local community. The suggested benefits are: More people would visit this area and it would be tidier; there would be more birds in the park that eat harmful rodents; birds would nest unhindered; the population of bird species would rise in Banat region. Unfortunately a high percentage of pupils (40.67%) consider that the local community would not have any benefits from protecting Rusanda lake and the spa park.
B. More than half of pupils (55.56%) consider that the local community would have huge benefits from protecting Rusanda lake and the spa park. The following benefits were suggested: The environment would be better protected; economy of this area and wellness tourism would be improved. The remaining respondents consider that the local community would not have any benefits.

C. Very high percentage (90%) consider that the local community would have various benefits from protecting this area: the improvement of local tourism, water management and the protection of biodiversity with rare species.

Question No. 16: Are you a member of some society connected to nature (scouts, societies for nature protection, hunting, fishing)? If your answer is positive please give the name of society.

A Only one of 20 pupils is a member of the local fishing club.

B. Very low percentage of pupils (8.89%) are member of some section or society connected to nature: Biology section, Fishing club "Rusanda", Society for nature protection. Unfortunately, the majority is not a member of any society.

C. Of all respondents only 1 is a member of the local fishing club.

Question No. 17: Do you have any suggestion related to protection and maintenance of the spa park and Rusanda lake? If you do, please write it down.

A. The majority of pupils (70.83%) did not have any suggestion. The remaining respondents suggested that there should be more trees and flowers, less pollution (sewage outflow, leaving livestock corpses) and a stop to tree felling.

B. Of all pupils that participated in the survey, 57.78% did not have any suggestion related to protection and maintenance of the park and Rusanda lake. The remaining respondents suggested that this area requires to be observed by rangers, the sewage outflow and the formation of waste dumps need to be stopped. Some of the pupils also suggested that reeds on the lake should be cut. It is evident that pupils are not informed about the importance of reeds as a habitat for reed warblers and buffer zone protecting the lake water from artificial fertilizers and pesticides coming from adjacent fields. .

C. From the total number of respondents, 40% of them suggested that there need to be constant water monitoring, improvement of ecological consciousness and adherence to laws.

Concerning the frequency of visiting the park (question No 11), most seventh grade pupils visit it several times a week, eighth graders mostly once a week, while the inhabitants and hospital workers are there daily. Hospital workers accompany very often patients who stroll through the spa park and lake shore as part of the therapy.

Our opinion survey showed a generally positive public attitude towards NP "Rusanda". This is significant since in every project concerned with nature protection, the participation of the public is of vital importance [8]. The respondents possess a basic knowledge of the local bird species, however, they should be further educated in this respect as this area was protected as a NP because of its rich bird fauna. The respondents, adults more than the pupils, believe that the development of tourism within the NP would be a benefit for the local community. It is necessary to harmonize the particular interests of the local community, agriculture and tourism in order to minimize negative effects on the quality of the local environment [9].

CONCLUSION

Nature Park "Rusanda" as an Important Bird Area (IBA) requires continuous conservation efforts to sustain natural habitats and biodiversity. Unfortunately, this area is facing many problems such as sewage outflow, the formation of waste dumps and uncontrolled agricultural practices which lead to water and soil contamination. In order to effectively manage this area, the local community needs to be more educated in sustainable agricultural practices and the natural heritage of the surroundings.

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ECOLOGY THROUGH THE PRISM OF GLOBALIZATION

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ABSTRACT

Rapid technological development and the application of modern scientific achievements in different areas, positively influencing the quality of life in most of the world. But at the same time, modern civilization is facing major challenges which increasingly threaten life and health, environment, material, cultural and other resources of the states.

Worldwide global security is in direct connection with environmental security, which affect the overall climate change plan, desertification ravages forests, pollution of all media eco-soil, water, air, migration, military conflict and many other factors. Regarding environmental safety related and criminal activities related to the disposal of radioactive waste, illegal trafficking in protected species of animal and plant species, the actions of the forest mafia and so on.

Ecological security is linked to international, national and personal security and in this context it is necessary to study the factors that cause and affect the ecological safety.

The research will be made analysis of the impact of the industrial revolution and environmental warfare on climate change. It will then be considered the application of professional knowledge in order to raise the level of The Security, and finally to be given draft measures for successful problem solving, decision and implementation of quality decisions aimed at greater environmental security as well as prospects of sustainable development future according to rights of use of resources by today's generations, while taking into account the rights of future generations.

Key words: ecology, globalization, environment, climate change.

INTRODUCTION

The modern world is increasingly facing non-traditional types and forms of risks such as terrorism on a world scale, trafficking in drugs, arms and people, danger from the use of weapons of mass destruction, infectious diseases and epidemics of larger scale, unemployment, poverty, consequences of global climate change, natural disasters and disasters of natural phenomena, environmental degradation, technological failures and other. Their main characteristic is that they do not recognize state borders and have global impacts.

History abounds with many accidents and disasters, which unfortunately have caused unforeseeable consequences and grave suffering of human civilization. Such occurrences are not rare nor today, because, as never before, the world mobilize and undertake joint efforts to reduce the effects of such phenomena, which are becoming more frequent, more aggressive and cause great human casualties and material losses, on all continents.

DEFINING ON THE ECOLOGICAL SAFETY

Learning of security, is directed towards three basic conceptual framework: individual safekeeping, national security and international safety.

When the disruption and endangering to the environment, are covered all three entities that felt for consequences of Pollution, degradation, and the disruption to the environment. Namely, the man just as individuals, and national and state international community are subjects that are threatened at the ecological disaster. The individual directly go again feels the impact of the ecological crisis, this represents a victim of a certain crisis materializes. As part of certain states, in whose territory the event is happening or territory in which regard themselves consequences, the very countries This precise appears to affect the subject.Frequently dispersion on the substance or territory that is afflicted by the ecological crisis, not within the framework of one state, but has a border character. Therefore international intervention is needed. Any conflict or crisis which, between that and the ecological crisis, will have security implications and on the security international Thereby International factor often times I decide whether it has a role.

Global problems in the sphere of the protection to the environment also apply to the security aspect of certain phenomena. Hence the ecological security is defined as the state protection of the humans of ecological threats and threats originating from environmental management.

The main actor in the promotion of the protection of the country is, the reason that environmental management will fit a security problem in the moment when the state will be forced to use special measures for dealing with the ecological pressures.

World Commission on Environment and Development, in the report Brundtland 1987, connecting the security as environmental management and emphasizes that Man is facing two huge threats, such as: the dangers arising from the possible use of nuclear arms and degradation to the environment that veḱe at the moment is present everywhere in the world.

According to other authors' represents the ecological safety of public safety against threats to environmental management caused by natural or human processes.

Means the ecological security situation of the dynamics between Man and the Environment, which includes recovery to the environment damaged by military activities and improvement of the Resource shortages, degradation of the ecological and biological threats that can lead to social tensions and conflicts. That is the ecological safety represents notion which theoreticians and practitioners go kind used to indicate the link between the conditions of the environment and security interests. "

In the academic sphere of the ecological safety is defined as the relationship between security that applies to armed conflicts and to the environment. This precise the broader definition of environmental security, enumerate the three elements: prevention or reparation of the damage on the military nature; prevention or response to conflicts caused by environmental reasons and protection of the environment as a moral value.

The ecological safety is public safety from environmental hazards caused by natural or human processes due to lack of information, crash, malversations originating in or across a national border. According to the United Nations security can be defined as a "situation in which States feel that there is no danger of a military attack, economic or political coercion coercion such as are free to develop." Who will be taken into account to the definition of security as the absence of threat, the ecological security can I definition as a condition in which the living world there was no threat or is threatening to the environment. In the definition it is stated that the ecological security is a state, when it is not stated whether this condition applies to the individual, the state or the like, because its under the general definition of "situation" shall mean the situation of national or international plan. Further under "alive world" include all living beings on planet Earth: Man, animal and flora world, as the site for there is a need of preserving to the environment that will enable a healthy and proper growth and development. Under the "threat" shall mean any threat to the environment and from it: political, economic, military or other nature, which may imply negative consequences on environmental management.

And at the end of "endangering" may be a potential or real, which, as a result of the realization of the threat can lead to degradation, contamination or other disruption to the environment. For such a method can be defined by the ecological safety at when it would be taken into account and determining a specified poimni, and in relation to the international dimension to environmental problems and the need for overall living world on a global level to be protected from possible is threatening.

THE IMPACT OF THE INDUSTRIAL REVOLUTION ON CLIMATE CHANGE

The man existence, Finances, and no life, every day, and threatens to "mother nature". So its negligence and Pollution of nature ever since the industrial revolution, as a consequence of CII and den gi We feel today, Man probably has created The most powerful long-term enemy. We witness the drastic changes in climate in the last hundred years. We are aware of the visible climate change, and remains not only the question, whether and to what extent we can quickly learn the will that I have kept the Earth for future generations. Despite controversies over the question of global warming of d and can confirm that there is a consensus learned under which climate change has implied negative impact on the climate because of industrial development. The modern science, unfortunately not at such a level of development in that climate that I can adapt to Man. Only you can make at this moment that you easier and as painlessly go adapt Man on climate. The question is how to adjust to the climate and its changes.

ORGANIC WARFARE

Today there is no single typology of Organic Warfare (ecocide). She more or less can be based on several different criteria and classifications. Given the global character of the global effect, is possible to distinguish tactical and strategic combat environmental effects (for analog general classification of combat operations). Certainly in relation to that is clearly more and scope of action are, as well as the scope of the consequences arises in the natural environment. That is in direct relation to the possibilities for differentiation in an environmentally military activities for sustainability of their consequences for the environment.

CONCLUSION

The connection of the the protection of the environment and security is evident and is confirmed by the ecological disaster that is going on in continuity in global terms, and have security implications. Because, it is necessary to manage risks and crisis situations arising from the persistent and serious threats to the environmental management, while it Considering all the climate change and that, tsunamis, hurricanes, earthquakes, volcanic eruptions and other similar events.

In that regard, it is necessary preparation of standard operating procedures that will be applied in an environmental disaster on a national but also an internal level, as much as in today 's terms of environmental disasters have global dimensions and takers of the framework of the nation-state and cross-border incidents represent. When it appears as a problem and the question of the sovereignty of the nation state, transferring of certain responsibilities to the international organizations and institutions and the need for controls and sanctions. It is indisputable is the importance of the protection of the Environment koešto him shall be given to the international plan, foremost in the European Union.

The huge world organizations, such as the Organization of the United Nations (UN), European Union (EU), NATO and others, within their institutional mechanisms, is taking an increasing attention to planning, to undertake some measures and activities directed towards prevention and reduction the risks of accidents and disaster world wide.

We live in a decade (2005-2015) that the UN, as a mass world organization, I dedicate on strengthening the resilience of the nations and communities as opposed to more frequent occurrence of various accidents and disaster.

The man has always lived and give lives in the presence of various sources to insecurity, danger surrounds you do not constantly be changed and unfortunately are larger causing harm, consequences and damages.

Our common responsibility is it better order to inform and is prepared to face up to them!

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SOCIALLY RESPONSIBLE CONDUCT OF SERBIAN IN THE USE DISPOSED WASTE

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ABSTRACT

Countries such as the Republic of Serbia if they develop have to learn how to use all their natural capital and resources on smart and sustainable man-near means moving to a new concept managing the economy, philosophy as the basis of observation of the economy, agribusiness, waste processing, and other useful products in . The gradual transition from classical postulates of neoliberals, especially in transition countries, among other means realistically deal with the issues that have global significance. From such a set framework, a new approach to business, should contribute to the strengthening of certain new industries, which are a function of economic growth, on the one hand, and on the other the acceptance of such economies means the Improvement of Living and general human living and working conditions of the observed broad layers of the population of a state. In this paper, the authors draw attention to just a new way of managing the economy of the Republic of Serbia.

Key words: natural resources, the economy of the state, development.

INTRODUCTION

A new approach to managing the economy of the Republic of Serbia should contribute to poverty eradication, sustained economic growth, while improving the living conditions of people at all levels, from local to state as a whole, and beyond. This approach is often called the green economy. This is the basis of sustainable development. Therefore it should be a lever of global change processes, which will lead to the betterment of the country. More and more authors observe multidisciplinary process economics, for example in the context of socio-economic processes (Popović, 2014, p.30). Therefore, a new approach to economics should allow Get better management of natural resources, and in a sustainable manner, with less negative impact on the environment with higher degree of recycling of discarded objects and products.

Such observation forcing companies to take action to develop sales of its products and services at inexpensive and widely accessible way widest range of consumers (Popović et al. 2014). Such observation requires recognition of the social responsibilities of each company to the local community.

Today is part of the references to socially responsible behavior, primarily companies, greatly facilitated the rapid development of information technology (Fletcher, 2003, p. 490). In transition economies, such as the Republic of Serbia, a lot of questions, including questions related to the "green economy" by many authors (Holscher 2009 Filipović, 2014; Filipović and Miljković, 2014; Ljubojević, 2012), primarily observed in terms of economic growth. Planning represents the primary stage of the process management (Williams, 2010, p. 76), in all industries, and in the whole economy, while adapting quickly to market environment (Hisrich and al., 2011, p.199).

The gradual transition from classical postulates of neoliberals, among other means realistically deal with the issues that have global significance. From such a set framework, the green economy approach, should contribute to strengthening of certain new industries, which are a function of economic growth, on the one hand, and on the other the acceptance of such economies means the Improvement of Living and general human living and working conditions of the observed broad layers of the population of a state.

Green economy should contribute to poverty eradication, sustained economic growth, while improving the living conditions of people at all levels, from local to state as a whole, and beyond. The green economy as a tool for sustainable development should be a lever of global change processes.

Accordingly, the green economy should allow Get better management of natural resources, and in a sustainable manner, with less negative impact on the environment with higher degree of recycling of discarded objects and products, observation should be facing in the future (Greuning, H., 2006, p. 4). The whole previously disclosed must be viewed in the context of real presentation of the financial statements and on several levels within a state (Soltani, 2010, p. 10). In addition to the above, the authors point out that it is important to find your model to run a good, such as compost, in a socially responsible and socio-friendly manner (Popović and al., 2014).

In addition to the above, the last phase in the real business approach the company must be realistic valuation of property companies following an economic activity (Popović and al., 2015), ie after the economic activities of all procedures are subject to revision (Gritsenko and Skorba; Panchuk; Skrypnyk and Vygivska 2015) . The audit process in the coming years will increasingly come to the fore, especially in those branches that are faster and better developed than the average. Faster development of a sustainable economy will surely be, especially in developing countries, who want to catch up with the fast developing economies.

MATERIALS AND METHODS

This research started from the application of basic research process first with the SWOT analysis of the current situation, which can significantly affect the industry that can be a driver of a large number of processes to create new global conditions for sustainable and socially responsible economy of the Republic of Serbia. In this context authors give an overview of the situation in table no. 1.

Table 1. SWOT analysis of the current state of the industry that can become a chance for development of the economy in the Republic of Serbia

The available options and the existing power	**Weaknesses**
- Just the existence of quantities that are can the industry and other production methods turn into useful products, recycling industry, - Tradition eliminating unnecessary waste in the continuity of the utility companies of local governments, - High-quality raw materials for the production of useful products,	- Lack of information, - Lack of interest of local governments, - Insufficient interest of the local utility company for innovation in production and processing, especially less hazardous waste, - Lack of interest of local companies to increase cost-effectiveness in the work, because financed from the budgets of local governments, - A weak relationship between enterprises of local government, for example, companies that remove plant waste and waste stored at the local and regional landfills
Opportunities	**Threats**
- Permanently increase the demand for products that are produced by recycling, - Extension of the areas that cities maintain and cultivate, - Development of new products on the basis of the obtained raw materials recycling, - Introduction of product recycling industry across the EU, - Strengthening the institutional capacity of local government, - Strengthening the capacity of waste processing on the basis of association at all levels	- The suppression of domestic enterprises by foreign companies that have introduced similar innovations long before they come on the market of recycling in the Republic of Serbia, - Negative impact of certain legal provisions in the field of ecology and local governments.

Source: *Author's calculations.*

On the basis of the present authors have made representations general availability, they showed any weakness, gave presentation opportunities that can realistically be related to the increase in future demand for the products of recycling and sustainable industry and eventually pointed out some of the main threats to the development of this new type of socially responsible approaches industry.

RESEARCH RESULTS

Basic research results which were obtained by the authors of this paper, based on the available data of the Federal Statistical Office of the Republic of Serbia, are given in Table 2, and are related to the display of the amount of heterogeneous wastes can be chance of development of a whole group of new processing industry in the Republic of Serbia. The authors give the table display the amount of hazardous waste from the point of impact on the environment, by groups 2010-2013.

Table 2. Total waste generated by groups of waste, from the point of hazardous operation on the ecology of Serbia, EWC-STAT in the Republic of Serbia for the period 2011-2013, in tons.

Groups of waste according to the EWC-STAT	2011	2012	2013
Mineral and Waste	12.732.526	14.329.800	16.674.243
The chemical and medical waste	57.154	56.129	85.320
Waste recycling	1. 957	406	234
The animal and vegetable waste	0	0	0
Mixed waste	1.772	632	466
Sludge	0	0	0
Electronic Equipment	3.381	3.385	1.960
Total	**12.796.188**	**14 .457.990**	**16.762.223**

Source: *Author's calculations based on the Statistical Yearbook of the Republic of Serbia for 2014.*

Amounts shown different categories of waste, which the authors have shown in Table 2, and can be used industrially processed into useful products, and as such presented to the market. The same products can be sold abroad thereby Republic Serbia could make tens of millions of Euros, selling only 10% of some of the displayed categories. That is, the products can be sold on the market, which confirms the social responsibility of a state.

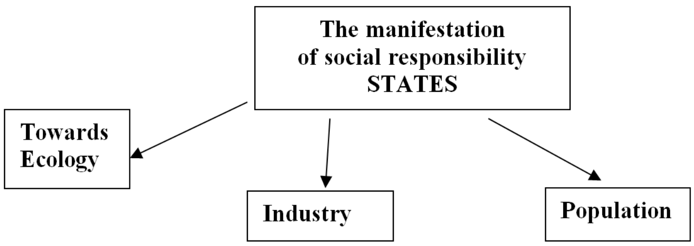

Figure 1. Social responsibility of the state and main impacts

Products obtained by processing at some of the ways of recycling have their value, which is measurable in the domestic and international markets. If you can not produce on its territory, they are imported, while waste slaughter industry, as well as vegetable waste generated in a particular area must be deposited, noting that for the delay must allocate funds.

CONCLUSION

The authors point out that the approach of the Republic of Serbia EU, increasing importance will be on renewable energy sources, the use of waste as a raw material base for processing in the form of recycling and others. The economic value of the recycling industry can be at the state and several hundred million euro's, which is the Republic of Serbia so far cast and burying in landfills.

Through this work, the authors draw attention to the economic exploitation of waste and the amount that is now unnecessary to throw, deposit and disposal of that waste for residents allocate funds. In addition exploitation of discarded waste could be employed and labor. In addition to the classical labor force may be employed, and the inhabitants on the sidelines so far in our country.

Employment of marginalized groups of the population would be performed even one of the essential functions of socially responsible economy and socially acceptable.

At the end of a number of different development paths exist. They were not disclosed, but each state according to their vision needs to develop its economy. With this work the authors are trying to draw attention to a wider observation of ecology, but also socially responsible economy. Proper consideration, it can make life easier for the common man, which can be included as a worker in the recycling industry, or as a taxpayer without a job, who will only pay for waste disposal local government, which is certainly not socially responsible and acceptable behavior of society towards the man.

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IMPORTANCE OF GEOGRAPHY IN EDUCATION OF YOUNG PEOPLE WITH SPECIAL EMPHASIS ON THE TEACHING CONTENT OF THE ENVIRONMENT

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ABSTRACT

Geography is of great importance from the lowest ages of education in order to create the image of the country, tourism, local environment and ecology.[1] Analyzing curricula subjects the world around us and science and society I tried to find out what is the status between the geographic and ecological topics in order to real observation needs the introduction of national geography and environmental groups object on high vocational schools. Besides geography elements in these subjects permeated the theme of environmental protection as an important carrier of ecological education for future generations. Ecological approach the most fit in courses in biology and geography, but it is possible and necessary and other subjects (physics, chemistry and technical education). The role of education of students is important, first of all due to the increasing consciousness of environmental protection its preservation and sustainability.

Key words: education, geography, environment, environmental awareness.

INTRODUCTION

The setting partly in science societies and partly in natural sciences Geography is marginal or bridges Sciences which helps us to realize complex nature, society and economy, in order to rationally exploit natural resources, uniform distribution productive forces and protection of human environment. The traditional approach Geography, like a complex science, is destined for a diverse understanding of complex phenomena of the world. The local environment is spatially restricted area, where the school is with its closest environment which includes a number of elements physical-geographical, anthropogeographically and biological character which assert man and landscape. We live in a time of climate change and destruction of ozonosphere so it's important to know what those processes are and what their consequences (fires, floods, UV radiation). It is no longer an academic issue but planetary ecological reality which is strongly reflected in the local environment. Considering that educators and teachers were holders pedagogical-educated processes and organizers cultural events It is knowledge of

[1] Pecelj M. R., Pecelj M., Pecelj-Purković J., Pecelj D. (2013): „The importance of geography in afore-school education“, Subotica.

homeland of particular importance. That is why the educators needed a higher level of knowledge in the field of geography[1].

The development of environmental awareness of students during the teaching process depends on: program content, organization of teaching and extracurricular activities application of textbooks and other teaching aids, as well as some properties and preparedness of teachers. (Klemenović J., 2004).

Pedagogical reaction on existence of a global ecological crisis reflected in the development of environmental education that developing environmentally conscious individual, should contribute to its mitigation and resolution. During training young people should be offer relevant information about environmental problems and provide an understanding of the principles that are taking place in it. In addition to forming the system of ecological knowledge, during the educational process, young people should develop the right relationship to natural and anthropogenic values that surround them, positive emotions towards the environment, a sense of personal responsibility towards the environment, awareness of the seriousness of environmental problems and confidence in the possibility of solving them. The ultimate goal is to develop the students' willingness to actively participate in environmental actions and habits ecological behavior during the performance of daily living activities (Andevski M., 1997).

Geography can contribute to contemporary research ecological character where it is desirable that a larger number of experts from different scientific disciplines, establish universally compatible relationship between nature and man. Today there is no science that uses only their research techniques and methods, or only one method, so the reintegration existing scientific knowledge necessity, especially when it comes to finding solutions of global character (Lješević AM, 1987).

CONTENTS AND ANALYSIS GEOGRAPHICAL ELEMENT IN SCHOOL SUBJECT (WORLD AROUND US AND, NATURE AND SOCIETY) FROM I TO IV CLASS PRIMARY SCHOOL

Beside two regular geography subjects, world around us (in I and II class) and nature and society (in III and IV class), we have elective, geographical and ecological subject, guards of nature (in I and II class).

In order to objectively insight is carried out empirical research about representation of geographic content in teaching the subject: world around us and nature and society. We analyzed the curricula subject the world around us (from first to second grade) and science and society (from third to fourth grade). Geographic contents were separated from other and are structured for quantification per teaching and geographic disciplines.

In research were used descriptive methods and techniques, plan and program of education, textbooks cases; the world around us (first and second grade) and nature and society (third grade and fourth grade) of primary school. Statistical data shows the results in the Table no.1.

Table 1. The representation of geographic content by regions in relation to other content and society according to the plan of 1997. Modified April 2015.

Class	*Geographic content*		Other *content*		*Total*	
	Number teaching units	%	Number teaching units (f)	%	Number teaching units (f)	%
I WAU	41	56,94	31	43,06	72	100
II WAU	48	66,67	24	33,33	72	100
III NAS	40	55,56	32	44,44	72	100
IV NAS	33	45,83	39	54,17	72	100
∑ (I-IV)	162	56,25	126	43,75	288	100

Source: *M. Pecelj, 1999. page 147.*

For spatial literacy of children in lower grades from I to IV grade, used subjects the world around us (grade I and II) and the nature and society (grade III and IV). In the first two classes of subject world around us, realized with a total of 72 hours per year. In the third and fourth grade subject of nature and society realized with 72 hours per year.

On realization teaching content, (288 teaching units), 162 hours or 56,25%, belongs subject of geography and other 126 horus or 43,75% belongs other education contents. This means that the geographical content are dominant. This leads us to think seriously about the necessity interceded introduction of geography at the high vocational schools, Teachers and Pedagogic faculties dealing with education.

In the structure of geographic content, per teaching, observed in all grades topics from geography homeland. In the first grade geographic elements are processed in the framework of topics: objects around us, animate and inanimate nature, connection between animate and inanimate nature, and orientation in space and time. In the second grade geographic elements are processed in the framework of topics: living and inanimate nature, connection between animate and inanimate nature, where a person lives, the movement in space and time. In third grade, geographical elements are processed in the framework of topics: nature-man-society, movement in space and time, our heritage. In fourth grade within the topic: my homeland is part of the world, meeting with nature, explore natural phenomena, retrospective look-past.

Such an attitude would not disturb the usual university teaching from the subject knowing nature and society whose realization of teaching content processed usually pedagogues. They pedagogues are not problematic when we talk about methodical-didactic practice, but should be respected scientific field and glossary which is geographically. Analysing of the curricula of nature and society in primary schools, we tried to define what is the status of geographic content In order to assess needs the introduction of national geography and environmental groups object at the high vocational schools, the Pedagogical Faculty of Education.

Teaching subject the world around us is a regular subject, is represented in the first and second grade of primary school. In the lectures, in the first grade, applied twice a week. The annual number of hours is 72. The theory consists of 53 hours, and 19 hours of practice, repetition, determination) and (2 hour evaluation and self-evaluation). In this case there are standards:

1. Basic level (knowledge and understanding) which has completed 80% or more students.

2. Medium level (application and analysis) which has completed 50% or more students.
3. Advanced level (synthesis and evaluation) which has completed 25% or more students.

The school subject, nature and society is a regular subject, which is represented in the third and fourth grade of primary school. In teaching, the third class, applied two times a week. The annual number of hours is 72 of which (introduction 1 hours), (51 hour processing of materials), (10 hours a repetition, reinforcement), (2 hours systematization of the material) and (8 hours of evaluation and self-evaluation). In this case there are standards:
1. Basic level (knowledge and understanding) which has completed 80% or more students.
2. Medium level (application and analysis) which has completed 50% or more students.
3. Advanced level (synthesis and evaluation) which has completed 25% or more students.

The school subject, nature and society is a regular subject, which is represented in the third and fourth grade of primary school. In teaching, the third class, applied two times a week. The annual number of hours is 72 of which (introduction 1 hours), (51 hour processing of materials), (10 hours a repetition, reinforcement), (2 hours systematization of the material) and (8 hours of evaluation and self-evaluation). In this case there are standards:
1. Basic level (knowledge and understanding) which has completed 80% or more students.
2. Medium level (application and analysis) which has completed 50% or more students.
3. Advanced level (synthesis and evaluation) which has completed 25% or more students.

The school subject, nature and society is a regular subject, which is represented in the third and fourth grade of primary school. In teaching, the fourth class, applied two times a week. The annual number of hours is 72 of which (51 hour processing of materials), (14 hours a repetition, reinforcement), (5 hours systematization of the material) and (2 hours of evaluation and self-evaluation). In this case there are standards:
1. Basic level (knowledge and understanding) which has completed 80% or more students.
2. Medium level (application and analysis) which has completed 50% or more students.
3. Advanced level (synthesis and evaluation) which has completed 25% or more students.(Sitarica R., Tadic M. 2013).

GUARDS OF NATURE (GEOGRAPHICAL AND ECOLOGICAL) SUBJECT

By creating better teaching, introducing the subject guards of nature, increase the level of environmental awareness with children. Protection and conservation of nature indicating to children endangered environmental quality. It is of great importance that younger generations have in mind the increasing number of environmental problems: (climate change over, global warming, greenhouse effect, ozone hole, more frequent natural disasters, etc.).

Guards of nature are optional subject in first and second grade of primary school. In this case, environmental education of young people, grow and reached a good basis for further progress in this area. Teachers themselves are not sufficient to deal with the environment, because in High vocational school and Teachers and Pedagogical faculties the theme of environmental protection is not sufficiently processed. Faculty of Geography in Belgrade has a way geospatial base environment whose graduates are eligible to teach this subject in school.

In the exposed environmental content is dominated by information on: forms human impact on nature, the consequences of human activities on the environment, environmental contaminants and the measures for its protection (S. Jovanovic, Zivkovic Lj., Andjelkovic S. 2010).

TEACHING OF GEOGRAPHY AND PROBLEMS OF ENVIRONMENTAL EDUCATION

On the basis of the curriculum defined aims and outcomes of school significant for the development of methodology of environmental education. Of the thirteen general objectives that are defined in this document two relating to education for environmental protection.

They emphasizes the need to have knowledge about natural resources, their limitations and Sustainable Use, as well as the need to have knowledge about the protection, restoration and advanced of the environment. It is noticeable lack of goals from the sphere of educational influence environmental education in the direction of development value attitudes responsibility, emotional, ethical norms and habits ecological behavior. The general outcome of compulsory education, defined the same document, determine that the student after completion of primary education:

- understand the limitations of natural resources on Earth;
- understand the positive and negative impacts, as well as local and global consequences of human activities in nature;
- understand the essence and importance of the sustainable use of natural resources;
- understands the importance of having a diversity of life and habitats for the ecological balance and human survival;
- understand the importance of, protection of individuals, species, habitats and ecosystems in general;
- understand the importance and the possibility of personal participation in the protection, restoration and improvement of natural and artificial ecosystems (Andevski M. Kundačina M., 2004).

CONCLUSION

Analyzing curricula subjects the world around us and nature and society in primary schools I have identified what is the status of geographic content in them in order to observe the needs of the introduction of national geography and courses on environmental protection at the High vocational schools, the Pedagogical Faculty of Education.

Curricula Geography at the High vocational schools, the Pedagogical Faculty of Education it's necessary to modify and adapt to new requirements and modern IT multimedia teaching technologies. It is necessary to introduce subjects that deal with National Geographic geography or geography homeland local environment, objects on the protection of the environment and the same professional cover. Through these facilities provides enough information and knowledge in environment protection and tourismology. Finally, this science is in many ways intertwined with basic knowledge of biology, helping teachers to be incomparably better understand and implement school activities in nature. No matter which has so far marginalized geography, it is time that the concept of curriculum these educational institutions set geographic scientific field, what is the reason for this initiative, which we believe is useful to note that those who participate in drafting the curriculum.[1]

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DEVELOPING ENVIRONMENTAL AWARENESS

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ABSTRACT

According to the current state of education in Serbia, environmental protection is not sufficiently represented. But young people in Serbia still have the ability to create specific education in the field of ecology. Starting from an early age, through the improvement of environmental knowledge later in life, and to be able to applied all knowledge about ecology throughout life. Education is extremely important in every inhabitant of our planet, knowledge of adaptation of living things to the living conditions, the methods of pollution of water, soil and air, aware of the need to conserve forests, have great significance for the development of everyone in planet. Knowledge of opportunities for every individual to contribute to the preservation of the environment is essential, each individual needs to give its best, to protect the environment in order to change the negative trend of the global nature of pollution.

Key words: environmental, nature, ecology, conversation, ecology crisis.

INTRODUCTION

To redeem continuous disturbance of the natural environment, we need proper measures of prevention. One of those measures in the field of ecology, in response to the ecological crisis is to educate the population about the harmful effects of man on nature. At the global level, ecological crisis is extremely present, which occurs as a result of disruption of the ecological balance, the development of science and technology. All the benefits that science and technology contribute and thereby improve the life of man, on the other hand has left serious consequences on nature. The causes that led to the ecological crisis can be found in the disturbed balance between natural life-support systems and industrial, demographic and technological needs of humanity. The ecological crisis is reflected in the depletion of natural resources and environmental pollution. In the contemporary world is more dominant and more and more accepted knowledge that the ecological crisis and environmental disasters can lead to the destruction of humanity. And precisely because the environmental problems have become global problems which significantly mark and characterize modern society slowly transcend political differences that exist between countries in order to find solutions to already accumulated environmental problems. Ecology should be studied as a whole, made up of elements that exist in all subjects [1]. Environmental education, can be divided into education in the school period (primary school, secondary school, university), and education and training of government (state, local government, media, literature).

ENVIRONMENTAL PROTECTION AS A WAY OF CULTURE

Ecological culture, at the present time has a very important role in every individual. Environmental education is actually understanding of environmental problems of a society, such education provides the necessary knowledge and skills in the field of natural and social sciences. The process of education to the protection and improvement of the environment is the planned development of man's knowledge of the environment in the course of his life, which is aimed at raising awareness about the basic relationship between man and nature, so that people will strive to preserve and enhance the environment. Education have a lot of influence on the formation of a critical attitude towards the pollution of nature, educate us how much we actually went away with uncontrolled exploitation of natural raw materials, and to what extent is our endangered planet. Education is not intended to convey individual information only, but to successfully prepare that their actions affect the environment throughout their life, and that such knowledge can be transferred to the next generation. Education of the formation of ecological way of thinking begins in early childhood, and is thus very important role of education and educational organizations at all levels of knowledge acquisition.

EVNIRONMENTAL EDUCATION IN SCHOOLS

Education in schools is crucial, which is still in early youth educates and forms ecological way of thinking. Environmental education is understanding of the general greening of material and spiritual activities of the company. A wide range of environmental education provides a necessary synthesis of knowledge and habits from the natural and social sciences. School is the basic factor of education in general, and therefore environmental education. With the established program contents wagon offers the greatest opportunities in the construction of ecological awareness of students. Environmental education in elementary school, in addition to regular classes, may be exercised within the framework of free community service activities, departmental and other community activities. The most important are the environmental sections in the school. Through the activities in sections youngest shows that the environment is greatly degraded and covered with waste, but that there are ways and ways of how it can be protected.

Ecological education should be based on a global, holistic and systematic principles.

Environmental education requires different sources of knowledge. Which source of knowledge will be favored depends on the teacher in the educational process. Highlights of the following sources of knowledge:

- The immediate reality - means the specific environment in which the student exists. This is a family home, a kindergarten, school, university, military barracks, general urban or rural area. It plays an important role in the formation of environmental awareness, although it is largely filled with neekološkog, but the knowledge he acquired through her the highest quality;
- Textual materials - school books, fiction editions, short stories, novels, etc. School textbooks are the basic source, but in terms of ecological and educational insufficiently aligned with the work programs, environmental activities they are under-represented and non-functional;
- Teaching aids and objects - models, preparations, models, pictures, drawings, tables, graphs, photographs, slides, video cassettes, etc. They replace immediate reality;
- Teacher - appears as a significant factor in the realization of the goals and tasks of environmental education: selects the curricula, assesses the environmental aspects of the curriculum, organize and manage the process of acquiring knowledge, forming attitudes and habits of students, organized and carried out extra-curricular activities and direct their actions acting on personality students;
- Print, television, radio and other means of mass communication media are engaged in the field of information, activation of citizens in environmental protection. In that way, an informal environmental education and upbringing.

Eco content should ensure that students in elementary school learn: basic concepts (the concept of disturbance of the ecological balance, the term degradation of environment, etc.); to gain knowledge about the negative influence of polluted air, soil, water, about how to prevent and protect against any adverse environmental impact [2] .

Understanding the personal responsibility of individuals, whose activities are changing the environment, and transfer this knowledge to students, is one of the most important tasks of environmental education. Environmental education is an integral part of our educational system. The aim of education is to preserve and enhance a man with his environment, to become an integral part of his life, work and biological survival. To the individual could expect and demand ecological behavior, it is necessary to pre-educate, which can only be achieved by introducing environmental content at all levels of the educational system of education. Therefore, we should force the classes with an environmental theme, in schools. Quality Education of Youth will affect building the value of thr systems, which will encourage the formation of attitudes on which to emerge positive patterns of behavior and responsible decision-making. From this it can be concluded that education for the protection of the environment will be more successful if they can be implemented as soon as possible [3].

GOVERNMENT EVNIRONMENTAL EDUCATION

Local governments need to have better cooperation with its citizens in order to function flawless. Municipalities should have as many workshops and training, in order to encourage the inhabitants of the municipalities to create an environment in which environmental protection is one of the development priorities of each community. Environmental problems have to deal with city and state authorities, but we should not neglect the role that the individual has in the entire system. The consciousness of the individual, of the potential dangers surrounding nature, in addition to himself and all other living beings, and his behavior are a key factor in changing the overall environmental picture of Serbia. Public participation in decision-making on the various activities that are of importance for the environment is one of the central issues of contemporary politics and environmental law it is also closely linked to issues of democratization, respect for human rights, the rule of law. With adequate aid local authorities, the population should be activated in order to successfully decided on very important issues in the field of environmental protection. That the joint action of citizens and authorities get the best solutions for the growing problems of the environment. In recent years, the Serbian Parliament passed several laws governing the environment. The adoption of these laws and regulations is of major importance for the country, but it is important that the behavior of the population should be in accordance with the regulations for a long time to see results. In addition to the application of the law is essential to implement the programs of environmental education at all levels, where over them should encourage people to engage in activities aimed at environmental protection. Environmental problems are becoming one of the hottest topics in the world, so information in this field are very important. The development of ecological culture is achieved when the entire society is working synchronized, in order to protect the environment, not just individual performance.

To manage to achieve influence the consciousness of the whole society in the country, it is necessary right across the local governments, activation and participation of citizens successfully changing awareness of nature. Municipalities in Serbia will only then be able to line up with where environmental protection that become an important factor of economic and social development, and will as a positive result in the creation of an environment for a comfortable and healthy life in a landscaped area.

CONCLUSION

Environmental education has the task to raise critical awareness of the necessity of preserving and improving healthy, ecologically clean environment, and to inform them about the consequences of technological development and uncontrolled impact of this development on ecosystems and human health. This is achieved both institutional and out of institutional education. These two methods of environmental education must be linked together in harmony, because they are naturally directed to one another.

The need for experts in the field of environmental protection in modern society, science and technology is extremely important, and the need for more versatile and complete knowledge of changes in the ecology. Raising awareness about the need and possibilities of personal engagement in environmental protection, adoption and application of the principles of sustainability, ethics and the rights of future generations to surviving the environment are extremely important. Then, the study of environmental issues is an essential part of sustainable development, and application of acquired knowledge and influence on daily life. Training the right awareness and education are of crucial importance, which involves taking into account the ecological interdependence of urban and rural areas. Providing opportunities to each person to acquire the knowledge, values, attitudes, commitment and specific skills that are needed to protect and enhance nature. Creating and implementing new patterns of behavior of individuals, groups and society as a whole, directed towards the environment, should be used and developed until it reaches a high level of awareness and knowledge that are consistent with sustainable development for all citizens of our country.

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EDUCATIONAL ROLE OF THE `ARBORETUM OF THE FACULTY OF FORESTRY` - EXAMPLE OF GOOD INCLUSIVE PRACTICE

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ABSTRACT

The paper gives a brief account of the educational potential of the natural protected area `Arboretum of the Faculty of Forestry` in Belgrade. The Arboretum setting has been successfully used for the purpose of practical inclusive teaching of Belgrade Secondary Vocational School students. Here, they attend workshops and get practical training for the educational profile of florist-gardener. The work is carried out in groups and individually and meets the needs of each pupil or attendee. Teaching process, which has elements of occupational therapy, is designed to improve motor, sensory, perceptual, cognitive, affective and psycho-social skills of the pupils. Thematic gardens with the elements of healing or therapeutic gardens were built in the zone of the arboretum extension in 2014. Plant material, with its texture, color and smell, is purposefully used to help enhance human senses and give this space a multiple educational, medical and therapeutic purpose.

Key words: natural protected area, inclusion, horticultural therapy.

INTRODUCTION

Time keeps moving on. Distances are reduced, new fields of activity are created, spaces are given new purposes. All of these process apply to urban green spaces, which are constantly undergoing 'the boldest changes to the mechanisms of nature`. In the past few years, the natural protected area 'Arboretum of the Faculty of Forestry' has used its authenticity and eco-educational potential[1] to contribute to the development of a program of practical training and inclusive education[2,3] of people with disabilities. This program is implemented in cooperation with teachers and pupils of the Secondary Vocational School in Belgrade and users of the Center for housing and day care of disabled children and young people in Belgrade. Apart from that, the program supports popularization of social or therapeutic horticulture (STH), through designing, establishing and maintaining of healing gardens. In the developed countries of the West, especially in America and Canada, social horticulture has already become a common practice in preschools and schools, schools and institutions for education and rehabilitation of persons with special needs, nursing homes, botanical gardens and many other green areas. The slogan of this therapeutic programme, which has now grown into a real movement, is *'environment without barriers'*. This form of occupational therapy is in our country still rare and uncommon. The yards in schools and institutions are usually designed only for the passive involvement of the users. It should be mentioned that the healing garden built in 2010 on an area of 10 *ha* of Ada Ciganlija[4] in Belgrade was designed by the students of the Department of Landscape Architecture, Faculty of Forestry in Belgrade.

HISTORY OF HORTICULTURAL THERAPY

The knowledge of therapeutic benefits of gardening dates back to the ancient times, but the first written records of horticulture being used to treat psychiatric patients originate from the French monastery of *Clairvaux* in the 12th century[5]. The first "green house" used in the treatment of persons with mental illnesses was built in 1879 by the Pennsylvanian Asylum for Persons Deprived of Their Reason, now known as Friends Hospital. At the beginning of the 19th century, Dr. Benjamin Rush, signer of the Declaration of Independence and the "father of American psychiatry," wrote about positive effects of occupational therapy in the gardens. The increasing number of hospitals for veterans opened by the US federal government in the period between the two world wars contributed to the development of HT programming. In 1955, Michigan State University offered the first university degree in HT. However, Alice Burlingame was the key person in the development of horticultural therapy in the United States. This scientist unified the fields of psychiatry, occupational therapy, landscaping design and nursery production. Together with Dr. Donald Watson, she published her first book on horticultural therapy, *'Therapy through Horticulture'* in 1960. Today, the American Horticulture Therapy Association (AHTA) is the organization with the main role in the promotion and development of social horticulture, which it has gained through its long experience in establishing and landscaping therapeutic gardens, as well as in educating horticultural therapists. Today, many different research disciplines and professions have different theories about the effects of healing people using horticultural therapy[6,7,8]. They largely belong to three different schools: 1. School of healing gardens, in which users realize health benefits by simply experiencing the garden space through its design and the amenities it offers; 2. School of horticultural therapy, in which users gain health-related benefits through their engagement in horticultural activities; 3. Cognitive school, where the health effects are achieved by being in the garden environment and by taking part in the garden activities.

ABOUT THE PROGRAM OF INCLUSIVE PRACTICAL TRAINING

Practical training of the Belgrade Secondary Vocational School pupils, which has been carried out in the protected natural area 'Arboretum of the Faculty of Forestry' since 2010, includes the realization of one part of the curriculum planned for a two-year educational profile: florist-gardener. This school is designed for special vocational training of people with disabilities. The training uses the inclusive approach to teaching and it is realized by the students and their teachers, together with the professional staff of the Arboretum and the students of the Faculty of Forestry in Belgrade and the Secondary International School of Belgrade. The work is carried out in two phases: indoor and outdoor creative educational workshops (Figure 1) and practical training in several thematic settings of the protected area: inner zone of the arboretum (Figure 2), greenhouse, nursery, zone of extension, zone of theme gardens and park zone.

Figure 1. Creative workshops

Figure 2. Participants of the practical training of the vocational school in the Arboretum of the Faculty of Forestry

The work is carried out in groups and individually and meets the needs of each student or attendee, taking into account their capabilities, mental capacity and degree of disability. Teaching process, which has the elements of occupational therapy, is designed to improve motor, sensory, perceptual, cognitive, affective and psycho-social skills of pupils. In a safe and quiet environment, they gain positive learning experiences by taking part in outdoor practical work with a multidisciplinary educational approach. Furthermore, the time spent in the natural protected area established in the vicinity of the city forest Košutnjak with its valuable sanitary-hygienic and health functions has relaxing and antidepressive effects, raising the levels of neurotransmitters - serotonin and norepinephrine in the organism. Other benefits of this school in nature are reflected in: (1) physical effects: improving physical health of the pupils by increasing their motivation, developing fine motor skills, decreasing the muscle tone, improving coordination and balance, increasing muscle strength; (2) mental effects: increasing their independence by developing professional skills, giving them opportunities to use their skills in problem-solving situations, stimulating creativity, reducing and eliminating stress and negative emotions; (3) social effects: inclusive teaching and interaction with students and schoolchildren, acquiring skills of cooperation and team work, mutual support, coping with success and failure, challenges of competition and confrontational attitudes.

Establishment and maintenance of therapeutic gardens

`*Forest Classroom in the Green Oasis of Belgrade*` (2014) is a project launched by the Students' Association of the Faculty of Forestry in Belgrade in the protected natural area 'Arboretum of the Faculty of Forestry'[9]. The project is implemented as part of the 'TOGETHER FOR THE COMMUNITY' competition (2014), co-sponsored by the City of Belgrade and NIS Gazprom Neft doo Novi Sad. The overall objective of the project was to promote the protection and conservation of rare, endemic, endangered and protected plant and insect species and to enhance new modules of environmental protection, through the inclusion of vulnerable social groups. Thus, the pupils of the Secondary Vocational School in Belgrade and the users of the Center for housing and day care of disabled children and young people Čukarica in Belgrade, together with the students of the Faculty of Forestry in Belgrade, students of the Faculty of Geography in Belgrade, and the pupils of the Technical School Drvoart in Belgrade, took active part in creative and educational workshops on environmental issues and raised thematic gardens in the extension zone of the arboretum. The gardens have elements of therapeutic gardens (Figure 3). The concept of these gardens is to create specific ambient space, elements and activities that will improve the health of groups of people with specific needs[10]. This improvement may relate to physical or cognitive rehabilitation, social interaction of people suffering from social phobia or antisocial behavior or people suffering from memory loss, PTSD, *etc*. The area intended for the establishment of thematic gardens (field 5 within the extension zone) is easily accessible from other parts of the protected area. It is rimmed with conifers and other natural forest vegetation, which directly abuts on the park-forest Košutnjak. The topography is suitable for a number of different treatment activities which not only provide the benefits of the time spent in a pleasant natural environment but also offer a view on the most prominent landmarks of the city (Ada Ciganlija, Ada Bridge, New Belgrade, the Sava and the Danube rivers, Kalemegdan, *etc*.). Consequently, this area has become a multipurpose social setting that offers different content programmes and includes various exterior elements: 5 wooden pergolas with flower pots and plantations of medicinal, aromatic, herbal, rare, endemic, endangered and protected plants; collection of live insects (`insect hotel`), collection of fungi, water ecosystem, appropriate labels, signs and notices and park mobile furniture. Pedestrian communication between the elements is made of log wood slices and sawdust. Each pot contains plant material whose texture, color and smell stimulate different senses - smell, sight, touch or taste. The following plant species are used to stimulate different senses: the sense of sight - nasturtium (*Tropaeolum majus*), African marigold (*Tagetes* sp.), common marigold (*Calendula officinalis*), sunflower (*Helianthus* sp.); the sense of smell - lavender (*Lavandula officinalis*), rosemary (*Rosmarinus officinalis*), immortelle (*Helichrysum arenarium*), cotton lavender (*Santolina chamaecyparissus*), marigold (*Calendula officinalis*); senses of taste and smell - sweet basil (*Ocimum basilicum*), parsley (*Petroselinum crispum*), oregano (*Origanum vulgare*), chives (*Allium schoenoprasum*), dill (*Anethum graveolens*), mint (*Mentha* sp.), celery (*Apium graveolens),* thyme (*Thymus serpyllum*); the sense of touch – lamb`s ears (*Stachys byzantine*), sage (*Salvia officinalis*), blue fescue (*Festuca* sp.), houseleeks (*Sempervivum* sp.), *Sedum acre*. All these things together support the ability of the visitors to organize the stimuli from the environment and their own bodies and make this area both stimulating and relaxing. The existing woody species (Turkey oak, chestnut, *Zelkowa carpinifolia*, birch, catalpa, forest fruit trees and a plantation of Douglas-fir) also contribute to the visual-aesthetic effect and educational and therapeutic role of the setting. Through their active or passive participation in educational workshops, the users learn about plant species through monitoring of phenological phenomena and ecological processes in all seasons, through practical work on planting and maintaining thematic gardens, recycling plant material and making compost. At the same time, these activities, which are a part of inclusive practical training and teaching, develop their social and professional skills, create the sense of responsibility, and develop creativity and teamwork spirit. The plant material can be used in creative workshops, as well as for the preparation of medicinal teas and health food. In addition to other elements of the area, thematic therapeutic gardens contribute to the harmonization of the whole site as a protected natural area.

Figure 3. Establishment of thematic therapeutic gardens

CONCLUSIONS

Multifunctionality of the protected natural area 'Arboretum of the Faculty of Forestry' is reflected in the implementation of inclusive vocational training of secondary school pupils intended for the education of people with learning and developmental disabilities. As a special mode of practical training and occupational therapy, thematic gardens were built with elements of healing gardens and horticultural therapy. With the slogan of the modern education system that 'every child can learn, these new landscape and architectural elements are considered valuable for their contribution to inclusive education, fostering the voluntary work of students and other users, raising the environmental awareness and, above all, awareness of the community to the needs of vulnerable social groups.

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GAS MONITORING IN THE ENVIRONMENT, FOLLOWING A FIRE IN AN UNDERGROUND TOURISTIC FACILITY

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ABSTRACT

In the last decades of the twentieth century were highlighted the medical therapeutic effects of mines, Speleotherapy's beneficial effects have been proven, namely: high degree of air purity (sterility, relatively high air humidity (vapor content), vapor condensation favorite content, constant air temperature, low air flow rate, high content of carbon dioxide in the air, high negative ionization (high number of micro ions).
For some events, INCD-INSEMEX Petrosani as specialized institute and national authority is empowered to carry out technical valuations under GD. 1461 / 18.10.2006, Annex no. 1 "development of methods for technical valuation of events caused by explosive atmospheres and / or toxic and / or explosive materials."
This paper presents the monitoring of environmental factors parameters preceding a fire that took place the fresh air inlet circuit of a treatment saline, as well as measures taken for reopening the tourist area of the underground salt mine.

Key words: environment, fire incident, touristic, salt mine, gas monitoring.

HEALTH EFFECTS RELATED TO SPELEO THERAPEUTICAL TREATMENT

The therapeutic effect of caves and underground excavations (galleries and abandoned operating rooms), has been known for centuries. In scientific and medical terms, the effects on the respiratory system were determined only in the last decades of the twentieth century. In the cave "Klutert" of Westphalia (near the town of Ennepetal) during the Second World War, a bombproof shelter was set up. Among the refugees there were some that were ill, suffering from asthmatic disorders. After a certain period of staying in the cave, the patients showed some signs of improvement in respiratory disease [6].

The salt mines of Ukraine, at "Solotvino" ("Aknaszlatina"), the practice of speleotherapy treatment for respiratory diseases is ongoing since 1968. Patients are placed in abandoned operating rooms, corresponding to hospital rooms with 2-3 beds at a depth of 206 m, attending four-week treatment cycles [6].

According to doctors who looked into speleotherapy is not about particular medical factors, but about a set of manifesting physical, chemical and biological conditions, causing complex effects on the human body..

HYSTORY OF THE TOURISTIC AND SPELEO THERAPEUTICAL TREATMENT FACILITY

The positive therapeutic results obtained in the salt mines abroad, at the analyzed mine, speleo therapeutic treatment began in 1960, in one of the chambers of the old exploitation. Salt extracting was performed at the same level with the treatment rooms, at an appropriate distance [3].

In operating rooms abandoned, were organized many events and events such as painting and sculpture competitions and camps were organized, who's works even these days, adorn as drawings and bass relief the saline's walls [1].

Subsequent the treatment base moved from the underground to a higher mine level, located at 120 m depth from the surface in a drier chamber system, where it functions even today [4].

Currently, treatment rooms and annexes are electrically illuminated and have continuous general ventilation. They are also equipped with playgrounds, chairs and sun loungers, pool tables, ping-pong tables, internet club, historical museum, coffee terrace and souvenir shop, an ecumenical chapel and bathroom facility, all to make the mandatory minimum 4 hours of underground treatment daily more bearable and more varied [4].

The next few years they intend to expand this base on a new level (at the bottom of the current one), thus creating an underground complex for tourism and treatment.

Figure 1. Picture made in the treatment of tourist attraction

CHARACTERISTICS OF THE ANALYSED TOURISTIC FACILITY'S AMBIENT AIR

The physical, chemical and biological characteristics of the tourist attraction ambient air are:

- low concentration of allergens and pathogens, the number of germs varies between 180-270 germs / cm^3, thus observing the condition of fresh air. There are present certain fungal strains (Mycromicetes) some of which may have the same effects as antibiotics (eg. type Penicillium),
- relative vapor content is 45-50%, which is maintained in all seasons, ensuring a constant hidric environment, regardless of outside conditions,
- 50% of microscopic particles of salt (NaCl) in ambient air are under 5 microns in size
- During the cold season air temperature is 16.4-17.4^{0}C and 20.8^{0}C during summer,
- Salt rock temperature covers the range between 15.4 to 16.4° C,
- Air velocity is 0.1-0.2 m / sec, independent of outside weather conditions,
- CO_2 content varies between 387-775 mg / m^3,
- Ionization level varies between 413-580 ion / m^3, the share of negative ions being higher during summer,
- The low value of air pH varies between 6.5 ÷ 6.9.

From the statistics stated, resulted that in recent years in the case of the patients present for treatment 3-4 times / year, the number and intensity of asthma attacks decreased, convulsion cough was improved, quantity of eliminated secretion and it's viscosity decreased and the body's respiratory capacity increased. Results show that underground speleo treatment and climatic therapy are simple and effective natural methods that contribute to rapid improvement of the condition of patients suffering from respiratory diseases, maintaining and restoring mental balance and neurovegetative system's tonus.

The results of monitoring gases from underground treatment tourism objective's air after a fire

On 07.30.2013 at the mining unit from which belongs the tourist and treatment objective, in an abandoned gallery located at 190 m surface (two floors down to that objective) a fire broke out. Through this gallery, was ensured the fresh air supply to the mine, including the treatment area.The unit immediately triggered a general alarm, following which hundreds of people, tourists, patients and workers were evacuated after gases and odors were infiltrated in the objective area. Fire outbreak manifested in an area of 30 square meters of wood and beams abandoned gallery.

To extinguish the fire the area was flooded by rescue teams However, the management of the mine ordered intensive ventilation in tourism objective and the control of air quality so that they can be reopened only after the gas will be below the limits permitted by the rules of protection of public health.

The fire was located at a distance of 240 m from the main station AXC 1250-7/28-9 fans and at a distance of 140 m from the AXC 630 fans site, which serve the treatment and visiting area horizon. Ventilation of the visiting the treatment area is provided from the + 339m horizon, through an air shaft (suitor de aeraj), located in the cross-cut gallery, linked to the gallery 617, which is accessible through the blind extraction shaft INCD INSEMEX – Petroşani made a technical expertise to this fire, setting the occurrence of the event (fire) due to a short circuit produced at the power cord from the underground ventilation system, from which were lit wooden beams.

In order to check the air quality INCD INSEMEX Petrosani was asked for monitoring residual gas remaining after the fire till their placing below the permissible standards.

Since the fire occurred on 07/30/2013 and fire-rescuers intervention and ventilation of the objective lasted several days, measurements were performed in two stages during 02 ÷ 04.08.2013 and 19 ÷ 20/08/2013.

The results carried out in two steps close to fire are given in Table 1.

The analysis results show the following:

- CO concentrations (190 mg / m^3) determined on 08.02.2013 in the fire and at 100 m from the fire scene (180 mg / m^3) exceeded the limit of 10 mg / m^3 established by Law 104/2011 on air quality ambient 18- 19 times,
- CO concentration determined on 20.08.2013 in the fire was reduced to 31 times on 02.08.2013, thereby falling into admissible concentration of 10 mg / m^3,
- SO_2 concentration determined on 08/02/2013 at fire exceeded the maximum permissible concentration (MPC) of 350 mg / m^3 established by Law 104/2011, 1.1 times. At the determination made on 8/20/2013 the concentration decreased to 320 mg / m^3, falling within the permissible limit,
- for NO_2 and CH_4 were identified only traces,
- O_2 and CO_2 were enrolled in normal atmospheric air.

From Fig. 1 can see how the CO concentration decreases over time below the maximum permissible limit specified in Law 104/2011 (on 08.19.2014). During 07 ÷ 19/08/2013 determinations were not made because the ventilation was increased.

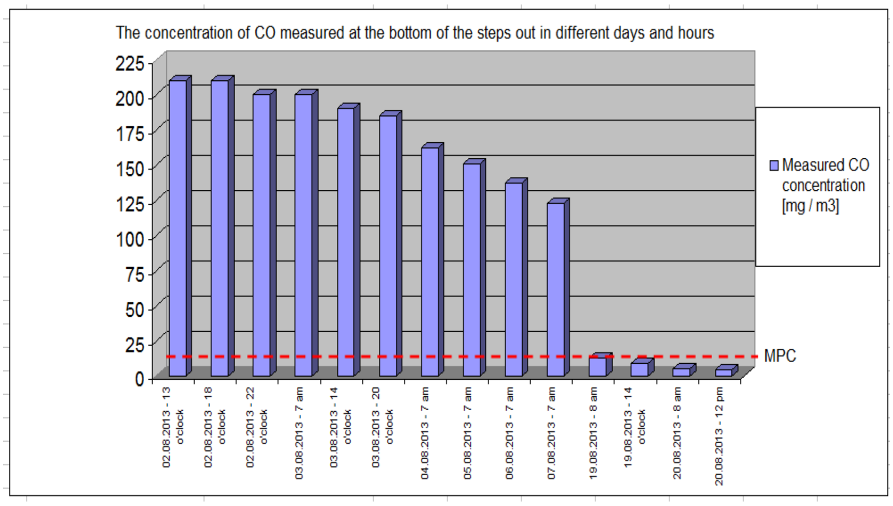

Figure 1. Concentration of CO due to the different time intervals and the at different tours.

The determination results are shown in Table no.2.

Table 1.

Gas sampling location	Gas analyzed	MU	Maximum permissible concentration (MPC) according to Law 104/2011	Gas concentration determined on 02.08.2013, after the fire of 30.07.2013	Gas concentration determined on 20.08.2013, after the fire of 30.07.2013	Decreasing the concentration of gas in 20.08.2013 to 02.08.2013 Col 4 / col 5 [times]	Comments
The area of the fire incident, lower floor gallery	SO_2	µg/m^3	350	**400**	320		
	NO_2	µg/m^3	200	traces	traces		traces
	CO	mg/m^3	**10**	**190**	6	↙ 31	6 < MPC
	O_2	%		20,2	20,1		
	CH_4	%LEL		traces	traces		traces
	CO_2	%		0,02	0,01		
At 100 m from the fire place, to the area exhaust air from the lower floor gallery	SO_2	µg/m^3	350	**380**	330		
	NO_2	µg/m^3	200	traces	traces		traces
	CO	mg/m^3	**10**	**180**	5	↙ 36	5< MPC
	O_2	%		20	20,1		
	CH_4	%LEL		traces	traces		traces
	CO_2	%		0,03	0,02		

Table 2.

Gas sampling location	Gas Analysis / climate conditions T, Wr	UM	Maximum permissible concentration (MPC) according to Law 104/2011	The concentration of gases and climate conditions determined on 02-04.08.2013, after the fire incident of 07.30.2013		The concentration of gases and climate conditions determined on 08.20.2013, after the fire incident of 30.07.2013	Decreasing the concentration of gas in 20.08.2013 to 02.08.2013 Col 5/col 7 [times]	Comments
				02-03.08.2013/ time	04.08.2013 7.00 am			
1	2	3	4	5	6	7	8	9
Entry into recreational basis. Waiting Room (pt. M1)	SO_2	µg/m^3	350	330	280	260		
	NO_2	µg/m^3	200	traces	traces	traces		traces
	CO	mg/m^3	**10**	**140 -** 02.08.2013- 13 o'clock	**120**	4,0	↙35	4,0 < MPC
	O_2	%		20,2	20,1	20,3		
	CH_4	%LEL		traces	traces	traces		traces
	CO_2	%		0,02	0,01	0,04		
	T	°C		17,2	24	23,3		
	W_r	%		39,1	38,4	35,6		
Playground, before passage (pct.M2)	SO_2	µg/m^3	350	190	160	150		
	NO_2	µg/m^3	200	traces	traces	traces		traces
	CO	mg/m^3	**10**	**190 -** 02.08.2013- 13 o'clock	**175**	4,5	↙42,2	3,5 < MPC
	O_2	%		20,1	20	20,3		
	CH_4	%LEL		traces	traces	traces		traces
	CO_2	%		0,02	0,03	0,06		
	T	°C		18,1	20,6	20,7		
	W_r	%		41,1	46	47		
1	2	3	4	5	6	7	8	9
The gymnastics area (pct.M3)	SO_2	µg/m^3	350	300	340	200		
	NO_2	µg/m^3	200	traces	traces	traces		traces
	CO	mg/m^3	**10**	**160 -** 02.08.2013- 13 o'clock	**145**	3,5	↙ 45,7	3,5 < MPC
	O_2	%		20,1	20,2	20,3		
	CH_4	%LEL		traces	traces	traces		traces
	CO_2	%		0,02	0,05	0,09		

	T	°C		18,7	24,3	20,6		
	W_r	%		43,2	45	47		
At the bottom of the exit stairs (pct.M4)	SO_2	µg/m³	**350**	340	320	320		
	NO_2	µg/m³	200	traces	traces	traces		traces
	CO	mg/m³	**10**	**210** - 02.08.2013- 13 o'clock **210** - 02.08.2013-hour 18 pm **200** - 02.08.2013-hour 20 pm **200** - 03.08.2013 – 7 o'clock **190** - 03.08.2013-hour 14 pm **185** - 03.08.2013-hour 20 pm	**180**	4,5	✓ 46,6	4,5 < MPC
	O_2	%		20,1	20,3	20,3		
	CH_4	%LEL		traces	traces	traces		traces
	CO_2	%		0,001	0,009	0,08		
	T	°C		19,9		21,5		
	W_r	%		45,3		47		

***Note:** T- air temperature [°C], Wr - relative humidity, [%]*

We chose four target locations analyzed as follows: Pt. M1. Waiting room, Pt M2 the playground before passage, Pt. M3- Flatbed Gymnastics, Pt. M4- At the bottom of the stairs out.

From Table 2 shows the following:

- CO concentrations determined on 08/02/2013 at 1 PM in four locations M1, M2, M3, M4 were 140, 190, 160 and 210 mg/m³, exceeding the limit of 10 mg / m³ 14, 19, 21, or 16, times
- CO concentrations determined on 04/08/2013 at 7.00 AM in four locations M1, M2, M3, M4 were 120, 175, 145, 180 mg/m³, exceeding the limit of 10 mg / m³, 12; 17.5; 14.5 and 18 times,
- CO concentrations determined on 20.08.2013 in four locations had values of 4; 4.5; 3.5; 4,5, reducing 35; 42.2; 45.7 respectively 46.6 times the concentrations determined on 02.08.2013 at 1 PM
- SO2 concentrations determined in 02 and 08.04.2013 in four locations M1, M2, M3, M4, did not exceed the limit of 350 mg / m³ established by Law 104/2011,
- for NO2 and CH4 were only traces identified in the four locations M1, M2, M3, M4,
- O2 and CO2 were scored within the normal range of air in four locations M1, M2, M3, M4,
- Temperature (T) in four locations M1, M2, M3, M4 had values between 17.2 and 19.9 ° C,
- Relative humidity (Wr) ranged between 39.1 and 47% specific of dry air.

CONCLUSIONS

- Research by doctors who were occupied with speleotherapy have demonstrated the beneficial effect of physical factors, chemical and biological from underground excavations on human respiratory tract.

In Romania there are several underground facilities, where due to the air quality were designed to treat patients with respiratory diseases.

- On 07.30.2013 at the mining unit from which belongs the tourist and treatment objective, in an abandoned gallery located at 190 m surface (two floors down to that objective) a fire broke out. Through this gallery, was ensured the fresh air supply to the mine, including the treatment area.
  Because of fire hundreds of people, tourists, patients and workers were evacuated after gases and odors were infiltrated in the objective area.
  To extinguish the fire the area was flooded by rescue teams However, the management of the mine ordered intensive ventilation in tourism objective and the control of air quality so that they can be reopened only after the gas will be below the limits permitted by the rules of protection of public health.
- In order to check the air quality INCD INSEMEX Petrosani was called for monitoring residual gas remaining after the fire till their placing below the permissible standards.
  Since the fire occurred on 07/30/2013 and fire-rescuers intervention and ventilation of the objective lasted several days, measurements were performed in two stages during 02÷04.08.2013 and 19 ÷ 20/08/2013.
- Measurements of SO_2, NO_2, CO, O_2, CH_4, CO_2 conducted between 08.20.2014 and 02÷04.08.2013 close to fire showed that only CO exceeded the limit. Thus CO concentrations determined on 08.02.2013 in the fire and at 100 m from the place of fire exceeded the limit of 10 mg / m3 established by Law 104/2011 on ambient air quality, 19 and 18 times.
  Determinations dated 08.20.2013 in the fire area showed that CO was reduced by 31 times from the date 02.08.2013 and at 100 m from its the area of 36 times, falling under admissible concentration of 10 mg / m3 .
  For NO_2 and CH_4 were only traces identified and O_2 and CO_2 were enrolled in normal atmospheric air.
- Measurements of SO_2, NO_2, CO, O_2, CH_4, CO_2 conducted between 08.20.2014 02-04.08.2013 in four locations M1, M2, M3, M4 showed that only CO exceeded the limit upheld.
  Thus the concentration of CO due on 08/02/2013 exceeded limit of 10 mg / m3 determined by the Law 104/2011 14, 19, or 16, respectively, 21 times
  CO concentrations determined on 20.08.2013 in the four locations M1, M2, M3, M4 decreased to values of 4; 4.5; 3.5; 4,5, reducing 35; 42.2; 45.7 respectively 46.6 times from the concentrations determined on 08/02/2013 at 1 PM falling below the limit of 10 mg/m3.
  For NO_2 and CH_4 were only traces identified and O_2 and CO_2 were enrolled in normal atmospheric air.
  Temperatures in four locations M1, M2, M3, M4 had values between 17.9 and 19.9° C and relative humidity between 39.1 and 47% specific of dry air.
- Based on the report of mine air parameters monitoring conducted by INCD INSEMEX - Petrosani, by reducing the concentration of CO under the the limit of 10 mg/m^3, the management ordered the reopening of the treatment area.

- To avoid risk of fire that may affect the treatment center is recommended that in the future, imbuing power cables along mining workings is done in such a manner that there is no contact between them and any combustible material, the salt mine ventilation network should be upgraded and simulations necessary for ventilation network should be performed, simulations modeled and solved in order to identify optimal solutions under fault conditions.

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TOURISM ACTIVITY AND SHALE GAS EXPLOITATION IN BUZIAS, THE SPA RESORT IN TIMIS COUNTY, ROMANIA

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ABSTRACT

People in holiday seasons wish to relax and to restore health, to find out and know new places and cultures and to escape from the polluted environment and stressful living from day to day. All of this should be enough to determine a sustainable tourism development in areas without pollution or danger of pollution.

The energy resource crisis triggered a search for new resources such as shale gas, but their exploitation is controversial. Their existence in the Buziaş area, near the spa resort and the possibility of exploitation raises the question of using the area for future tourism.

Key words: tourism, sustainable tourism, mineral waters, shale gas, pollution.

INTRODUCTION

Tourism involves movement and accommodations for people outside of their homes and for their own leisure. In the opinion of the World Tourism Organization (WTO) "Tourism comprises the activities of persons traveling outside their home for a short, specified time and whose purpose is other than the exercise of a paid activity from the visited place."[1]

Key elements that define tourism are:

- Trip;
- The destination;
- Time;
- The absence of paid activity.

This activity is based on natural and anthropic resources, which means that keeping them unaltered is essential.

The increase from year to year of the worldwide number of tourists can have negative effects on the environment. In this sense, sustainable tourism development is the current solution.

1 Conferinţa Internaţională asupra turismului şi statisticii turismului de la Ottawa, iunie1991

According to the World Tourism Organization (WTO) "sustainable tourism develops the idea of serving the needs of present tourists and the tourism industry and at the same time protecting the environment and the opportunities for the future. It is considered to meet the tourism "actors" needs of economic, social, aesthetic, etc. of travel, in the meantime maintaining cultural integrity, ecological, biological diversity and all ecosystems that support life. "[2]

Protecting the environment and the tourism potential is required for both areas already in the tourist circuit and for the non-integrated so that they continue to attract tourists.

Tourist motivations are diverse, personal, subjective and caused by endogenous and exogenous impulses.

For every tourist the reasons for traveling can be pleasure, business, health (thermal treatment, thalasso-therapy) or attending a professional meeting or sports events, religion, etc..

Spa tourism is the type of tourism that has been practiced since ancient times, even if we consider it as a phenomenon of our times. The forms of the practice have improved and multiplied in time, even if the type remains the same as in ancient times. Mostly this type of tourism is practiced locally and nationally.

Traits of spa tourism:

- The relatively small number of participants (involving suffering population more and very little the rest of the population);
- Takes place with significant fluctuations throughout the year, even if it has a regular character;
- Attracts tourists both urban and rural;
- Length of stay is medium and long;
- Has a high social and economic efficiency;
- Benefits from specific features.

Natural resources that contribute to the development of curative tourism are:

- Mineral waters;
- Mud treatment;
- Mofetarian gas treatment;
- Salt mine therapy.

In order to have beneficial effects on the body these natural elements must have certain qualities and to exist in certain amounts.

Indicators tracked at mineral waters are:

- total Mineralization ≥ 1,000 mg / L
- CO_2 (free or bound in bicarbonate) ≥ 1.000 mg / L.
- Iron ≥ 10 mg / L
- Iodine ≥ 1 mg / L.

2 *** WTO, WTTC, The Earth Council-Agenda 21 for the Travel an Tourism Industry: Towards Environmentally Sustainable Development, 1995.

- Sulfur (titre) ≥ 1 mg / L.
- H2S ≥ 1 mg / L.
- Arsenic ≥ 0.7 mg / L.
- Bromine ≥ 0.5 mg / L.
- Radioactivity ≥ 80 uM / L.

In mud treatment we track, in terms of:

- Quality:
  - The density;
  - The pH;
  - The RH index (potential oxidation - reduction);
  - Specific heat;
  - Texture;
  - Slip resistance;
  - The content of organic matter;
  - The degree of decomposition of peat;
  - Mineralization and ionic composition of the soaked solution;
  - The content of hydrogen and sulfur.
- Quantity:
  - Certified reserves ;
  - Reserves in the balance sheet B and C category.
- Mofetarian gas use in therapy is conditioned by:
  - CO_2 content;
  - The content of H_2S;
  - The content of other gases;
  - Radioactivity.
- Spa tourism includes salt mines for therapeutic usage, in the mean time also monitoring:
  - Thermo-hydro-barometric indicators;
  - Indicators for air quality;
  - Physical indicators;
  - Ionization;
  - Concentration of aerosol particles;
  - Radioactivity;
  - The content of gases (CO_2, F_2S, N_2, O_2, SO_2);
  - The content of the chemical elements (Na, Cl, K, Ca);
  - Microbiological indicators (air, micro-conservatory, fungi).

In bathing treatments carbon dioxide is also used which can be found in areas of volcanic and geological moffetic halo , in which case we speak of free gas emanations and carbonated mineral water that is captured and separated from those waters.

Buzias – Spa resort

The town is situated in Timis county, 34 km from Timişoara, in a transition area with hills and piedmont plain at the contact between the eastern Banat plains and the Banat hills (Silagiu Hills) in western Romania. The climate is moderate continental and has Mediterranean influences.

Figure 1. Positioning Buziaşului on the map in relation to Timisoara
Source: *www.ccserban.ro*

GPS Coordinates: 45 ° 39'N 21 ° 36'E. Access can be made either by road or by rail.

In Roman times in this region there was the Ahibis fort (dr. Gheorghe Popovici, eng. Adam Cucu), also known because of carbonic acid springs.

Some specialists say that the town had been documented in 1072, others in 1320.

Buzias is one of the spa resorts in Romania that treat cardiovascular diseases, central nervous system, neuro-endocrine disorders, nutritional and metabolic diseases, kidney and urinary disorders, digestive problems and has been declared a spa resort from 1819. Treatments have prophylactic, therapeutic and recuperative purposes. This resort uses the slogan "The resort of your heart."

Water temperatures in Buzias ranges from 14 to 15 ^{0}C.,and the depths are between 75 and 110 meters and have highlighted three mineral horizons, all aerated with CO_2. These layers are:

- groundwater at shallow depths of 7-10 m;
- Aquifer depth, meaning 17-70 m, containing water with a high hydrostatic ascension of 2.5 m;
- Artesian aquifer in connection with the crystalline of less than 80 m, amounting to 25 to 30 m above the ground and the CO_2 2g / l - 2.4 g / l.

Mineral waters from Buzias have the following chemical composition Iron (Fe), sodium bicarbonate, chloride (Cl), calcium (Ca), magnesium (Mg), bromine (Br) and carbon dioxide (CO_2) and are hypotonic. Currently there are seven springs, 6 being exploited for therapeutic purposes, the seventh being operated by the company "PHOENIX" commercially.

In addition to these waters, in the major crystalline fractures carbon dioxide rises to the surface. Mofettes (natural density) are present in the western part of the country only at Buziaş. In its composition, the weight of carbon dioxide is 91.5 to 98%, 0.02-0.04% of argon, methane of 0.4 to 3%, the rest being oxygen and nitrogen. They are indicated and used in external treatments to treat cardiac, circulatory, neurological and rheumatic disorders.

SHALE GAS

More and more there is talk about shale gas, the possibility of their exploitation and the benefits obtained from exploiting it.

Shale is metamorphic sedimentary or waterproof rocks that are able to unfold quite easily in sheets or thin plates with parallel surfaces.

Shale gas is natural gas (methane) trapped between the plates of shale or coal seams, but at a greater depth (3-5 km) than conventional gas fields. These gases are considered to be unconventional because they cannot be found in compact areas in the form of pockets.

Recent studies (2013) made by the U.S. Energy Information Agency about shale gas resources in Europe have revealed that Poland, France and Romania hold the largest such reserves.

The idea to exploit such gases started from the states needs to have independent energy.

Currently, the U.S. have developed a technology to extract shale gas and have already started exploitation. The method of extraction combines drilling and hydraulic fracturing digging vertically and then horizontally until they reach depths of 3-6 km. In order to make holes in the probe an explosion is made in the horizontal shaft.

For fracturing the rocks at each drilling there are introduced, under a very high pressure of 1000 atmospheres, millions of gallons of water mixed with sand and chemical additives. The released gas is withdrawn through the probe tube, being pushed along by the drilling fluid injected through the internal pressure in the rock.

Figure 2. Scheme hydraulic fracturing method for shale gas
Source:*Energy.gov (Ziare.com)*

The issues that arise with the use of such a method to exploit shale gas are multiple and have major repercussions on the environment and human health.

The risks of such operations are:

- Diminishing the fresh water supplies (declining resource) by the huge consumption with each drilling operation;
- Pollution of groundwater and surface streams with chemical fluid that exist while fracturing ;
- Increase in radioactivity in the area with chemicals used in fracturing and while passing the clay asphalt deposits that are naturally radioactive;
- The possibility of explosions and blasts all over extraction;
- Tectonic risk, landslides and earthquakes amplification;
- Air pollution by various chemical elements emitted by drilling station chimneys;
- The appearance of the greenhouse effect from the huge quantities of methane that are emitted into the atmosphere (about 7% of the amount of methane is lost in extraction);
- Leakage of toxic substances, particularly containers used for the storage of recovered fluid;
- Biological risk, meaning the destruction of vegetation and fauna on very large surfaces and the occurrence of cancer in the population and workers in the area;
- Noise pollution;
- Sealing off large areas of fertile land;
- Destruction of existing infrastructure.

An area where exploitable shale gas will be filled with many probes, and their life length is low, between 5 and 8 years.

Worldwide, according to Greenpeace shale gas exploitation was banned in France, Bulgaria, Ireland, South Africa and several states in the U.S. A.

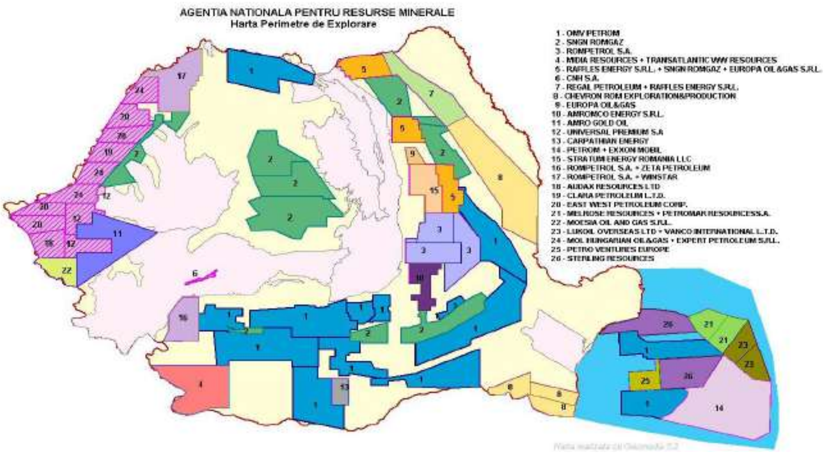

Figure 3. Operating perimeters and companies which have been leased

***Source:** Stopfracturare.ro*

In Romania a few perimeters have been defined and assigned by the National Agency for Mineral Resources that can be exploited naturally. A large number of companies are on this map.

CONCLUSIONS

In Buziaş, Timis County, there are reserves of shale gas and a company ready to exploit them, Universal Premium SA

The Romanian Government has approved in the government decision nr.1188 the petroleum agreement and concession for exploitation, development in the EX-11 Buziaş perimeter.

The western part of the country, in terms of seismic hazard is the most important active seismic region, (the focal depth points are between 5 and 30 km).

Typically, where there is natural gas there are radioactive processes as well. Now, following global gamma evaluation being conducted in Buziaş by members from the Hobby Club (Eng. Golosie Mircea- coordinator), the following results were obtained:

- Probe Baia 1 = 0,6pci/l
- Probe Baia 2 =2,4pci/l;
- Probe 3 = 1,2pci/l
- Probe 4 = 2,4pci/l.

The uranium values are still within legal limits allowed (up to 15 pci / l), but the exploitation of shale gas and hydraulic fracturing will change these values. Given the fact that Buziaş is a treatment resort of national interest the results of drilling activities would mean the disappearance of this city. The small distance from Timisoara would affect this city, too.

A prohibition, at least until we observe the effects of such operations in other parts of Europe would be welcome.

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IMPORTANCE OF LANDSCAPE CHARACTER IN THE PROCESS OF ESTABLISHMENT OF EDUCATIONAL (NATURE) TRAILS IN FUNCTION OF ECOTOURISM

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ABSTRACT

The great potential of natural and cultural tourist resources in Serbia is not adequately exploited. Modern trends in tourism are more and more based on alternative forms in accordance with the principles of sustainable development. Taking into account that tourist activities are not carried out independently from the landscape, landscape values are reflected in its character, integrating various landscape dimensions (natural, cultural, visual, historical); therefore it can be considered a potential for forming of educational trails in function of development of ecotourism as well.

Key words: ecotourism, landscape character, educational trails, nature trails.

INTRODUCTION

Special forms of tourism that have been developed in recent decades are based on activation, preservation and coordination of tourist activities with natural and cultural values, as well as with the values of local community, that have a possitive effect on the environment. Ecotourism is an alternative form of tourism that has recently appeared as one of the courses of tourist development, defined as “ecologically responsible travel and visiting of relatively intact natural areas, with an aim to enjoy and admire the nature (as well as all accompanying cultural characteristics from the past and the present) and to promote preservation, with minimized impact of visitors and provision of socio-economic benefits for the local population which is actively engaged in ecotourist business” (Ceballos – Lascurain, 1996).

Protected natural resources are the potential for development of eco-tourism in Serbia, making approximately 5% of the territory of the Republic of Serbia, viz: 5 national parks, 17 nature parks, 16 landscapes of exceptional forms, 5 Ramsar sites, 69 nature reserves, 1 biosphere reserve, 3 protected habitats, 325 natural monuments and 42 protected areas of cultural and historical values. Natural resources with certain international status are the areas nominated for the Emerald European ecological network, 61 Important Plant Areas, 42 internationally important areas for birds (within the program of Important Bird Area / IBA) and 40 selected Prime Butterfly Areas/PBA (according to the data provided by the Institute for Nature Conservation).

According to Page and Dowling (2002), the five key principles on which ecotourism is based are as follows: foundation on nature, environmental sustainability, offering environmental and cultural education, improtance for local population and providing satisfaction to tourists.

Educational paths (nature trails) support all the above mentioned principles and therefore their formation can be considered important for the development of ecotourism offer in Serbia. First of all, they are important at the local level, they require systematic valorization and planning actions based on sustainable development. Tourism, being a specific human activity, is directly connected or depends on the environment (Gunn, 1988), whereby not only that it occupies certain space, but it influences the environment (positively or negatively) in numerous direct or indirect ways. Landscapes and their values integrated in a unique character represent the capital of the populationm and landscape quality is a precondition for tourist activities. Landscape character integrates various landscape dimensions and values and to this effect they can be considered as the basis for planning and arrangement of educational paths and development of ecotourism program.

The aim of this paper is to gain new knowledge on the role and importance of landscape character in the process of establishment of educational paths. Landscape characterization forms the information base that enables making strategies and decisions on the courses of future development and conservation of unique characters, while their interpretation in the context of creation of educational paths network makes it possible to establish a conceptual framework for their implementation and realization of designs and projects defined by planning documents.

This paper shows a conceptual dependence between educational trails and landscape character, being the initial potential in the process of their establishment, whereby the basis for realization of ecotourism development goals is laid.

EDUCATIONAL (NATURE) TRAILS

Educational trails (nature trails) are specially marked trails connecting different natural or cultural - historical facilities. Their primary function is acquisition of new knowledge or renewal of the existing one, as well as recreation and tourism. They are designed as pedestrian routes in natural environment and most frequently refer to protected areas. Educational trails have been developed as the consequence of urbanization and alienation of man from the nature, with the aim to turn the mankind back to natural values and to make contact with the nature, to raise awareness about the importance of natural, ecological and cultural values.

Educational trails can be theme paths, which, in terms of content, functionality, symbolism, include several facilities, namely, several elements in space, and whose theme is related to natural sciences (botanical, zoological, ecological, geological trails etc.) or to forestry, geography, history and culture and other fields.

The first official trail of this type was created in New York in 1925, and already in 1930 in Germany. There are over 1,000 nature trails in Germany nowadays, most of which are formed in forest environment with an aim to point out the importance of conservation of forest ecosystem by the principles of sustainable development and management, preservation and importance of biodiversity.

Nature trails are arranged and marked paths with accompanying infrastructure and they can include environmental and educational centers, places for rest and fittings, information desks and boards with accompanying photos, maps, multimedia contests, and they often include programs of thematic events during the year. Organization and design of educational trails include the following stages (Fig.1) (Kedra, 2003, according to Ferchmin, 1993).

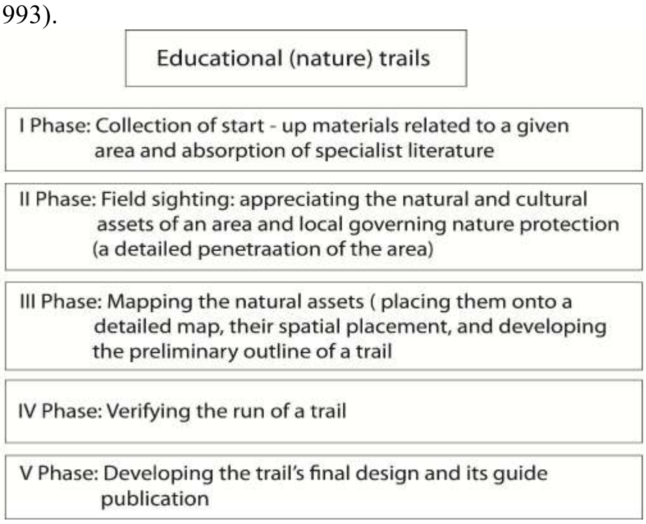

Figure 1. Organization and design of educational trails

Important issues during establishment of educational trails are: which theme or type of trail can be formed, what are the natural and/or cultural resources that can be connected and what is their correlation with a particular theme, in which way it is possible to physically connect and group the facilities and spatial environments, ownership and legal status of resources, competence for protection and conservation of resources, planning and statutory legislation, what capacity and how many visitors can be accepted without disrupting natural values and/or the protected area, conflicts with other methods of use, guidelines for design of trails and accompanying elements (what materials, contents and path elements will not disrupt the environment, trail routing and length, how long it takes to go through the entire trail).

Trail formation is carried out in an environment, in a certain landscape and enables development in accordance with its unique character, whereby the route design requires considering of the environment and atmosphere characterizing the route. Structure elements, indicators of landscape character represent the framework for formation of educational trails, and since they are most often formed as nature trails in protected areas, the analysis of potential influences is necessary as well.

Greenways and cultural paths have a similar conception. Greenways are defined as multifunctional trails intended for non-motorized users (pedestrians and cyclists) that can be local, urban and interurban, connected with green corridors, historical routes, rivers and railway lines. They refer to the local level and they are managed by local population, offering the framework for local initiatives and projects which aim to protect and promote the nature, cultural heritage and sustainable forms of tourism (Central and Eastern Greenways /CEEG/).

Cultural trails connect tangible and non-tangible cultural assets, taking into account the natural values within the itinerary as well. Their conception primarily refers to a broader framework and national or international level, and they also include motorized traffic. Educational trails can be incorporated in a broader framework by networking with greenways and cultural trails whereby a network of trails with different contents and themes is formed, being of importance at both regional and national levels.

LANDSCAPE CHARACTER AS THE BASIS FOR ESTABLISHMENT OF EDUCATIONAL TRAILS

Taking into account that ecotourism is developed in areas of high natural value, and forming of new contents and trails includes interventions that affect the environment, their planning and implementation need to be carried out in relation to the environmental potentials. Trail (trail network) development must enable the connection between tourism and the local population, as well as the connection with natural characteristics in a way that would not bring them into conflict. If not realized in accordance with the environment, new contents and elements may lead to disruption of landscape appearance (visual dimension and beauty being one of the factors based on which protected areas are evaluated), as well as to negative impacts upon biodiversity by intersection of important habitat types.

Landscape character consists of a certain combination of geology, relief, land, method of use created by action and interaction of natural and/or cultural factors, and it incorporates integrated interpretation and reflection of physical, aesthetic, social-cultural and historical influences and space values. (Fig.2).

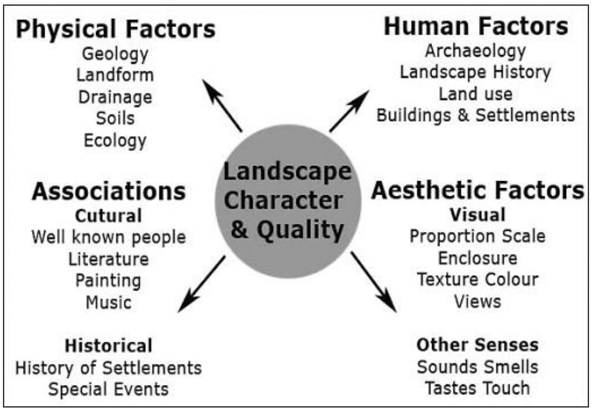

Figure 2. Landscape character and quality
(Credits: Cranborne Chase, Area of Outstanding Natural Beauty)

Natural and cultural-historical conditions are analyzed on the basis of geological and geo-morphological characteristics, characteristics of vegetation and forests, hydrographic and hydrologic properties of the terrain, climatic conditions, areas of nature protection and relief modification resulting from anthropogenic activities and modern geodynamic processes, further, on the basis of infrastructure, architecture, history and archeology of the area, previous local and foreign landscape typologies, planning documentation and corresponding legal regulations.

Anthropogenic influences are defined through three dimensions: land use and management, character of settlements and facilities, field scheme and type. Therefore, landscape character is the exponent of identity in which it is necessary to look for the interest, and at the same time it is the level at which problems are observed and solved (Васиљевић, 2013).

Landscape characterization is used in early phases of planning and design. The obtained results and data provide valuable and determining information for bringing decisions regarding the scope and nature of future development (Cvejić et al., 2008).

Identification and interpretation of a specific landscape character and value and quality assessment are crucial in modern space planning and management. Among other, the method of landscape character assessment provides for the following: *forming of guidelines and rules carried out through plans and programs in the field of environmental protection, tourism, forestry, protection of natural and cultural heritage, as well as defining and forming of planning and construction rules, programs and special development plans* (Васиљевић, 2009).

The procedure of landscape character assessment is carried out through two phases; the phase of *landscape characterization* meaning the interpretation and classification of landscape character types, and the phase of evaluation or *"decision making"* which is carried out in relation to the set goals and purposes in terms of forming strategies and guidelines.

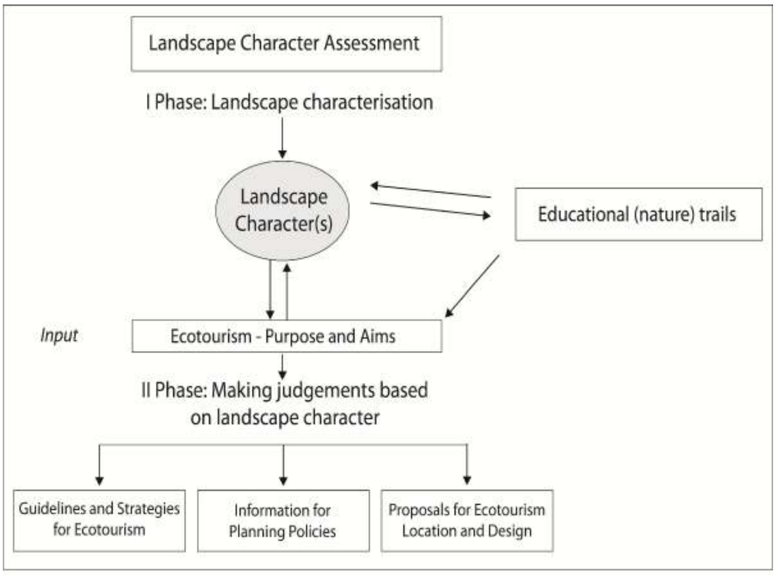

Figure 3. Relationship between landscape character, educational trails and ecotourism

In the context of development of educational trails, through landscape characterization, in the first phase, the information basis is created providing organization and design of educational trails (see the diagram Ferchmin, Fig.1.), whereas in the second phase of landscape character assessment, strategies and guidelines for development of ecotourism are formed (Fig. 3).

CONCLUSION

As a form of sustainable tourism, ecotourism requires minimum strain and impact on the area where it is realized.

Landscape characterization provides for a systematic valorization of all natural and cultural resources of a certain area, whereby the development of tourist location identity is directed according to the features and identity of the environment.

Not only does the landscape character directly enable integration of educational trails of various themes as a form of tourist offer (which implies development of ecotourism), but the educational trails also promote and increase the recognizability of landscape character where they are formed (Fig.3). In that way ecotourism supports and promotes landscape character at the same time.

Since forming of educational trails refers to the character of the landscape where they are created, active participation is required in further landscape management. Conservation and protection of the unique landscape character are set as an imperative of future development and new initiatives.

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STRATEGIC PLANNING OF TRANSPORT INFRASTRUCTURE AS BASIS OF ECOTOURISM DEVELOPMENT IN NEGOTIN

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ABSTRACT

Developed transport network is a precondition for economic and tourism development of areas. Strategic planning of transport infrastructure is of great importance for both, Municipality development and for to achieve development of tourism. The basic potentials of the tourism industry are based on an integrated combination of natural, anthropogenic and spiritual potential of space. The tourism industry has not yet reached full recognition and various travel resources are under-valued, although the area is part of a wider tourism region Timocka Krajina.. The main strategic orientation is that the sustainable tourism development is an important developmental perspective for Negotin area while the basic concept of tourism development is based on functional networking of tourism and activities in the wider regional level and internal organization of tourism at the local level.

Key words: Transport network, Tourism, Development, Negotin.

INTRODUCTION

The specific situation and historical development of the Municipality, as well as resources and values and developmental processes that occurred in the past, especially in the last few decades have affected the structure and use of space. Besides natural, the development was influenced by anthropogenic factors, often disturbing the natural conditions and opportunities.

Negotin is located on a plain surrounded by mountain ranges (Miroč, Crni Vrh, Deli Jovan) and open space on the eastern and southern sides. Developed transport network is a precondition for economic and tourism development of areas and largely follows and allows the development of human activities. In municipality of Negotin are conceived all modes of transport: road, railway, river, air, intermodal and bicycling, so that it has a significant transport potential. The paper will present the mutual interaction and functional connectivity of planning solutions for development of transport infrastructure and development of tourism.

The survey was conducted using the integral method, with equal and interdependent observation of three basic dimensions of the spatial development of transportation infrastructure: physical - ecological, economic and socio-cultural in real and assumed context of economic and tourism development in the Municipality

For the analysis and definition of solutions in the field of tourism, the different indicators were taken into account. Considering the complexity of the tourist system structure, it is understandable that in the previous researches a large number of indicators related to the relevant phenomenon have appeared. The factors affecting the selection of indicators to be used in the management of a tourist destination are: approach to sustainable development (minimal or complete), measurable indicators, the available financial and human resources, the interests of the key stakeholders of tourism in a given destination, public support, political influence, etc. (R. Butler, 1999).

RESEARCH RESULTS DEVELOPMENT OF TRAFFIC INFRASTRUCTURE

Adequate development of traffic infrastructure in Negotin is defined on objective basis and in an optimal manner follows the development of other urban functions vital to the economic development and quality of life. Organisation of Municipality, as well as its spatial development and integration into the wider regional systems in the region, largely depends on the development of adequate traffic infrastructure.

Project of Pan-European transport corridors, defined in 1994 on Crete, and later amended in Helsinki in 1997, is of great importance for the Municipality which ultimate goal is functional inter-regional integration, with a simplified and accelerated traffic flows that include open borders and also improved and harmonized transport networks and services (Grčić M., Ratkaj I., 2004.). Related to this, **the position on the Danube** (Corridor VII) and the relative proximity of the two other **European multimodal Corridors** - X and IV, whose full exploitation and activation of developmental potential is still expecting, opens possibility for more perspective planned development of tourism. Connection with Corridor VII is realising through the port in Prahovo and transportation activities that are taking place on this river transit route, while the Municipality is associated with the corridor X through road directions (state roads of I and II category).

Road traffic

The basic conceptual orientation is traffic opening and increasing of area accessibility, primarily by rehabilitation, reconstruction and construction of existing network and by quality connection with the state roads network of Serbia. Spatial Plan of the Republic of Serbia defines the corridor of the highway E-771, which follows the route of the SR of I category No. 25, as a activity beyond 2014. The corridor, width of 500 m, is kept until further notice, bearing in mind the uncertainty of its realization.

State road network will consist of two SR of I category and seven SR of II category, which will liaise with regional centres in Zajecar and Branicevo district, Belgrade, Nis and the Corridor X. The road network is necessary to complete with network of municipal roads, which need to be reconstructed, modernised and upgraded with new sections, while the unclassified road network will develop together with evolvement of the settlements and capabilities of the local community.

Spatial Plan of the Republic of Serbia defines the development axis as developmental belts that will contribute the integration of spatial and functional relationship of regional entities in order to improve territorial cohesion. Model of polycentric development of the Negotin local economy includes three development zones of economic development: Negotin valley, the Danube development belt and the northwestern (mountain) belt with centres at different levels:

1. Centre of I level - Negotin, commercial and industrial centre of the diversified structure of the economy;
2. Centre of II level – Prahovo, industrial and port centre;
3. Centre of III level - small development centres in rural areas – Jabukovac, Stubik, Kobisnica with the manufacturing and service activities, and Mihajlovac and Rajac as tourist centres; and
4. Rural settlements with facilities for the storage and processing of local raw materials and complementary services to tourism, agriculture, etc.: Milosevo, Dusanovac, Karbulovo, Popovica, Aleksandrovac, Kovilovo, Bracevac, Samarinovac, Jasenica, Srbovo, Sikole and other.

Traffic concept of road network development in the urban area of Negotin is contained in functional roads segregation. Considering the importance of the streets, they are classified into the following categories: city highway; collecting street, access roads and car-pedestrian walkways and parking lots. The existing road network is updated with new routes, which follow a planned urban development from the perspective of the establishment of new residential and commercial zones.

One of the solutions that will contribute to cost-effective flow of goods is relocation of route of SR No. 25 to the position of a road that leads from Bukovo to Kladovo along west part of Negotina. In addition, it is proposed the rehabilitation of sections from border with the Zajecar to sattlement Bukovo in length of 12.0 km, with reconstruction of pavement and signalisation together with pavement widening, aimed to safer transport of heavy trucks that gravitate to the port "Prahovo".

The eight SR of II category run through Municipality in total length of 143.0 km. Their expanding, rehabilitation of the pavement and signalisation is proposed at the sections that lead to the most attractive spots. In order to improve the efficiency of origin-target and transit traffic is defined a new road of II category at the location of relocated route of SR No. 25, on section Samarinovac - Dusanovac - Mihajlovac - Plan boundary, in length of 26.12 km. It is necessary to build following sections of the SR of II category:

- SR of II category No. 248a on section Kovilovo – Bracevac – Jasikova, in length of 21.3 km; and
- SR of II category No. 260 on section Sikole – Plavna, in length of 16.0 km.

The most important interventions are planned on **local road network**, which has the role of linking villages and tourist sites with the centre of the municipality and with the road network of higher rank. Increase of transport accessibility and connectivity with centres in the network of settlements, economic potential, tourism offer in the area and rural regions will be achieved through reconstruction and construction of municipal roads. The rehabilitation / reconstruction of municipal public roads are planned with total length of 154.07 km. Priority activities will be directed to the reconstruction of pavement or installation of vertical signalisation.

Railway infrastructure

Affirmation of rail transport is possible by modernization of all capacities, in order to become more competitive in the distribution of requests for transportation, especially for long distance. The existing single-track railway line (Nis) – Crveni Krst - Zajecar- port "Prahovo", in length of about 37.7 km, has a special role and importance because it connects the port "Prahovo" with Nis region. Economic evaluation and transport efficiency of the railway line implies:

- Reconstruction and modernization of railway line and facilities in order to enable railway line for the allowed load of 22.5 tons per axle and a speed of 60 km/h;
- Electrification with system of 25 kV, 50 Hz and the construction of power plants and substations;
- Provision of free profile UIC-C and enabling use of all technology for intermodal transport without restrictions;
- Modernization of security system for line and stations; and
- Arrangement of stations and securing of road-railway crossings.

It is also necessary to denivelate crossings at the intersection of railway line and SR of I category No. 24, in the area of Negotin and Kobasnica and intersections with municipal road between settlements Rajac and Zlokuce, as well as recession of the four road-railway crossings in SR No. 248 and one at the municipal road Rogljevo - Kovilovo.

River traffic

The Danube River represents basis of the river transport in the Republic of Serbia, and as the European corridor VII represents link between the countries of Western, Central and Eastern Europe, the Mediterranean and the Middle and Far East.

The economic development of the municipality, but also and wider area, largely depends on adequate development of port "Prahovo" as an intermodal centre in Eastern Serbia and ports in Donji Milanovac, Tekija and Kladovo, while in the Municipality is envisaged construction of piers and marinas in areas of settlement Prahovo, Mihajlovac and Radujevac in order to enrich the tourist offer.

Bicycle traffic

Bicycle traffic is expanding with the intention to minimize the negative effects that are carrying other modes of traffic. Under the patronage of EU, the European

Cyclists' Federation (ECF) was launched in 1998 the project of cycle route network throughout Europe (EVP). The cycling transversal EuroVelo 6 is planned through the valley of the Danube. The path leads along the main road from the Djerdap to Negotin continues to Bulgaria at the border crossing Bregovo.

The directions of bike paths in the municipality are along major road corridors:

1. Negotin - Monastery Bukovo - Majdanpek municipality, along the corridor of SR No. 24 in length of 35.2 km, that joins the track EuroVelo 6 in Negotin;
2. Stubik - Monastery Vratna – Slatina, in length of 17.4 km;
3. Sarkamen - archaeological sites "Vrelo", in length of 10.5 km;
4. Plavna – Sikole – Stevanske livade, in length of 17.3 km;
5. Negotin – Mokranjske stene, in length of 15.7 km;
6. Mokranje (connection with EuroVelo6) – wine cellars in Rajac, in length of 10.9 km.

Alignments of the bicycle paths follow largely the tourist movements, which complete the tourist offer in accordance with the principles of sustainability and standards of EU.

THE BASIC POTENTIALS FOR DEVELOPMENT OF TOURISM

Tourism in the Danube basin has become one of the most important branches of the economy and the driving force of the development of tourism and complementary activities. In order to tourism become one of development component of the Danube basin in Serbia, it is necessary to valorise the potential and values of tourism, where the tourist function also affect the development of other sectors of the economy (Milijić S., Basarić J., 2011). The main strategic orientation is that the sustainable tourism development is an important developmental perspective for Negotin area while the basic concept of tourism development is based on functional networking of tourism and activities in the wider regional level and internal organization of tourism at the local level.

It is possible to develop different types of tourism in Municipality such are: excursion, ethno, transit, sport, nautical, educational and hunting tourism, along with the potential activation of spa tourism. Besides good network of primary roads, whose importance is reflected in the inter-regional connections, a precondition for further valorisation of tourism potential is realization of a road network of secondary importance. In this regard is foreseen rehabilitation, modernization and reorganization of the network of SR of II category and municipal roads, which will enable implementation of the following projects:

- *Excursion tourism.* In the village Vratna-Jabukovac area around Sikola (Stevan meadows) Mokranjac rocks, and other attractive parts of the Municipality (sub Miroc zone, the Danube area);
- *Negotin wine callars (pimnice).* With already acknowledged Rogljevac and Rajac wine callers, it is necessary to reconstruct and activate Stubicke wine callers;

- *The Danube area.* Combination of sports and recreational activities on the water along the beach in Mihajlovac, Radujevac and other suitable places. Using port Prahovo and marinas in Mihajlovac and Kusjak, as well as in other locations, and
- *Itineraries.* Independently or with neighboring municipalities and in cooperation with Romania and Bulgaria will be defined more itineraries that would be found in the tourist industry (wine route, food rout, farm route, bike paths, etc.).

The environment is well preserved in the largest part of the territory. Additionally, the area is rich of natural and cultural values and rarities especially in hilly and mountainous areas. These benchmarks, together with manifestation, traditions, customs and ethnic composition, are basis for the development of tourism, as seen in the broader system of tourist itineraries in European (Danube), national and regional level.

We can be distinguished potential tourism areas that include items relevant to tourism (Ristić N, et all, 2013):

- The Danube area – the development concept is based on the combination of sports and recreational activities, fishing, nautical tourism and transit tourism;
- Area of urban settlement Negotin – except the indigenous architecture, cultural and spiritual objects (museum, Mokranjac house, monuments Mokranjac and Hajduk Veljko, monastery Bukovo and others.), this area is the basis for the manifestation, convention and educational tourism;
- Mountain (sub Miroč zone) - located in the western part of the Municipality that is regionally observed in the system with the municipalities of Bor and Majdanpek. Extremely rich natural and cultural heritage of the area (monastery Vratna, Zemna and Vratna prerast, canyon Zemna, Jabukovac village and all along to Stevan meadow and Mokranjac rocks at Sikolska river), suitable for hunting, formation of marked mountain trails, excursion tourism; and
- Timok (ethno) zone – with centre in Rajacke and Rogaljske wine cellars is predestined for the development of ethnic tourism (with special emphasis on traditional products of wine), European bike paths and others.

It is necessary to connect the zones with the tourist itinerary at local and regional level based on the routes: cultural and historic sites, traditional products (wine, food, fruit), manifestations, etc. incorporated into a wider regional system of daily or multi-day organized tour.

CONCLUSION

Tourism values in the Negotin municipality are not adequately valorised because of among other things and small degree of availability and lack of quality road network and other modes of transport. The important role is the existence of a modern, safe, reliable and efficient transportation system. Planned development and solutions provide better activation of resources in a responsible and sustainable manner, taking account of endangering their characteristics.

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DJAVOLJA VAROS – A NATURAL PHENOMENON

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ABSTRACT

Đavolja Varoš (”Devil’s Town”), a peculiar formation described as ”earth pyramids” or ”towers”. This attractive area consists of two rare natural phenomena. The first one is presented with 202 rock formations created by strong soil, topped by andesite blocks/caps weighing as much as 100 kg, appearing unreal and yet lasting for centuries. The second geo-attraction consists of two springs (Đavolja voda/ Devil’s Water and Crveno vrelo/Red Well) of extremely acidic water with high mineral concentration.

Key words: Đavolja Varoš, legends, unique geomorphological phenomenon, tourism, traditional beliefs.

INTRODUCTION

Đavolja Varoš is located in southern Serbia, in the hearth of the Radan Mountain, on the northern slope of Sokolov Vis, hidden in the valley of the brook Žuti Potok (tributary of the river Velika Kosanica, in the basin of the river Toplica). It is located 27 km from Kuršumlija and 9 km from the Prokuplje–Kuršumlija–Priština highway, of which the final kilometre has to be crossed on foot.

Figure 1. The entrance to the Đavolja Varoš

On the hillside, densely overgrown with forest, the erosion has destroyed the cover and revealed a unique natural phenomenon, the only one of its kind in our country and very rare in the world. Đavolja Varoš is currently ranked 1st on a New Seven World Wonders of Nature list in the caves, rock formations and valleys category. In support of the initiative of the New7Wonders Foundation, founded by Bernard Weber, the Municipal Tourist Organisation of Kuršumlija and the Joint-Stock Company Planinka of Kuršumlija have nominated Đavolja Varoš in the contest to select the seven wonders of nature. The nomination has been supported by the Serbian Ministry for Diaspora and the Tourist Organisation of Serbia.

Figure 2. Map of Đavolja Varoš

Figure 3. Đavolja Varoš (Devil's Town)

ĐAVOLJA VAROŠ (DEVIL'S TOWN)

The wider area is known for the volcanic activity during the recent geological past, and today it is an ore-rich area known as the "Lece andesite massif", with hydrothermally altered andesite rocks later destroyed by intensive processes of kaolinisation, silicification, and pyritisation. Besides changes in petrographic composition and colour, these processes have caused significant changes of mechanical properties of andesite rocks. Their inner connective capacity is weakened, so that they have become very susceptible to processes of physical and chemical destruction and decay, and to runoff influenced by disorganized surface waters and rain torrents. The quartz and quartz-breccia veins, as well as lenses of volcanic tuff, breccias, and agglomerate are fitted into the hydrothermally altered andesites. The steepest slopes in the valley of the brook Žuti Potok are made of these dark, reddish rocks.

Figure 4. Earth pyramids

In their surface layer, the watershed area and the higher parts of the slopes in the valley of the Žuti Potok, particularly in the trenches Đavolja Jaruga and Paklena Jaruga, are made of diluvial material of Quaternary age, up to 20 m thick. This is a heterogeneous, relatively poorly bonded material, in the composition of which blocks, large fragments, and fine particles of different volcanic rocks (andesite, its varieties, and pyroclastite) take part. However, the basic connective substance is made of yellowish clay component. The contact line between the diluvial layer and the foothill is steeply inclined towards the riverbed of the Žuti Potok, and can be traced along the open profile in the trench Đavolja Jaruga.

In the middle part of their longitudinal profiles, the beds of the trenches are getting closer to a distance of only 50 m, due to which their watershed is narrowed and the erosion has its maximal effects at this point. Right here is the place where the earth pyramids started to form. They are irregularly scattered, forming a true "forest" of turrets and pyramids, and in this area they can be traced from the initial forms to the degree of maximal development, when they start to crush. They are up to 15 m tall, and their width is around 4-5 m at the base, and 1 m at the top. Most of the turrets have a cap or a head –

an andesite block that protects them from destruction, while some of them have lost such shield.

The primary, initial agent in formation of the earth pyramids is the rain and its runoff. Mechanical destruction occurs under the strokes of the rain drops, after which the clay components are being dissolved and removed from the surface layer, and the initial, miniature erosive furrows, as well as removal of the more and more large quantities of the loose material. However, the material under the rocky blocks was protected from this "bombardment" of rain drops and runoff, so that it remained on the slope in the form of short primary pillars with "tables". Runoff of the material and cutting of the trenches occurred not only by gravitation, down the trenches, but transversally as well, between the pillars.

In this way, more than 200 earth pyramids, towers, and turrets were formed, 2 to 15 m tall, 3 to 5 m wide, with andesite cones at the top, positioned between the two trenches, Đavolja Jaruga and Paklena Jaruga, as well as in the local watershed between them.

Apart from this geomorphological erosive phenomenon, there are two hydrological rarities in Đavolja Varoš, specifically two highly mineralized springs. In the upper part of the trench Đavolja Jaruga, upstream of the earth pyramids, there is a spring the locals call"Đavolja Voda" (Devil's Water). The analysis of the water revealed that it is extremely acidic (pH is only 2.7), and that the concentration of aluminium, iron, copper, rubidium, manganese, lithium, and sulphur is 10 to 100 times greater than maximum allowed for drinking water, which makes it unpotable.

The other spring, known as "CrvenoVrelo" (Red Spring) is a source of highly mineral water. This water is so mineralized with iron that it takes on a distinctly reddish colour, with the mineralization index as high as 17 mg/l. This water is undrinkable, but it can be used to wash one's mouth, and it tastes very sour and bitter. The locals say that the water is medicinal and that it should be used to wash one's face, eyes, affected body parts, etc.

Figure 5. "CrvenoVrelo" (Red Spring)

Owing to the isolation from road traffic and its limited accessibility, Đavolja Varoš has remained preserved and has not undergone changes caused by excessive presence of human activities. The only factor of degradation is the erosion itself, which progresses backwards, cuts slopes, destroys large pyramids, and constantly creates new ones.

The influence of man is the strongest in the wider area and it is most prominent in the condition of the forest vegetation. The valley of the right riverbank of the Žuti Potok is overgrown with sprout oak stands of low quality, poor health, and of incomplete and scarce canopy cover and timber volume. They are devastated by excessive and inadequate usage, by both felling and pruning for the purpose of supplementary cattle feeding. The southern exposition, steep slopes, and the character of the geological substrate slow down and prevent the natural restoration of these forests.

The left side of the valley, with northern exposition, is covered with beech forest, and occasional hornbeam trees can be found by the brook. Within the area of the bare headwater, the presence of the birch, as a pioneer species, is evident.

LEGENDS OF ĐAVOLJA VAROŠ

The unreal picture of oddly lined towers on the hillside, extremely sour-tasting mineral water, as well as traces of human activities in their immediate vicinity have strongly influenced the imagination of the locals, and that is how several legends about Đavolja Varoš came to be.

The first legend says that once upon a time here lived humble, quiet, and devout people. This was a thorn in the Devil's side, so he concocted the "devil's water" to make them forget about their kinship. After they had drunk the water, the stunned villagers decided to marry a brother to his sister. The Fairy, who, according to the legend, still holds the entire area under her protective wings, tried to thwart the Devil's plan. However, the Fairy failed to reason with the wedding procession, and they continued after the bride and groom towards the church for the ceremony. Desperate, she started praying to God to somehow prevent such incestuous affair. God answered her prayers, uniting heaven and earth and sending a strong cold wind to petrify the entire procession together with the bride and groom.

The second legend says that the earth pyramids represent petrified devils, which some people used to carry on their backs for a long time, receiving only evil and trouble in return. The people got rid of the devils by spending a night near the Church of Saint Petka, located in the immediate vicinity of theearth pyramids.

The third legend says that some school children, who preferred having fun to studying, made a wager with the devils that they would outsmart them. Having lost the wager, the devils turned into hoodoos, and the children, having broken their vow, turned into devils.

The fourth legend says that in the distant past there was a heavily fortified settlement in these parts, whose residents did not want to serve a terrible ruler, who was as evil as the devil himself. Their disobedience angered the ruler, and he gathered a massive army, destroying the settlement and turning the people into stone figures.

The fifth legend says that the earth pyramids represent wedding guests from two families, which long ago entered into a feud over the same girl. Both families sent their wedding guests for the girl, but they crossed paths at the site of Đavolja Varoš. Both families wanted to claim the girl for their respective grooms, so in order to avoid bloodshed, a mysterious force punished them by turning them into stone.

Almost no one dares to spend a night at Đavolja Varoš, because the locals keep spreading the story that after midnight, the entire area resonates with deafening and unreal screams and roars, almost as if they were coming from the very depths of the earth. There are mixed screams of men, women, and children, but, either due to fear or seeing things, the locals even claim that they saw silhouettes of some creatures, which are taller and much more hunched than humans. Many of those who wanted to verify this story ran in panic, scared by the choir-like screams and sounds. They recounted that they had felt a strange flow of air even though there was no wind and that pictures of the distant past, a wedding procession, music, song, and merriment had flashed before their eyes only to be interrupted by a terrifying silence, which scared them immensely.

TRADITIONAL BELIEFS

Near the upper viewpoint, on the remains from the 13^{th} century, the Church of Saint Petka was built five years ago. There is a belief that various diseases can be treated at Đavolja Varoš by placing ah and kerchief or a tissue soaked in medicinal water over the affected body part, and then tying the handkerchief/tissue to a nearby tree. Tissues can be also placed in front of the church. The belief that disease is left behind at that place has been around as long as Đavolja Varoš itself. It is believed that one week after the tissues have been tied to a tree, they should be buried deep into the ground to free the person who tied them of all their troubles.

Figure 6. Church of Saint Petka with a tissue-covered tree

TOURISM

As a tourist destination, Đavolja Varoš includes the ethno restaurant "Galerija" (Gallery), which is characterised by colourful ethno music, a specialty dish – lamb roasted under the bell, and very drinkable and healthy Prolom spa water.

A ticket for Đavolja Varoš costs only 350 dinars (3 euro).

The price of visiting this natural phenomenon is truly symbolical, and at the entrance tourists can buy a variety of souvenirs with motifs from Đavolja Varoš.

Figure 7. "Galerija" (Gallery) restaurant

Figure 8. View from "Galerija" restaurant

CONCLUSION

As a unique geomorphological phenomenon of outstanding magnetism, and a genuine geomorphological laboratory in the open, with particular scientific, educational, and cultural significance, Đavolja Varoš has been protected since 1959 as a natural rarity across the area of 3 ha. Later, in 1981, the protected area was expanded to 26 ha, and in 1988, this geomorphological natural monument was given the protected perimeter of

64.6 ha. Finally, in 1993, it was designated a natural asset of exceptional significance, covering an area of 67 ha, with the level of national significance.

The area is included in the Inventory of the Geoheritage Objects in Serbia (ProGEO) at the European level and in the national list of five areas that should be nominated for the UNESCO World Heritage List.

Today, Đavolja Varoš is on the UNESCO World Heritage List.

Figure 9. Earth pyramids

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POSSIBILITY OF TOURIST VALORIZATION OF VLASINA LAKE

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ABSTRACT

Based on the fact that the area of Vlasina lake is located in the southeastern part of Serbia, which is one of the economically most underdeveloped in the country, and has very modest tourism infra and superstructure, the aim of this paper is that the current plan to gain insight into the current situation and propose solutions to affirmation of the observed area. The task is to, with respect of laws and other legal acts in the sphere of protection and sustainable tourism development, comply proposals and plans, in order to establish a harmonious relationship of tourism development and environmental protection in the future.

Key words: tourism, protection, sutainable development, area planning, Vlasina lake.

INTRODUCTION

The Vlasina lake is located in the southeast of Serbia, in a valley elliptic as the lowest part of Vlasina plateau. Plateau is located at an altitude of 1230 m, area of 400 km^2 and is known by the name of today's artificial lake, and the earlier mud that was in the bottom. It is located between the high peaks of Rhodope mountain massif. On the western edge of the landscape mosaic and rounded Chemernik (1638 m) in the north, gradually giving way to the gentle mountain range Plane (Gramade) with Vrtop peak (1721 m). At the same part of the plateau rises lookout Bukova Glava (1472 m), and to the south the plateau is elongated and surrounded by mountain branches Vardenik, whose most prominent ridges Plesijevac (1664 m) and Stresar (1876 m). [1]

The lake covers an area of 16 km^2 at an elevation of 1213.8 m. In administrative and spatial terms located in the municipality of Surdulica (Pcinja district), not far from the border with Bulgaria. From the international road E-75 road and railway (linking Central with South Eastern Europe), in the valley of South Morava, 29 km away from the direction Vladicin Han - Surdulica and 51 km from the direction of Leskovac - Vlasotince - Crna Trava. From the border crossing Strezimirovci has only 17 km, where the road continues over a mandrel to the Bulgarian capital Sofia and 42 km across Bosilegrad, towards the border crossing Ribarci.

In the distant past in place of today's lake was the largest peat bogs on the Balkan Peninsula, Vlasina or peat soils of mud that was unique in its hydrographic regime and the living world. The construction of a large earthen dam and reservoir formation altered the characteristics of the entire area. However, located away from major roads and Balkan industry, which could collapse the beauty of the place Vlasina plateau has long remained almost untouched part of the nature of our country. More Jovan Cvijic spoke on the region in his book *Origins, peat bogs and waterfalls Eastern Serbia from 1896.* Conditions for the formation of peat bogs are leaking because of the high altitude due to lower air temperature was reduced evaporation. Because of such conditions, land is affected by moss and marsh vegetation which makes it more than affordable for education ponds and peat bogs.

However, human-hand the peat disappeared in 1949, and the place where the river Vlasina stood out from Vlasina peat dam was built, the so-called Vodojaza. Basen filled with water until 1954. The primary objective of creating Vlasina lake was exploiting the hydropower potential for the needs of HC "Vrla I, II, III, IV". Also nearby is the accumulation of Lisa from which water is over 4 channels switch to Vlasina lake. [2]

On the lake there are two islands - Stratorija (250 m long and 115 m wide) and Long part (480 m long and 150 m wide) as low forward cape. Physical - chemical characteristics of water Vlasina lake show that the water is neutral to slightly alkaline, low-mineralized, soft and rich in dissolved oxygen. Not burdened by the presence of heavy metals and can be characterize as water first class.

The lake has three functional units, as follows: [3]

- Vlasina Dumplings - the first point of contact with the lake, and functionally represents a kind of crossroads that directs visitors to the east and north. Most public office in this resort (post office, police, shops, bakeries, health center, the property of the Ministry of Defense), so logically viewed as a point of entry at Vlasina lake in the direction of Surdulica. Within the resort except public function is a motel and two resorts, and residences.
- Vlasina Rid - located on the north-western side of the lake, is available through regional R122. Zone Vlasina Rid is the most urbanized in comparison to other functional parts of the lake, with a large number of private houses (some 400), which partly used for living and work to rest. In the area there are shops, a post office, two hotels and several resorts. This part is leaning on the sports - recreational facilities (Chemernik the west and the football stadium and support facilities to the south) and the camp Mutt, so that whole zone makes it a functional unit. Access is possible from the direction of Vlasina Dumpling and from the direction of grasses;
- Vlasina Stojkovica - located on the eastern part of the lake and is regarded as a point of entry to Vlasina lake from the direction of the Gorge highway M1.13 (from the direction of Bulgaria). In the field is located about 100 houses partly for life and partly to rest. From public functions there are only two shops, but it is in this area farm the company Simpo from Vranje.

DEGREE AND TOURIST VALORIZATION OF VLASINA LAKE

Landscape character Vlasina plateau and its eco-climatic complex are the essence of its proper tourism value and quality, and water accumulations lake itself is the most recognizable motif - travel decoration and image of the Vlasina area. The main eco-tourism potentials and valuable recreational and attractive motifs of this area are: [4]

- The natural landscape of diverse ecosystems and high aesthetic values;
- fresh and stimulating recreational landscape and climate
- Vlasina lake - hydrological and recreational tourism visokoatraktivan motive.

Master plan with business plan development of tourism on Vlasina lake [8] provides for tourism development in this area and emphasizes the complementarity of resources for tourism development. The main task of this project is to identify significant resources for tourism development, carry out an analysis of the development of tourism destinations and indicate the future direction of development of the destination. One of the main ideas of the concept master plan is a blending of diverse content, because the very nature of the Vlasina is such that it offers different opportunities, attractive both for winter and for summer tourism, benefits for passive recreation in silence and clean air, but also for preparation of elite athletes. In this respect such a decision, which should be implemented through eight are designed to meet these requirements. The greatest number are located on the west side area of Vlasina lake within the whole Vlasina Rid. The western side is given priority due to natural conditions, but also due to the fact that it takes the easiest access from both directions, ie from the direction of Surdulica and from the direction of the Crna Trava. These zones are located in small areas, where they have acquired a variety of tourist value, where the lake is dominant, but present and attractive facilities for winter sports. The eastern side is planned for the establishment of residential and regensy zone ("zone Regency"), which are intended to plan for the construction of facilities for a holiday on large plots (0.20 ha and above), with the necessary supporting facilities.

Tourism development project in the wider area of Vlasina lake is structure draws in five "experiential zones", which are connected with a boardwalk, berth with a docking platform for small electric boats, as well as the shuttle bus, which operates on a tour every time. Each of the zones is differentiated according to its structure and the dominance of the types of products and activities offered:

1. **Zone Vlasina Dumplings** - entrance area (info center and family hotels)
2. **Zone Vlasina Dumplings**- ski area (wellness hotels and villas)
3. **Zone Vlasina Rid** - Lake Resort (Event Center, tourist marinas and restaurants)
4. **Zone Vlasina Golf (**course with a golf club and villas on about 70 ha)
5. **Zone Vlasina Stojkovica Hotel** (catering facilities). [5]

Horwath HTL 2007 proposes the following portfolio of tourism products Vlasina: vacation in summer and winter, golf, MICE and special interests. [8]

ACCOMMODATION CAPACITY VLASINA LAKE

Actual storage capacity and the capacity for providing food and drinks, are not yet sufficiently developed and visibly meet the needs of the growing number of visitors Vlasina lake. If tourists decide to come, welcome them offer the hotel "Vlasina" and "Lake", Boarding house "Narcissus", resort " Flag PES", "Serbia forests", "Zele Veljkovic", "Nevturs" then resorts hydropower "Surdulica "electricity distribution" Leskovac "thermal power plant" Kostolac - mines, "Youth Association, Institute for Employment" Surdulica "and others. There are also many private villas and houses, as well as two decorated campsite - Fishing Camp and Camp "Vlasina". Accommodation facilities, except in "Narcissus" are poorly equipped and low categories are. Rest and recreation are generally low comfort and neglected. Most are closed, irrational use and operate seasonally, and is at the current state of facilities necessary to find a better organization of the business and provide a unified tourist offer.

Tourist traffic in 2011 recorded 4,238 tourists, of which 3,838 of domestic and 400 foreign, who have made 19,816 overnight stays, of which 18,997 by of domestic tourists and 819 by foreign tourists. The average number of overnight stays was 4.9 in favor of the home, while in the number of foreign 2.0. Among the foreign tourists prevail tourists from Bulgaria, Macedonia, Greece, Romania and Hungary.

Many home owners have a contract with the Tourist Organisation of Surdulica, to work together to facilitate the accommodation of guests. For Government rail lake, "Narcissus" There is a tourist information center, where workers tourism organizations welcome guests, provide them with detailed information about vacancies and indicate cottages in which to spend your vacation. [5]

According to the Master plan from 2007 to Vlasini have already confirmed some forms of tourism, and some still to be expected with further development. Important among them are: A resort, sports and recreation, rural, hunting, sightseeing, excursion, cycling, nautical, transit tourism. Depending on the possibilities of providing financial resources for reconstruction and modernization of existing tourist facilities and roads, construction of new facilities, utilities and sports infrastructure, will gradually complete tourist offer, and with it will strengthen the present and to take up new forms of tourism. Will contribute to the new financial incentives for the development of agriculture and other activities, physical development and equipping of tourist sites and centers, as well as organizational and business connections relevant subjects in local communities. [8]

Especially worthy of a transit tourist feature of this area is in complete dependence on the tourist traffic situation of the region and the quality of the roads. The traffic situation is peripheral, and will contribute to the modernization of roads little transit traffic, because the main road through Surdulica and Vlasina to transit Bulgaria frequent low, and the main role in the transit traffic will continue to keep the transit routes through the valley of Morava towards Greece and the valley of Nisava to Sofia . However, the increase in this traffic can be more affected by transit through organized itineraries, in which you can enter and Vlasina lake as a special destination.

THE PROTECTION AND SUSTAINABLE DEVELOPMENT OF VLASINA

In 2006, the Serbian government adopted a *Regulation on the protection of landscape is exceptionally quality "Vlasina"* which is categorized as a natural resource of great importance for the Republic - the first category. Regulation stipulates that a natural good old Public Company "Directorate for Building Land and Roads of Surdulica" from Surdulica. [7]

Area of exceptional importance "Vlasina" in a total area of 12,740,90 hectares, and based on criteria the protection of natural values, zoned to the three levels of protection, including:

Regime and the degree of protection:

1. Island Stratorija,
2. Long Island part.

Mode II degree of protection:

1. Vrtop - Jelicka rid,
2. Small Chemernik,
3. Large Chemernik,
4. Stream of Stevanov,
5. Long part of the peninsula,
6. Vlasina lake,
7. Wolf River Gorge,
8. Golden beech.

The third level of protection: all other localities within the natural resource. [10]

Regarding international status, PIO "Vlasina" is the decision of the Secretariat of the Ramsar Convention of 20 November 2007, included in the official list of internationally important wetlands, which is a very important international recognition of the values of national and natural heritage Vlasina and efforts for its preservation. PIO "Vlasina" is a particularly important area for waterfowl conservation, since it was declared as a European important bird area (IVA), by international organizations BridLife International, as well as a possible important area for plants (IPA), based on the criteria organizations Plantlife Europae. Area PIO "Vlasina" on the territory of Serbia recognized as an Emerald ***Site (Management Plan - Landscape of exceptional quality "Vlasina" from 2011 to 2021).***

CONCLUSION

Vlasina, the natural and touristic values, should be in the future that represents the area towards which will be directed strong tourist flow. Power tourist attractions of this area will not only be in the diversity and high quality of its natural values and attracting tourism accommodation and other conditions of residence, but also in a considerable expanse and plateau and the possibility of planning the construction of tourist resorts and facilities for tourists, who will visit throughout the Vlasina years.

The growing pollution of the urban environment creates a growing need for the original intact nature and its recreational properties. Due to its large and diverse recreational and therapeutic properties, Mountain gaining increasing national and regional significance. With the advancement of modern civilization, values Vlasina growth and should therefore be conceived, planning measures to revitalize and protect Vlasina of each type of pollution and the best use of its natural beauty. Only proper management of space Vlasina, as a resource for tourism, contribute to the increase of its economic, ecological and aesthetic value, which will provide long-term benefits at the local, regional and national levels.

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THE CONCEPT OF SUSTAINABLE DEVELOPMENT OF RURAL TOURISM

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ABSTRACT

An important part of tourism is rural tourism. Rural tourism is a specific economic activity in which the villagers are providing certain services to interested tourists. Also, rural tourism is one of the pillars of development in rural areas who actively promotes socio-economic transformation of rural settlements. Rural tourism is an area that is interesting to the tourists because returns urban man to the nature which has always belongs. Protected nature and clean and unpolluted environment in rural areas has always drawn, and more recently attracted a growing number of urban population. This paper aims to highlight the importance of sustainable development of rural tourism. Rural tourism should be developed in the family holdings in rural areas and is therefore necessary to define the concept of development with the aim to attract more tourists and generate additional revenues of the local population with the aim of economic development and to improve living standards in rural communities all over Serbia.

Key words: Rural tourism, sustainable development, tourism potenential, environment.

INTRODUCTION

Rural tourism is becoming more and more actual and has increasingly important place in the tourist trends in developed countries. The development of rural tourism has a significant impact on the transformation of economic, social and functional structure of rural areas, as evidenced by examples of some European countries (France, Austria, Italy, Slovenia) [1]. Clean and preserved nature, healthy environment and facilities that can provide an attractive and relaxing vacation become a need of modern man and he is trying to meet this need [2]. The rural areas of our country have enormous natural potential for tourism development. The very fact that Serbia has long been out of the main tourist attractions and is therefore largely preserved its natural and social characteristic [3]. The traditional way of life of the local population over time has become a recognizable layout for significant natural, biological, ecological and aesthetic values [4]. The aim of this paper is to define the basic concept of sustainable development of rural tourism in order to form the basis on which will be based sustainable development of rural tourism overall territory of the Republic of Serbia. The concept of sustainable development of rural tourism development should enable the development of local communities and regions, and should also provide for the preservation of natural resources.

CONCEPTUAL GUIDELINES OF RURAL TOURISM

Tourism as a general phenomenon of this century, is an activity that was first acquired on a global dimension. After the economic, sociological, psychological, political and other connotations of tourism is to express the phenomenon, which for the volume of transactions close to the oil and automotive industries. This is indicated by the fact that the economically most developed countries of the world, in the service sector, where there is tourism, employs on average 65% of the total number of employees [5]. Today, tourism is one of the world's largest generator of employment. It is estimated that tourism provide about 212 million jobs, both directly and indirectly.

Rural tourism is a concept that by definition that is listed in the Tourism Development Strategy of the Republic of Serbia and is defined as a range of activities, services and additional facilities that needs to be organized by the rural population. Rural tourism should be developed in the family holdings with the aim to attract more tourists and generate additional revenues. This product is based on the principles of sustainability and thus offers to the tourists the elements of the rural environment, nature, and presenting traditional hospitality and values of life of the local population, and as such is a lever for economic development and raising living standards in rural communities. Europe in the last few decades, is the world's leading provider of rural tourism and resulting trends indicate that it will remain in the next decade [6].

The development of tourism is gaining special attention because it can contribute to social and economic regeneration of rural areas. In this regard, tourism is seen as a way to overcome a series of problems in the development of rural areas throughout the world. Rural tourism is becoming the engine of economic development and raising living standards in rural communities, because it is based on the principles of sustainable development and conservation of natural resources [7]. In many countries of the European Union in the development strategy of the region rural areas and rural tourism has been included in the strategy, which helps in keeping the population in the place, creating new jobs and contributing to the socio-economic progress (residual) areas [8].

Rural tourism as tourism of local character, was initiated and controlled by the people who live in the local community, offers new chances and opportunities for economic prosperity of the local population, and also affects the positive attitude to the development of tourism in general [9]. Rural tourism should contribute to the preservation of the rural environment and cultural heritage, but also to economically motivate local residents to stay in the countryside. This form of tourism could contribute significantly to the protection of nature, but also to provide funds for the survival and development of villages. The main resource for the development of rural tourism is a nature, and is estimated about three-quarters of the world's total tourism demand is directed exactly towards the natural values and "untouched" areas. Because of the fact that natural resources are only one part of the natural conditions, it is a gift of nature, which is used in the reproduction process for creating new useful values [10]. While terms such as "natural capital" has long been established in the literature, specific term, rural capital 'has entered the academic discourse only in the last few years. Protected nature and the environment in rural areas has always drawn, and more recently attracts a large number of urban population, because of increased interest in travel to the village, and rural areas are included in the circle of interest of an increasing number of tourists.

According to that rural tourism accounts for 10-25% in all forms of tourism activities, it can be concluded that the "story of rural tourism began in the rural area and that in the future achieve a continuous rise" [11].

The development of rural tourism in Serbia can have positive effects in:

- Encourages the development of new tourist destinations,
- The creation of local entrepreneurship,
- Sustainable development of rural areas,
- Preserving indigenous values (local identity, traditions and customs),
- Conservation and enhancement of natural and environmental.

Rural tourism must be developed in accordance with the principles of sustainable tourism (derived from the concept of sustainable development) that includes environmental, social, cultural and economic sustainability with the aim of improving the quality of tourist destinations (preserved natural environment, cultural and historical heritage, cultural identity and a positive attitude locals - tourists). Due to the growing tourist demand, is increasingly considering about the justification of attracting an increasing number of tourists due to revenue growth, jobs and tourist traffic, but at the expense of environmental degradation. Sustainable Development underscored the fact that economic development and environmental quality are not mutually exclusive, because the use of modern technology and improving the behavior of tourists and local residents prevent damage to non-renewable tourist resources [7].

BASIC PRINCIPLES OF RURAL TOURISM

The concept of sustainable tourism includes integration with nature and cultural environment, where activities undertaken have an acceptable impact on natural resources. In this framework, tourism activities should be environmentally, economically, socially, as well as the welfare and cultural sustainable in the long term.

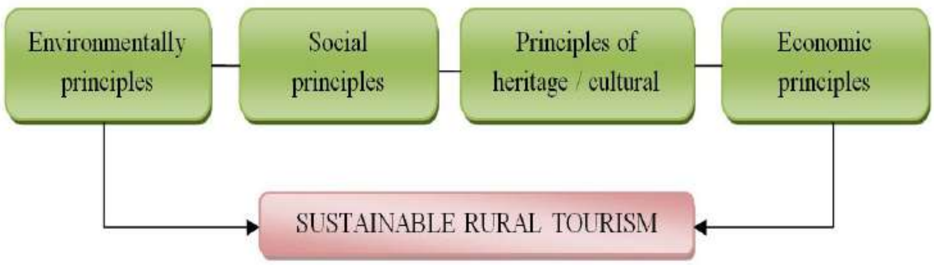

Figure 1. Basic priciples of rural tourism [12]

Basic principles of rural tourism are:

- ***Ecological Principles of protection of the environment***
  - Preserving nature and biodiversity conservation as a prerequisite for sustainable tourism. In this case, tourism activities should ensure integtitet ecosystem and habitat conservation.
  - Tourism activities such as hiking and construction of infrastructure in rural areas that are likely to have a significant impact on nature and biodiversity should be subject to prior assessment of environmental impacts.
  - In protected and highly sensitive areas and other areas that require strict protection, tourism activities should be limited to a tolerable minimum. − In coastal areas special attention should be paid to the preservation of endangered areas, such as small islands, coastal wetlands, beaches, etc.
  - Tourism in mountain areas should be managed with the aim of preserving biodiversity.
  - Sustainable tourism should be based on ecological means of transportation, and special attention should be given to environmentally sensitive areas.
  - Sports activities, such as hunting and fishing, especially in environmentally sensitive areas should be managed in a way that meets the requirements of nature in accordance with existing regulations on conservation of the species.
- ***Social Principles***
  - Ensure that tourism development protects and not destroys cultural diversity and local community.
  - Active discourage forms of tourism that cause and contribute to social problems.
- ***Cultural Principles (heritage)***
  - Develop tourism, which is typical of the (indigenous),
  - Avoid duplication,
  - Promote unique characteristics of culture and heritage areas [12].
- ***Economic Principles***
  - Restrain the exodus from rural areas and create new employment;
  - Conversion of productive activities towards more environment-friendly strategies and to the development of local and typical production;
  - Development of new professions, new management approaches and new agricultural methods;
  - To make the most of environmental resources through synergy and a less conflicting relationship between agriculture and the environment;
  - Economic development of local communities and general improvement of the quality of life [13].

As significant characteristics of modern tourist demand that are essential for the development of tourism in rural areas of Serbia, are the following:

- Increasing demands for environmental quality and health-recreational function of rural areas;
- Returning human to nature and its original values;

- Tourist market recorded a growth of green consumer movement whose behavior is determined by ecological motives and values;
- Increasing the demand for destinations, non-urban rural and protected natural areas and villages with important cultural and historical values;
- Refreshment expressed through the contrast between urban village, lowland mountains;
- Demand for rural and agro-tourism, which requires accommodation in various types of facilities (rural houses, small hotels, motels, etc.);
- Requests for clean and free space suitable for moving, self-expression and recreation;
- The growing interest for fun and leisure, religious and cultural features, ecological values (healthy environment and food);
- It is increasingly represented individual and family movement, which correspond to the manner of acceptance and accommodation in rural households;
- Greater domestic demand orientation towards rural areas, because of the economic situation and the low standard of living of the majority of the population.

It is difficult to determine the precise number of tourists who aspire to rural areas, although some estimates indicate that about 75% of world tourism demand is directed towards the natural values of the areas (in 2000, the number of participants in international tourist flows amounted to about 698 million, the realized foreign income from international tourism in the amount of 475.8 billion USD) [14]. According to recent research, rural tourism is growing three times faster than classic tourism and it is expected that its share of the tourism market in Europe in the next 20 years will be greater than 20%.

However, given that neither the World Tourism Organization (WTO) or the Organization for Economic Cooperation and Development (OECD) have taken appropriate measures, there are several limitations to provide precise and logical data on rural tourism and recreation:

- The differences in the definition and identification of data among different nations of one state can only counted farm and nature in this type of tourism, while others may consider that many economic activities outside urban areas is also part of the rural tourism;
- Many rural tourists and recreationists are Excursionist (one visit) and do not belong to those who use the services of nights, and whose volume is in this case could at least to some extent measured [15].

Contemporary trends in world tourism for areas of authentic or minimally preserved environment. Opportunity for Serbia, as the country's diverse and preserved nature in the direction of the development of eco and rural tourism. The commitment to these types of tourism and unambiguous quality of the natural environment of rural areas are a good way towards the ultimate formation of the strategy of development of sustainable rural tourism [16].

A large number of rural areas in the Republic of Serbia is characterized by depopulation and economic underdevelopment, while urban centers recorded higher concentration of population and economic activity. This trend is negatively affecting the development, so it is necessary to develop programs, projects and future strategic directions of sustainable development of rural areas, in line with their specific characteristics, economic and non-economic functions, as well as the demands of the domestic and international environment, and in particular, the development of agriculture as an important part of the regional economy.

An important priority for the sustainable development of rural tourism is the reconstruction and development of rural infrastructure (roads, water supply, sewerage, electricity, information and telecommunication services, etc.) which has a huge socio-economic and environmental importance. In doing so, the cross-border projects can significantly contribute to a better use of local resources, for example, a common road infrastructure, energy networks, tourist facilities, etc. [17]. Creating a stimulating environment by the state for development of small and medium sized enterprises in rural areas (tax incentives, subsidies, loans on favorable terms, etc.) contributes to the diversification of the rural economy and keep young people in the countryside, in agriculture and non-agricultural occupations.

Sustainable Development Strategy includes overall strategic development plan that provides guidance and incentives for future development. It defines sustainable development as a target-oriented, long-term, comprehensive and synergetic process affecting all aspects of life (economic, social, environmental and institutional). Document "Strategy for Sustainable Development" is prepared using a participatory approach which includes the involvement of all stakeholders in the process [18]. The strategy itself entails the need to ensure long-term economic growth, accompanied by increased innovation and technological progress, providing a social responsibility, increase employment, reduced poverty and adequate distribution of natural resources [19].

One of the essential elements of sustainable development of rural tourism is the sustainability of economic activity, which is based on different grounds. In the first place, there are strong reasons that today's generation descendants left a legacy no less likely to develop than it has now. This means that the current generation of people should not degrade the planet Earth, with all its resources. The right of the present generation to use resources and the environment should not endanger the same rights of future generations [20].

CONCLUSION

Rural tourism is a complex type of tourism, made up of different types of tourism that occur in rural areas. Rural, natural environment, traditional and cultural values are important preconditions for the creation of a competitive tourism offer. Rural tourism must be developed in accordance with the principles of sustainable development, which includes environmental, social, cultural and economic sustainability, but to improve the quality of tourist destinations (preserved natural environment, cultural and historical heritage, cultural identity and a positive attitude locals - tourists). Rural tourism as a specific economic activity in which the villagers by providing certain services to interested tourists, will be one of the pillars of development in rural areas because rural tourism actively promotes socio-economic transformation of rural settlements.

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SENSITIVITY ANALYSIS IN RADIOGENIC CANCER RISK ASSESSMENT

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ABSTRACT

Cancer mortality risk for general public along with measurement uncertainty was assessed, related to inhalation exposure to natural radionuclides from soil, using Monte Carlo method. Two sensitivity analysis techniques were compared in order to show influence of variability of input quantities on the measurement uncertainty. Regression analysis gave more conservative results, compared to results obtained with direct method for sensitivity analysis of applied model for cancer risk assessment.

Key words: radionuclides, cancer risk assessment, Monte Carlo method, sensitivity analysis.

INTRODUCTION

Cancer risk assessment related to general public exposure to carcinogens from the environment has great importance due to increased cancer incidence rates in populations. Various mathematical models are defined in order to explain relationship between concentration of carcinogen agent from environment and quantities that describe health detriment. Mathematical models that are used in cancer risk assessment enable researches to predict cancer incidence or mortality rates in population based on results from previous studies [1]. Cancer risks are usually expressed with point risk estimates in the case of preliminary research or screening. It is very important to treat risk as any other physical quantity, so statement of the measurement uncertainty should be accompanied by risk estimates [2].

Purpose of this paper was to assess cancer mortality risks for general public along with measurement uncertainty, related to inhalation exposure to natural radionuclides from soil using Monte Carlo method. Monte Carlo technique represents statistical method that is often applied in risk assessment because it implements uncertainty analysis [3], [4]. Also, method is very convenient because uncertainty and variability of all input quantities are treated in the same way. Mathematical models for risk assessment could be very complex so there is a need of their simplification, but without losing relevant information, for example, measurement uncertainty. Various sensitivity analysis techniques are used in order to determine influence of the specific input quantities on the assessed risk [5]. In this paper it was made attempt to use multidimensional regression technique as a tool for sensitivity analysis. Obtained results were applied in uncertainty analysis and discussed in terms of their influence of the overall estimate of measurement uncertainty.

METHODS

Cancer mortality risks were assessed related to inhalation exposure to radionuclides ^{238}U from soil. Five soil samples were collected at the location that belongs to meteorological station under control of Republic Hydrometeorological Service of Serbia in Sombor. Activity concentration of radionuclide ^{238}U in soil samples were measured using gamma spectrometry technique with high purity, low energy, germanium semiconductor detector (HPGe). The relative efficiency of HPGe detector was 28 %. Energy resolution was 2 keV in measurements at the second line of ^{60}Co energy. The expanded measurement uncertainty of radionuclide activity concentration was 15 % (coverage factor $k = 2$).

Risk was assessed using cancer risk coefficients provided by US EPA which are expressed as average risk per unit exposure of average member of a population [6].
Lifetime cancer mortality risk *per capita* for lifetime exposure via inhalation was calculated using (1) [7]:

$$Risk = R_c \times A \times C \times IR_i \times EF \times ED \times \left[ET_0 + \left((1 - ET_0) \times DF_i \right) \right] \quad (1)$$

where Rc - risk conversion factor (risk/Bq), A - activity concentration of radionuclide in soil (Bq/kg), C - concentration of dust particles from soil in air (μg/m^3), IRi - inhalation rate (m^3/day), EF - exposure frequency (day/year), ED - exposure time (year), ET_0 - fraction of time spent outdoor, ((1-ET_0) - fraction of time spent indoor), DFi - indoor dust dilution factor.

Probability cancer risk assessment and uncertainty analysis was obtained using Monte Carlo method [8]. Wolfram *Mathematica* software was used for numerical simulations. It was simulated 10^6 histories.

RESULTS AND DISCUSSION

Table 1 presents probability density functions that are assigned to input quantities in model. Choice of probability density functions (PDFs) should reflect exposure scenario, in the case of inhalation exposure of agricultural population to radionuclide ^{238}U.

Mean value of assessed cancer mortality risk is 0.0849×10^{-6}, with expanded uncertainty range of $(0.00233 - 0.625)\times10^{-6}$ for inhalation exposure to ^{238}U. Uncertainty range is represented with lower and upper bounds for confidence level of 95 %. Lower bound is defined as the 2.5th percentile and the upper bound as 97.5th percentile of obtained probability density function of risk.

Table 1. Probability density functions of input quantities for inhalation exposure to ^{238}U.

Input quantity	Probability density function
$R_c(^{238}U)$ (Risk/Bq)	Log-normal (-15.2; 1.12) [6], [9]
A (Bq/kg)	Uniform (37.3; 48.5)
C (μg/m^3)	p=3/4 for C=(5-15) μg/m^3 p=1/4 for C=(60-80) μg/m^3 [10]
IR_i (m^3/day)	Normal (17.48; 2.81) [11]
EF (day/year)	Triangular (250, 300, 350)
ED (year)	Uniform (40, 70)
ET_0	Uniform (0.3; 0.5)
DF_i	Single value of 0.4 [7]

*Uniform distribution is defined with minimum and maximum values of the distribution, Normal, with arithmetic mean and standard deviation, Log-Normal distribution with two parameters (arithmetic mean and standard deviation of corresponding Normal distribution), and triangular distribution, with lower limit, upper limit and mode.

Multidimensional regression technique is used for sensitivity analysis of the model where regression model contains more than one regressor variable. All numerical values of input quantities are normalized according to (2):

$$\begin{aligned}
(\log Risk)_{\mathrm{N}} &= \frac{\log Risk - (\log Risk)_{\mathrm{Mean}}}{(\log Risk)_{\mathrm{StDev}}} = y;\\
(\log A)_{\mathrm{N}} &= \frac{\log A - (\log A)_{\mathrm{Mean}}}{(\log A)_{\mathrm{StDev}}} = x_1;\\
(\log Rc)_{\mathrm{N}} &= \frac{\log Rc - (\log Rc)_{\mathrm{Mean}}}{(\log Rc)_{\mathrm{StDev}}} = x_2;\\
(\log Iri)_{\mathrm{N}} &= \frac{\log Iri - (\log Iri)_{\mathrm{Mean}}}{(\log Iri)_{\mathrm{StDev}}} = x_3;\\
(\log C)_{\mathrm{N}} &= \frac{\log C - (\log C)_{\mathrm{Mean}}}{(\log C)_{\mathrm{StDev}}} = x_4;\\
(\log EF)_{\mathrm{N}} &= \frac{\log EF - (\log EF)_{\mathrm{Mean}}}{(\log EF)_{\mathrm{StDev}}} = x_5;\\
(\log ED)_{\mathrm{N}} &= \frac{\log ED - (\log ED)_{\mathrm{Mean}}}{(\log ED)_{\mathrm{StDev}}} = x_6;\\
(\log ET_0)_{\mathrm{N}} &= \frac{\log ET_0 - (\log ET_0)_{\mathrm{Mean}}}{(\log ET_0)_{\mathrm{StDev}}} = x_7
\end{aligned} \tag{2}$$

Equation (1) was transformed to a form (3) that is suitable for the multidimensional regression analysis:

$$y = \alpha_1\, x_1 + \alpha_2\, x_2 + \alpha_3\, x_3 + \alpha_4\, x_4 + \alpha_5\, x_5 + \alpha_6\, x_6 + \alpha_7\, x_7 \quad (3)$$

Sensitivity coefficients α_i obtained from the multi-dimensional regression analysis are presented in Table 2. Residuals were analyzed in order to check model adequacy and assumption that residuals are approximately normally distributed with constant variance. Normal probability plot was constructed as check of normality and it showed that distribution of residuals doesn't deviate from Gaussian distribution.

It can be seen from Table 2 that the quantity *Risk* is the most sensitive on PDF for *Rc*, and the least sensitive on PDF for ET_0. Coefficients α_i are measure of influences on *Risk,* caused by variability of input quantities.

Table 2. Coefficients α_i obtained from multidimensional regression analysis for standardized input quantities.

Input quantity	Normalized input quantity	α_i
A (Bq/kg)	x_1	0.051
R_c(^{238}U) (Risk/Bq)	x_2	0.77
IR_i (m^3/day)	x_3	0.11
C (μg/m^3)	x_4	0.62
EF (day/year)	x_5	0.048
ED (year)	x_6	0.11
ET_0	x_7	0.031

Sensitivity of measurement uncertainty limits on the variability of parameters for PDFs of input quantities can be further analysed. Assessed risks as model output and uncertainty limits can be compared between two cases:

- when they are calculated using all defined PDFs for input quantities;
- when they are calculated by holding single value estimate (point estimate) for one input quantity, while PDFs are assigned to all other input quantities.

This direct method gives insight in the influence of variability of input quantities. Results from these comparisons are complementary with results obtained using multidimensional regression analysis and they can be used to check validity of regression analysis.

Fig. 1 shows PDF for assessed risk with lines that represent expanded measurement uncertainty interval for probability of 95 %. Line with label *Risk* represents uncertainty interval in the case where PDFs for all input quantities were used in the simulation. Line with label *A* represents uncertainty interval in the case where PDFs are assigned to all input quantities except for the quantity *A,* which was given single value (mean value). Same process is repeated for other input quantities. Central points on every line represent assessed risks (mean value). It can be seen from Fig. 1 that only variability of two quantities, *Rc* and *C,* have influence on the interval of measurement uncertainty.

Although regression analysis is often used as method for sensitivity analysis, the direct method applied in this paper showed that only variability of two quantities have influence on measurement uncertainty interval.

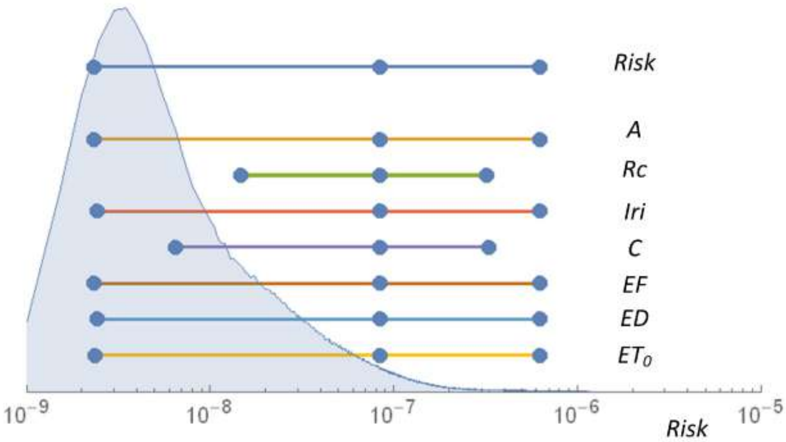

Figure 1. Probability density function of assessed cancer mortality risk with measurement uncertainty intervals regarding variability of input quantities.

CONCLUSION

Sensitivity analysis techniques are often used to simplify mathematical models leading to simplification of numerical experiments. In this specific model, as well as in other similar models for cancer risk assessment, regression analysis appeared to be conservative method. While regression analysis suggested that variability of PDFs for almost all input quantities (*Rc,* C, *A*, *IRi*, *EF*, *ED*) have influence on the measurement uncertainty interval of output *Risk*, direct method that was applied showed that only variability of two quantities (*Rc* and *C*) has practical influence on measurement uncertainty interval. Great effort should be invested especially in further analysis of mechanisms of cancer development related to low dose exposure to ionizing radiation. More precise insight into the mechanisms of cancer development and dose-effect relationship would lead to definition of cancer risk conversion factor, *R*c, with lower measurement uncertainty.

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FURTHER DEVELOPMENT OF OIL SHALE INDUSTRY IN SERBIA

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ABSTRACT

Basic geological exploration in Serbia detected 21 deposits of oil shale with resources of over 4.7 billion tons. Oil shale in these deposits is of various qualities and oil content. The biggest deposits of commercial potential are Aleksinac and Vina-Zubetin. Aleksinac deposit has been explored in more detail compared with other deposits, with reserves close to 2 billion tons with average content of organic matter of approximately 20% and with oil content of approximately 10%.

Considering the fact that oil production from oil shale becomes more and more important, and that 77% of raw oil in Serbia comes from import, and only 23% from domestic resources, while 86% of natural gas comes from abroad and only 14% from domestic resources, it is necessary to analyze possibilities of oil production from Serbian oil shale deposits, such as Aleksinac basin.

This paper highlights possibilities for development of oil shale production and processing in Serbia.

Key words: oil shale, extraction, technology, environment, economy.

INTRODUCTION

There are numerous basins and deposits of oil shale in Serbia, but they are explored at various levels. Most important basins of oil shale in Serbia are Aleksinac, Vranje, Senonian Tectonic Trench, Valjevo-Mionica, Western Morava, Kruševac, Babušnica, Kosanica, Niš and Levač [2]. Part of Aleksinac Basin and part of Vranje Basin (Goč-Devotin) have been explored in detail, while semi-detailed exploration has been performed at remaining parts of Aleksinac and Vranje (Vlase-Golemo Selo) basins. Other basins of oil shale are explored at basic exploration level, which enables planning of further exploration in order to reliably determine amounts of reserves and quality of oil shale. Serbian oil shale is of sapropel type (Aleksinac, Mionica and Petnica) and sapropel-coaly type (Babušnica, Vranje Basin, Senonian Tectonic Trench, etc.). Further activities related to geological exploration are of particular importance regarding determination of organic matter and oil content, necessary for planning of future activities in connection to mining, processing, utilization and environmental protection [7].

OIL SHALE RESOURCES AND THEIR QUALITY

Oil shale is a rock that contains kerogen, which is a complex organic substance that breaks down when retorted (heated) to form crude shale oil, gases, and char.

Basic geological exploration detected 21 oil shale basins and deposits of various qualities and potential, but only two deposits are explored in detail. These are Aleksinac deposit and Goč-Devotin deposit. Therefore, most of the oil shale potential in Serbia should be considered in terms of resources instead of reserves. Since Serbian legislation still has not regulated reconciliation of the reporting system, further on, reserves will be presented according to the current Serbian system. Locations of oil shale deposits are presented in Fig. 1, while basic data are given in Table 1.

Table 1. Basic data on oil shale deposits in Serbia

Basin	Deposit	Thickness of seam, m	Average thickness, m	Average content		Reserves/Resources (10^6 t)		
				Kerogen, vol. %	Oil mass (Fischer assay), %	Shale	Oil	Category
Aleksinac	Aleksinac	54–92	75.5	20.0	10.0	2000	200	A+B+ C_1+C_2
		7–29	20.2	25.0	12.5			
	Bovan-Prugovac	10–33	20.0	12.2	6.0	210	12.6	–
Vranje	Goč-Devotin	10–23	15.0	8.8	4.5	22	1,0	A+B+C_1
		2–6	3.9	5.9	2.1	13.8	0.3	C_1
	Vlase-Golemo Selo	6–13	9.7	5.5	3.4	38.5	1.3	C_1
		3–7	4.4	2.5	1.4	–	–	–
	Stance	–	4.0	5.6	2.6	45	1.2	D_1
		–	6.0	6.2	2.6	–	–	–
	Buštranje	4–13	9.0	8.2	3.4	46	1.6	C_1
		5–9.5	7.0	5.0	1.4	36	0.5	C_1
		4.2–9.0	6.0	5.2	1.4	30	0.4	C_1
	Klenike-Jastina Bara	1.3–13	7.5	5.6	3.4	42	1.4	C_1
		1.5–10	6.0	6.7	3.2	30	1.0	C_1
		9–11	10.0	5.2	1.3	–	–	
	Baraljevac	4–6	5.6	7.3	2.8	8	0.2	C_1
	Dražnica	8–10.7	9.0	8.5	5.1	35	1.8	C_1
		–	7.5	8.4	4.9	30	1.5	C_1
Senonian Trench	Veliko Polje-Rujiš	20–150	72.0	–	0.5	–	–	–
	Vina-Zubetin	20–80	31.0	5.4	2.6	850	22.1	C_2+D_1
	Podvis-Gornji Kar.	2–5	4.0	–	7.5	10	0.1	C_2
	Miran.-Orlja	5–33	12.0	4.5	2.2	70	1.5	C_2
	Man.-Okoliš	10–35	25.0	5.1	2.4	100	2.4	C_2
Valjevo-Mionica	Šuše-Klasnić	5–15	9.0	7.2	3.2	30	1.0	C_2
	Rad. Str. Svet.	4–15	9.0	8.4	3.9	80	3.1	C_2
Western Morava	Pekčanica-Lazac	–	4.4	5.0	1.3	38	0.3	D_1
		–	1.7	3.0	0.9		–	
	Paramenac-Riđage	–	2.3	6.0	1.3	18	0.2	D_1
		–	2.7	3.3	0.8		–	
Kruševac	Odžaci	3–11	7.0	6.8	1.7	20	0.3	D_1
Babušnica	Raljin	24–40	30.0	7.4	3.7	300	9.6	C_2
		9–15	12.0	5.2	2.6			
Kosanica	Rača	4–6	4.4	11.5	5.2	20	1.0	C_2
		1–2	1.4	3.6	1.6			
Niš	Paljina	–	15.0	–	3.2	500	16.5	D_2
		–	6.0	–	3.3			
Levač	Komarane-Kaludra	–	7.0	3.4	0.6	190	1.9	D_1
		–	2.0	3.0	1.4			
						4812.3	**283.8**	

Figure 1. Locations of oil shale deposits in Serbia.
1 Aleksinac, 2 Bovan-Prugovac, 3 Goč-Devotin, 4 Vlase-Golemo Selo, 5 Stance, 6 Buštranje, 7 Klenike, 8 Vlaško polje-Rujište, 9 Vina-Zubetin, 10 Podvis-G. Karaula, 11 Manojlica-Okolište, 12 Miranovac-Orlja, 13 Šušeoke-Klašnić, 14 Radobićka strana-Svetla, 15 Pekčanica-Lazac, 16 Parmenac, 17 Odžaci, 18 Raljin, 19 Rača, 20 Paljina, 21 Komarane-Kaludra.

According to data shown in Table 1, quality and grade of oil varies by deposits. Largest deposits with commercial potential are Aleksinac and Vina-Zubetin. Aleksinac deposit is explored more thoroughly than others, and estimated reserves reach 2 billion tons, with 20% of organic matter and 10% of oil. Table 2 shows comparative overview of oil shale quality from Aleksinac and Estonian deposits.

Table 2. Comparison between oil shale quality from Aleksinac and Estonian deposits

	Aleksinac oil shale	Estonian oil shale
Moisture, %	10-12	10-12
Ash, %	60-65	43-47
Sulfur, %	1,4-4,8	1,5-1,8
Heat value, MJ/kg	6-9	8-10
Oil content, %	8-12	15-16

Table shows that oil shale from Aleksinac contains higher percentage of ash and sulfur, lower heath value and lower percentage of oil. This could implicate that extra costs in environmental protection would be necessary in Aleksinac.

THE TECHNOLOGY

Oil shale can be exploited either by surface processing techniques or by in-situ technologies. Surface processing basically includes three steps: mining of the oil shale and ore preparation, thermal processing or retorting, and processing of the shale oil to obtain a refinery feedstock and value-added by-products. Mining of the oil shale also results in important investments in waste disposal and site reclamation. By in-situ techniques, the oli shale is not, or only partly, mined and the pyrolysis is conducted underground. The pyrolysis products are pumped to the surface and upgraded into fuel chemical by-products. Depending on the underground heating process and the type of kerogen, the obtained oil has to be stabilised and upgraded before further refinement or can be directly used as a refinery feedstock. Figure 2 illustrates the flows of oil shale from extraction to final products to consumers, in other words - the efficiency of the oil shale industry.

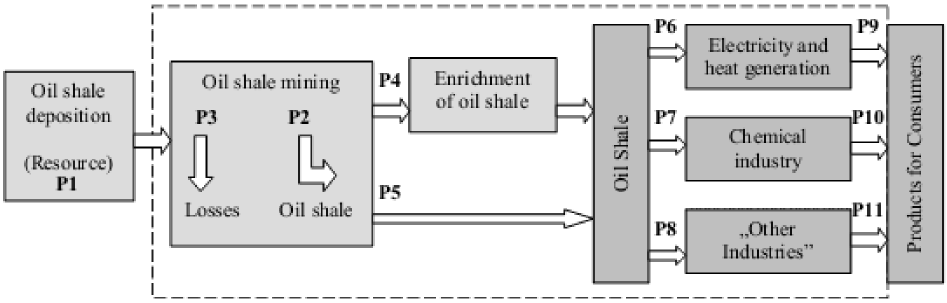

Figure 2. A scheme of material flows and efficiency of oil shale industry

The flows on the Figure 3 are defined as follows:

P1 - Oil shale reserves
P2 - Oil shale extraction
P3 - Oil shale losses in mining
P4 - Oil Shale to enrichment
P5 - Oil Shale to consumers without enrichment
P6 - Oil Shale for electricity and heat generation
P7 - Oil Shale for chemical industry (for shale oil production)
P8 - Oil Shale for "Other Industries" (cement)
P9 - Heat and electricity consumption by consumers
P10 - Products of chemical industry – shale oil etc. to the end-users
P11 - Products of "Other Industries" (cement) to the end-users

The principle of retorting, or extracting oil from oil shale, is to heat oil shale in the retort, or furnace, to 450-550 ^{o}C, when organic matter (kerogen) is extracted from oil shale. Organic matter is extracted into liquid component (oil), gas component (natural gas) and third component stays in oil shale in a form of carbon sediment (semi-coke).

In surface retorting, the retort is a furnace where prepared oil shale is placed.

In situ retorting is a process held in the deposit, where a room and pillar, limited by underground drifts or drillholes, are used as a retort. Oil shale is blasted inside them, or disintegrated without blasting, in order to become suitable medium for inflow of air and gasses, thus providing the process of retorting to develop. Recovery ratio in surface retorting reaches 90%, while in underground retorting it may go as low as 30%. Table 3 gives an overview of the world's commercial oil shale retorting technologies.

Table 3. Overview of the world's commercial oil shale retorting technologies [10]

Retort	Chinese retort	Kiviter	Galoter	Petrosix	Alberta Taciuk (Atp)
Country	China	Estonia	Estonia	Brazil	Australia
Location	Fushun	Kohtla-Jarve, Kivioli	Narva	Sao Mateus do Sul	Stuart
Configuration of retort	Vertical	Vertical	Horizontal	Vertical	Horizontal
Heat carrier	Gas	Gas	Ash	Gas	Ash
Size of oil shale, mm	10-75	10-125	0-25	6-50	0-25

One of the main hindrances to oil shale becoming a widely exploited resource is the difficulty of extracting and processing it. Consequently energy companies have been focusing on developing more efficient retorting technologies. Table 4 below summarizes recent developments in retorting technology.

Table 4. Advances in oil shale retorting technology [9]

Process Type	Advances	Status	Project
Conventional	Shale pre-heating increases gas and oil yields; extracts intermediate products before high temperature pyrolysis Combusting carbon residue on pyrolized shale generates process heat; reduces emissions and spent shale carbon content.Recirculation of gases and capture of connate water from shale minimizes process water requirements. Lower heat rates reduce plasticization of kerogen-rich shales	Demonstrated at pilot scale in ATP	Stuart Shale
In-situ	Slower heating increases oil and hidrocarbon gas yield and quality	Proven at field scale	Shell ICP
	Recovery of deeper resources enabled by heating technology	Indicated	
	Improved ability to cintrol heat front by controlling heaters and back pressure	Proven	
Novel processes	Supercritical extraction processes	Concept	ATP
	Higher heating rates	Research	
	Shorter "residence" durations	Proven	
	"Scavengers" (hydrogen or hydrogen transfer/donor agents)	Research	
	Solvent extraction of kerogen from ore	Research	
	Thermal solution processes	Research	

THE ENVIRONMENT

A commercial-scale oil shale project would reshape the social, economic, and political life of the communities in the oil shale region. Development will occur in remote, sparsely populated, and non-industrialized areas with only limited infrastructure in place. If development is rapid, the local communities may suffer from inadequate utility services and insufficient public services, such as public transportation, education, health care, and police and fire protection. Republic of Serbia should provide resources, such as planning assistance and money, in advance of development. Oil shale development could also have negative effects on air, land, and water in the oil shale region. Specific concerns include:

Mining – release of silica, metallic and organic salts, mercury, methane, carbon monoxide, nitrogen oxides (NOx), unburned fuels, and nuisance dusts during blasting, crushing, transportation, and materials handling; leaching of salts and organic compounds from disturbed overburden and oil shale.

Retorting and upgrading – release of hydrogen sulfide, carbonyl sulfide, carbon disulfide, sulfur dioxide, polycyclic organic matter, trace metals, NOx, and particulate matter, especially from the retorts during discharging and maintenance; Accidental discharge of process water condensates; Venting and loss of hydrocarbon vapors from poorly sealed storage tanks and pipelines; Discharge of heavy metals during catalyst regeneration.

Thermal energy and power systems – emissions of sulfur dioxide, NOx, and particulate matter in stack gases. Discharge of blow downs and water treatment chemicals.

Waste management – disposal of retorted oil shale, spent shale, spent catalysts, process waters and sludge, chemicals from treatment of water and wastewater, fly ash, and domestic wastes from worker facilities and related municipal growth. [8]

Recently, the technology of oil shale extraction has been improved. Entire oil shale volume and entire organic matter from them is used now. Water is no longer used in the process; ash is not toxic and can be used in the cement industry. Air pollution is minimized and below permitted values, while processing plants are equipped with CO_2 collectors.

THE ECONOMY

Economics of shale oil production strongly depends on price of conventional oil. In general, higher prices of conventional oil are more convenient for shale oil economic results. Besides, it is very important that price of conventional oil is stable and projections of price flow are reliable. The latter is especially important for large projects and building of ex-situ processing plants, due to huge investment requirements.

It is obvious that current situation at oil market is not favorable for shale oil production, nor for starting of new projects. Drastic decrease in 2014 has brought the oil price very close to break-even point of shale oil.

INDICATIVE MAIN PROJECT STAGES AND CORRESPONDING TIME SCHEDULE

According to global experiences, there are three main phases of oil shale industrial process development: preparation, construction and work. Preparation usually takes two years and includes feasibility study, preliminary design and solutions. Second phase usually lasts about three years and includes main project design, plant construction and test work. Final stage, steady work, begins in sixth year of project.

CONCLUSION

Geological reserves of oil shale in Serbia are significant. However, except for Aleksinac and Goč-Devotin deposits, most of the oil shale deposits have been explored at the level of basic geological exploration, which means that more detailed explorations are necessary. This activity is of particular importance regarding determination of organic matter and oil content, needed for planning of future activities related to mining, processing, utilization and environmental protection.

Potential of shale oil production in Serbia is huge. It could be one of the major energy sources in Serbia. Consequently, it would significantly improve economy and level of development in the regions around the plant. Also, domestic shale oil production means significant substitution for imported oil and a factor that improves country's energy independence.

However, concerns about economic justification of such project are rising after recent strong decrease of conventional oil price. So, there are still numerous challenges before the introduction of shale oil industry, related to technological, environmental and economical issues.

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TOXIC VIGILANCE DATA ON POISONING IN SERBIA

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ABSTRACT

The poisoning could have occurred as a result of an intake of or exposure to dangerous substances. In this paper we present some results of the research of adults and children affected by the poisoning. Presented results have shown that the leading causes were: alcohol, medications, corrosives and pesticides.

Key words: poisoning, intake, exposure, dangerous substances.

INTRODUCTION

Data about the poisoning in Serbia caries the information on adults and children affected by the poisoning. The poisoning could have occurred as a result of an intake of or exposure to dangerous substances which could endanger health and with sometimes fatal consequences. The VMA (Military Medical Academy) is a National Toxicology Control Centre – NTCC. They compile annual reports on cases of poisoning that include data collected from other medical institutions. The NTCC is a a Lead Institution, institution which provides the following services:

Medical help in prevention and treatment of acute poisoning; Detection of chemicals in the biological material, water, air and soil; Education in clinical toxicology and toxicological chemistry; Scientific research in toxicology and pharmacology.

The NTCC consists of the following units: Clinic for urgent and clinical toxicology; Toxicology and pharmacology Institute; Toxicology-chemical Mobile Units for bigger scale accidents.

With the help from the official bulletin "Godisnjak," it has been in production for 4 years now, this report analyses the data on cases of poisoning in Serbia in the year 2013. The data was collected from the National Toxicology Centre's Admission and Resuscitation department (OPR) and from the Intensive Care Unit.

Besides, there is a Toxicology Information Department as a database of available chemicals, their manufacturers and distributers and their storage locations. There is also data on acute self poisoning cases, occupational poisoning and cases of accidental poisoning in Serbia.

RESULTS AND DISCUSION

Table 1.* Available data from the Serbian National Statistics Office website – Statistical bulletin for Serbia and VMA

Year*	Population number	Number of registered cases	Number of cases per 1000 population
2010	7 320 807	3996	0,54
2011	7 120 666	3986	0,55
2012	7 291 436	4176	0,57
2013	7 186 862	7024 (4199 OPR 3492; 83% I Clinic 707; 17% + 2825)	0,97

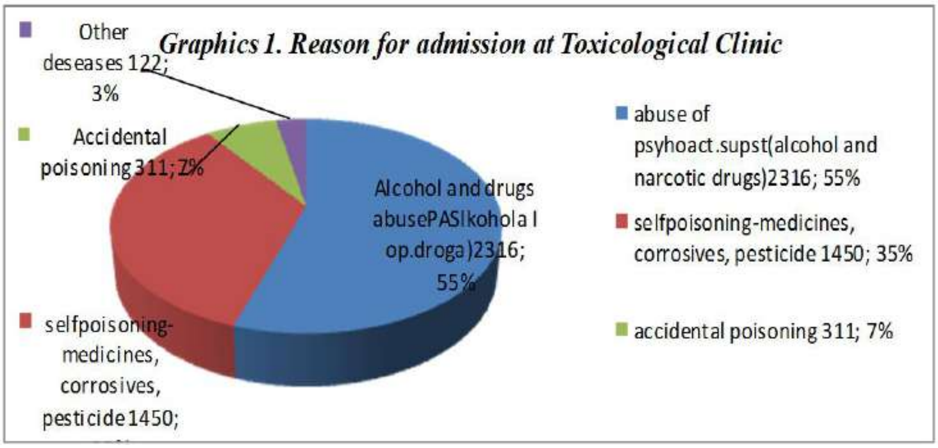
Table 2. Types of calls for admission - Intoxication of adults and children

Agents	Adults		Children	
	Calls from doctors	Calls from general public	Calls from pediatrician	Calls from general public
Medicines	107	17	112	9
Pesticides	84	30	35	5
Corrosives	40	10	26	4
Mushrooms	7	7	21	7
Gases	9	3	0	0
Alcohol	5	2	2	1
Misuse of funds	4	4	0	0
Others	46	57	91	27
Total	**302**	**130**	**287**	**53**

Adult Total: 432 Citizens Total: 183 (23,7%) Children Total: 340

Basic information about the number, age and sex/gender structure and representation of different types of poisoning and hospitalized patients are presented in subsequent graphic illustration.

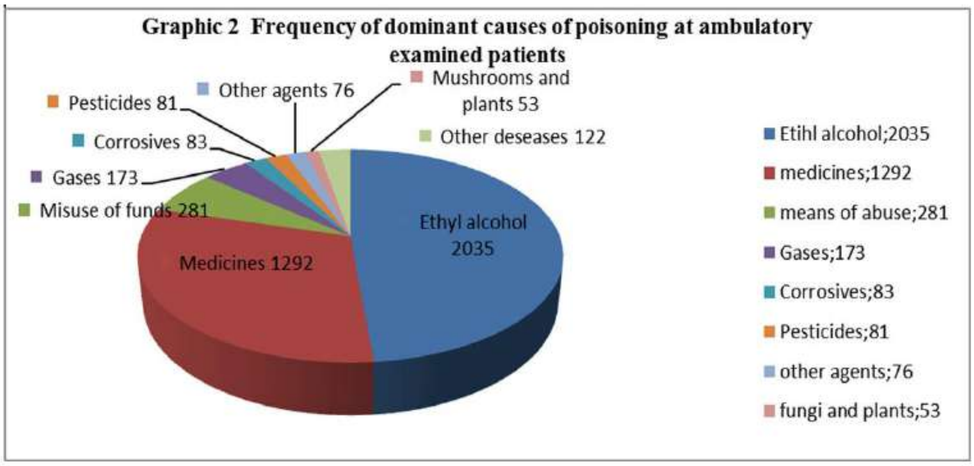
The National Toxication Centre's Admission and Resuscitation Department (OPR)



Graphics 1. Reason for admission at Toxicological Clinic

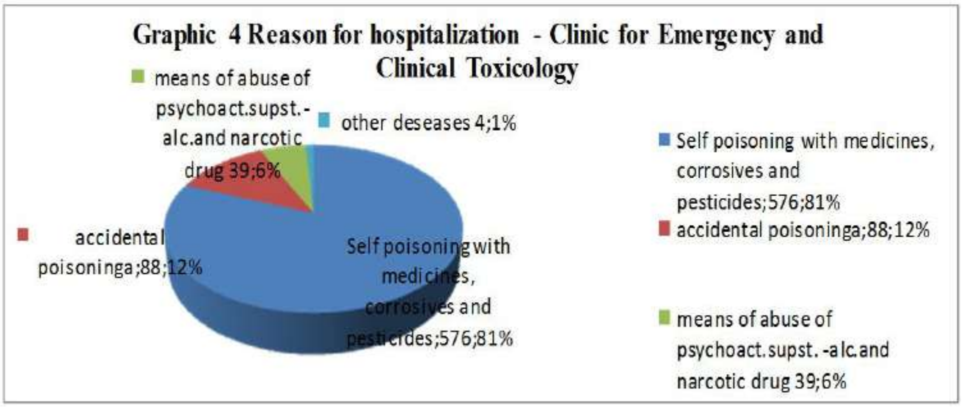
Table 3. Frequency of dominant causes of poisoning in relation to individual agents

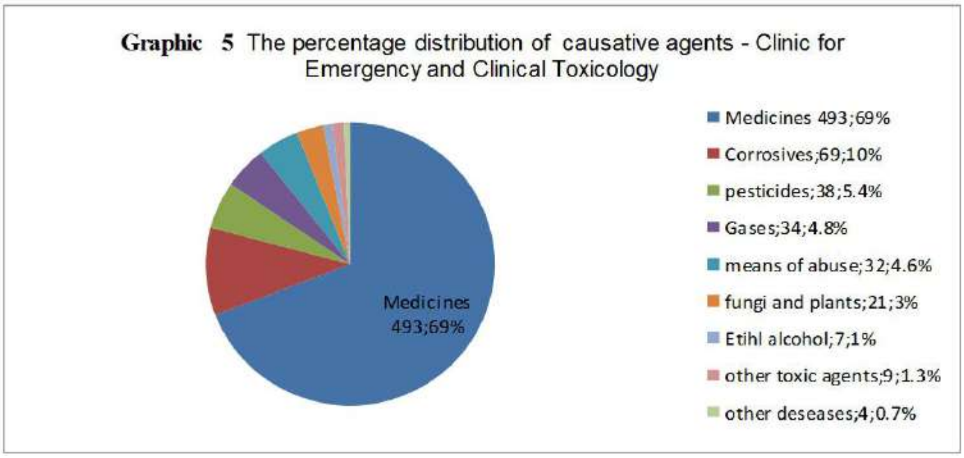
Dominant cause	OPR	Clinic	
	Number	Number	%
Alcohol	2035	7	0,3
Misuse of funds	281	32	11,3
Medicines Psychoactive Others	1292 1089 203	493 407 86	38,1 37,3 42,3
Gases	173	34	19,6
Corrosives	83	69	83,1
Pesticides	81	38	46,9
Mushrooms and Plants	53	21	39,6
Other agents	76	9	11,8
Other deseases	122	4	3,2
Total	4199	707	



Gender break down: 39% women, 61% man. Level of poisoning: Light PSS1 – 75,1%; Medium PSS2 – 13,7%; Heavy poisoning PSS3 – 7,8%.
Age break down: 19-65 years – working able population 82,2 %; over 65 years – 6,5%; till 18 years – 9,4%.

Clinic for Emergency and Clinical Toxicology – 707 patients





- Gender break down – 59% women, 41% men. Level of poisoning: light PSS1 - 53.9%, medium PSS 2-17,7% heavy poisoning PSS 3-22,9%
- Age break down: 19-65 –working able population 84,7%; over 65 – 10,8%; till 18 – 4,5%.

Using a similar methodology, other data can be analysed to show the breakdown in relation to the chemical agent causing the intoxication by cross-referencing the number of patients at the OPR and the Clinic for Urgent and Clinical Toxicology with the cause of the intoxication.

(Ethyl alcohol, medication – most used Benzodiazepini(bromazepam, diazepam), antiepileptic, means of misuse – most commonly heroin, marihuana, cocaine, fire related gases, chloride vapours from domestic cleaning products, carbon monoxide, bromine vapors, industrial gasses, pesticides, organophosphourus insecticides and herbicides, corrosives – vinegar acids, HCl, NaOH, bleaching and cleaning material, fungi, plants, other agents, other illnesses.)

CONCLUSIONS

Similar analysis was conducted in the period 2010 -2013 showing that similar types of causes were present in the same period. This report contains the data from 2013. It shows that the information produced for the update of the annual journal for the 2013. was more comprehensive compared to previous years.

There were 4199 people examined at the OPR department of which 82% were working-age population. The biggest percentage of poisoning came from the alcohol followed by the over consumption of prescribed medication and the miss-use of drugs. Following the examination, 707 patients were admitted at the Clinic. The leading causes were medications, corrosives and pesticides.

There were 30 deaths registered proven to be linked to effects of vinegar acid, Hydrochloric acid, benzodiazepine, fire related gasses, heroin, pesticides, paracetamol, etc)

The report includes data from other Medical Centres located in other bigger Serbian cities. They are as follows: Accident and emergency Unit of the Medical centre in Subotica, Clinical centre Nis, general Hospitals in Pancevo, Pirot, Sabac, Vrsac and Zrenjanin. The Health Centres "dr Dragisa Misovic" in Cacak and "Studenica" in Kraljevo, totaling 2825 people. Institute for health protection of children and youth and mother and child of Serbia, "dr Vukan Cupic" in Belgrade.

The main causes of poisoning are alcohol and over use of prescribed medication, followed by all other afore mentioned causes. Poisoning by over use of the prescribed drugs is the most common at the Institute for Mother and Child in Belgrade. Based on the high number of cases, poisoning is one of the most common cause of death in the Republic of Serbia.

The support from other Serbian health institutions is very important and it needs to improve in the following year in order to provide more comprehensive data. The new law on medical records and collection of health related information will also define required systems and questionnaires for obtaining the needed data on acute poisoning.

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THE ASSESSMENT OF HEALTH RISKS FROM MEDICAL WASTE GENERATED IN DENTAL PRACTICES

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ABSTRACT

Introducing and implementing adequate procedures to minimize the risk of medical waste in the first place to protect public health and reduce the impact on the environment. The first step in the management system is to identify potential risks. For good practice in management of medical waste is crucial that health care workers and staff know exactly what is expected of them in connection with the separation of waste, to be motivated and properly trained for the above activities, and that they have adequate cooperation with the management of health institutions on this issue.

Key words: medical waste, health risk, dental practices.

INTRODUCTION

Medical waste includes all the waste generated by the provision of health services in health institutions or elsewhere, regardless of its composition, characteristics and origin. The generation of waste in health care institutions is unbalanced. Quantity of wastes depends largely on the size and type of institution, ie. whether the institution has an infirmary and what kind of disease cures, if only perform examinations and minor interventions,etc.

Improper management of medical waste until recently was a significant problem because of the lack of separation of waste in health care institutions and their disposal in landfills where it is mixed with municipal waste. It is necessary to continue to implement the initiated process of mandatory classification of medical waste on the site where the hazardous and non-hazardous. All institutions of health care in which medical waste generated are required to draw up waste management plans and appoint a person responsible for waste management inaccordance with the law (1).

Types of medical waste, which must be required to separate from the general waste generated in dental practices from the moment they are produced to the moment they are passed to the authorized person for disposal and treatment are sharps (needles, waste from ampoules), pathological waste (extracted teeth) and infectious and potentially infectious waste (swabs, gloves,disposable syringes),as well as radioactive waste.Waste with high concentrations of heavy metals represents a sub category of hazardous chemical waste. In this waste group consisting of mercury, which is most often generated by amalgam fillings.

ASSESSMENT OF HEALTH RISKS

Risk assessment is a combination of various decisions and analyzes are obtained using methods of risk assessment with the aim of achieving security in the work. This process includes economic, legal, political, health and social aspects.

Risk is the probability that there is a load caused by accidents which can lead to injury, illness or environmental damage. Basic elements of risk assessment are the probability and consequences. Risk management means taking preventive measures and procedures, preparation for the incident and the response to it, as well as improving the current situation with the aim of reducing risk and creating conditions under which the risk is acceptable.

There are five basic steps in risk assessment: identify risk, to determine who might be harmed and how to assess the risks and decide whether existing precautions are adequate or should additional measures, record the results and conclusions of the assessment and check made assessments (2).

In the framework of the legislation, in the fields of health and medicine, as well as in environmental protection, there is a need for creating a risk assessment by all entities dealing with waste management. It is also necessary that the different departments there is ongoing cooperation of experts involved in waste management. The purpose of proceedings. Use of risk assessments is to assist in finding a reasonable decision in order to protect the population and environment. It is important that the assessment is carried out actively and with reflection, rather than simply round off to give answers.

For risk assessment it is necessary to consider how hazards and risks. Therefore, risk assessment is a process in which: identify hazards, identify and assess the threats that are linked with this, assess the risks and assess the significance of these risks in the circumstances discussed.

Inadequate management of hazardous medical waste, starting from the operation within institutions that provide medical or veterinary services to final disposal, is a very high risk to the health of staff, patients and the general environment.

Medical waste presents a risk to health care workers (doctors, nurses, technicians and paramedical personnel, pharmacists), patients in health care facilities or patients which provides home care, visitors to the health worker responsible for follow up and the general public in case of an infectious or toxic waste gets into the water system, or if animals or pests come into contact with infectious waste and thus transmit the infection to the general public (3,4).

The causes of the disease that, according to past experience of importance, are eg.: fungi, viruses hepatitis B and C, herpes simplex virus, HIV, legionella, mycobacterium tuberkulozis, pseudomonads, staphylococci, streptococci, viruses that can lead to infection of the upper respiratory system .

WASTE MANAGEMENT OF DENTAL OFFICES

Medical waste management system must be defined in the dental clinic. All team members must be familiar with the rules or plans, and procedures on medical waste management. In the dental clinic must be appointed the person responsible for the management of medical waste. Team members dental clinics have proper and timely use of personal protective equipment, in order to reduce the risk of infection (5,6)

Reduction of risks to health from the medical waste generated in the dental practice is solved by setting up an integrated system of medical waste management as well as developing effective and efficient system for the collection, storage, treatment and disposal of dental waste in accordance with Waste Management Law and EU Directives. The management system allows the protection of the health and safety of all persons in dental clinics and outside of them (staff, patients, visitors and residents), control of specific biological, physical and chemical properties of waste that can harm human health and the environment, protection of the environment by promoting proper waste from the place of origin to final disposal, reducing waste and especially hazardous medical waste, recovery, recycling and eventual use of waste (7,8).

Disposal of dental waste is given on table 1.

Table 1. Dental waste disposal guide

Dental waste	Disposal
Needles, blades, endodontic files, partially full carpules, carpules contaminated with biohazardous waste	-Sharps container treated by steam autoclave. -Sharps container disposed of via a registered medical waste hauler. - Alternate treatment technology (e.g. encapsulation). - Mail back sharps
Fluid blood in IV tubing, infectious tissues, cultures	-Red biohazard bag, stored inside a rigid container, treated by steam autoclave. -Red biohazard bag, stored inside a rigid container, disposed of via a registered medical waste hauler
Body fluids and liquid blood	-Sanitary sewer system
Waste of apparent medical origin that is not regulated medical waste, such as dressings with non-liquid blood	-Regular trash disposed in a dumpster or trash enclosure maintained in sanitary condition.
Iodine, lead, most cold sterilant solutions, isopropyl alcohols, cleaners that are corrosive, (with a pH $\geq$ 12.5 or $\leq$ 2.0). Lead foil, sludge from silver recovery unit (waste resulting from treating X-ray fixer onsite), dental amalgam, teeth with amalgam.	-Container with a hazardous waste label, a tight fitting lid and removed off site under a manifest by a registered hazardous waste hauler. -Store in an appropriate container and maintain records that indicate that the waste is managed by a legitimate recycler. - If not recycled, these wastes must be stored, labeled, and disposed of as a hazardous waste, as described above

It is very important to implement and train the staff in the dental practice in regard to the implementation of the Plan of medical waste management. Safety Precaution to avoid risks to health from include:getting acquainted with the rules of medical waste disposal,sorting of waste by source and origin,the use of protective equipment with additional hygiene steps,closing of packaging must be visibly marked with the internationally recognized color coding system as soon as they are filled with waste,storage of medical waste at dental clinics to disposal or transport at appropriate locations,careful transportation of medical waste to the place of disposal by an authorized organization (9).

ECO DENTISTRY

Eco dentistry or "green dentistry" refers to oral health care and dental treatments that use technology, procedures and materials that help not just dental health, but also to preserve the health and quality of the environment.

Eco dentistry, the term protected by the Eco-Dentistry Association (EDA), includes high-tech innovation to increase efficiency and effectiveness, while reducing the amount of waste and pollution. Dentists who use "green" technology in their practices incorporate technologies that have numerous advantages (10).

One of the most significant innovations of green dental office is a digital radiography, which eliminates the need for traditional recording X-rays. Digital X-ray technology drastically reduces the use of harmful chemicals, such as lead and mercury, which are released into the environment. In addition, the radiation to which patients are exposed is less by 90% compared with traditional X-ray imaging. The recordings obtained in this manner are available immediately, and better quality compared to X-rays, and can be enlarged for better diagnostics.

Green "dental practice also use biodegradable disinfectants and sterilization of high quality. These methods do not require ventilation, chemical fumes or permission for the disposal of toxic chemicals. Also, they use more energy-efficient washing machines and clothes dryers, in order to maintain the purity of the fabric used in the office. What is important is that all the napkins, towels, hats and other accessories used again, reducing the use of paper products, and thus preserves the forest from cutting (11).

At the present time, when they are available different materials for dental fillings, crowns and other restorative dental supplies, "green" binder dentists use of new materials, which do not contain metals, and white composite fillings. As well as these materials look more natural, they do not contain heavy metals. The benefit to the health of patients is large, and moreover, it is less hazardous waste, which threatens the health of the planet (12).

CONCLUSION

Proper handling of waste resulting from dental practice reduces the risk to health. Creating a plan for the management of medical waste from dental practice aims not only the motivation of employees to effectively manage mediicnskim management, but also the development of their awareness in the medical waste management. It is necessary multidisciplinary cooperation in order to determine healthcare waste management system, both at the dental clinics and the level of administrative districts.

Acknowledgements

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INFLUENCE OF EXPOSURE TO AIR POLLUTION ON USE PRIMARY HEALTH CARE AT WOMEN

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ABSTRACT

The objective of this paper was to estimate the use primary health care in female populacion because of exposure to sulphur dioxide and soot. The study sample included 327 non smoking women who were interviewed about upper and lower respiratory symptoms in the last year due to what came to visit health care facilities seeking professional help. The results showed that examines from exposed group to air pollution had statisticaly higher use of primary health care and absence of work because of upper respiratory symptoms, whereas there was not statisticaly higher prevalence of lower respiratory symptoms.

Key words:women, primary health care, air pollution, respiratory symptoms.

INTRODUCTION

The largest number of epidemiological studies have examined the impact of air pollution on health focused on the effects that occur in the respiratory tract (1,2).

Exposure to pollutants from air can lead to an increased prevalence of respiratory symptoms, mild lung function, increased absenteeism of work and increased hospitalization and mortality due to respiratory diseases (3,4). What will be the intensity of expressed effect on respiratory organs depends primarily on the characteristics of present pollutant or combination of pollutants, concentration and length of exposure, size and distribution of emission sources, local meteorological conditions etc.

Individual in response to exposure to air pollution depends on the properties persons (including genetic factors). Also, in response affect lifestyles and behavior, as well as the existence of some chronic diseases.

The aim of the study was to determine the frequency of occurrence of certain respiratory symptoms and disease, and the degree of use of primary health care in female population who expose to different concentrations of air pollutants

METHOD

The study included 320 women, aged 20-40 years, non-smokers and professional unexposed to air pollution. The group exposed to air pollution made up women who live at least five years in the area the measuring point in Nis (n=167) and the control group consisted of women who live in Niska Banja (n=153).

Data on the frequency of respiratory symptoms were obtained using a questionnaire originally constructed. The survey was conducted by the physician, through interviews in the period from May to June 2012. The survey included the date that are related to the presence of respiratory symptoms occurred in the women in the previous year and diagnosed by a doctor. The collected data are divided into: symptoms by upper respiratory tract symptoms and by the lower respiratory tract. Symptoms from the upper respiratory tract were recorded as stuffy nose, secretions from the nose, difficulty breathing through the nose, dry throat, sore throat, hoarseness and coughing. Chest tightness, wheezing, choking, and long-lasting dry cough are recorded as symptoms from the lower respiratory tract. Also, the questionnaire was included questions on the use of primary health care due to respiratory symptoms, as well as the length of absence from work.

Examination of the outdoor air pollution was carried out at the Institute of Public Health in Nis. For this study analyzed data for the period from 2008.–2012. The air samples were determined content of sulfur dioxide and soot and commented according to the Regulation on conditions and requirements for monitoring of air quality (Sl. gl RS 11/2010).

In order to determine statistically significant differences were used Mann-Whitney test, Student's t-test and $\chi 2$-test.

RESULTS

Analyzed and measured concentrations of sulfur dioxide and soot for the test period are given in Table1.

Table 1. Average annual concentrations of pollutants at measuring points in the period 2008–2012 (mg/m^3)

Pollutant	Measuring points		Mann-Whitney test	p
	Niš	Niška Banja		
SO_2	17.21±16.63	2.32±1.45	Z=23.88	p<0.01*
soot	24.45±19.34	5.67±9.37	Z=22.54	p<0.01*

* statistical significance

It can be noted that the measured average concentrations of pollutants listed in both measuring points were below the limit values of imission prescribed by the Regulation. However, it has been shown that concentrations of sulfur dioxide and soot at the measuring point in Niš were statistically significantly higher compared to the same of the measuring point in Niska Banja.

Between two groups of women showed statistically significant differences in the frequency of symptoms of the upper airways, while the frequency of symptoms of the lower airways statistically significant difference was not determined (Table 2).

Table 2. The statistical significance of differences in the prevalence of respiratory symptoms in the group of women

Measuring points	Respiratory symptoms	
	upper	lower
Niš	101 (60.475%)	43 (25.74%)
Niška banja	53 (34.64%)	35 (22.87%)
χ^2	$\chi^2 = 21.29$	$\chi^2 = 3.45$
p	p < 0.01*	p > 0.05
OR	2.89 (1.79 < OR < 4.67)	0.94 (0.87 < OR < 1.25)

* statistical significance

The exposed group of women was statistically significantly more frequently used primary health care (Table 3) due to problems with respiratory organs. Absence from work due to problems with respiratory organs were also more frequent among women exposed to air pollution (Table 4).

Table 3. Exposure to air pollution and visits to the doctor because of problems with respiratory organs

Group	*Number of the visits to the doctor* (n / %)				χ^2	p
	never	1-3	4-6	>6		
exposed (n=167)	11 (6.58)	131 (78.44)	19 (11.34)	6 (3.59)	56.24	p<0.001*
control (n=153)	63 (41.18)	78 (50.98)	6 (3.92)	6 (3.92)		

* statistical significance

Table 4. Exposure to air pollution and absence from work because of problems with respiratory organs

Group	*Absence from work* (n / %)				χ^2	p
	never	1-3	4-6	>6		
exposed (n=167)	15 (8.98)	105 (62.87)	40 (23.95)	7 (4.19)	47.97	p<0.001*
nonexposed (n=153)	65 (42.48)	59 (38.56)	24 (15.68)	5 (3.26)		

* statistical significance

DISCUSSION

Results of this study show that the prevalence of symptoms of the upper respiratory tract significantly higher in women who were exposed to higher concentrations of pollutants from the air.

The content of sulfur dioxide and soot in the air was monitored on the basis of the air quality indicators used in the evaluation of chronic exposure to harmful substances from the air. The average annual concentration of sulfur dioxide and soot in the air measured at the measuring point in Nis and at the measuring point in Niska Banja, during the test period were below the limit values laid down by national standards. However, using statistical test has been proven that the difference was statistically significant between these two sites, so it can be said that the female part of the population lives in Nis was exposed to significantly higher concentrations tested for air pollutants in relation to the female part of the population who live in Niska Banja. Studies done in the world have confirmed the fact that chronic exposure to low concentrations of pollutants in the air can affect the occurrence of respiratory symptoms and disease (5,6).

A study done in Switzerland (7) followed concentrations of particles in two years and proved that their fall concentration of 6.2mg/m^3 to 3.9mg/m^3 had not statistically significant effect on reducing the incidence of respiratory symptoms, especially the occurrence of secretion nose and difficulty breathing among the adult population. However, in chronic respiratory patients reporting these symptoms were significantly reduced. Bayer-Oglesby et al. (8) found that in adults living near busy crossroads and exposure to concentrations of pollutants in the air increased significantly more have persistent symptoms of upper respiratory tract. Nose secretion was statistically significant presenting in exposed persons who are non-smokers. Significantly higher prevalence of respiratory symptoms and reduction in lung function showed a study carried out in France (9) in chronic exposure to air pollution, as well as more frequent hospitalization of chronic respiratory patients in increasing the daily concentration of particulate matter and sulfur dioxide.

The prevalence of symptoms of the lower respiratorz airways does not differ statistically between two groups of women. It is known that a triad of symptoms - cough, wheezing and choking point the history of an allergic disease. Some studies have shown that allergic diseases are more common in areas with polluted air in relation to the clean areas (10,11). In addition, Niska Banja is the zone of rest and recreation with lots of greenery and is possible to expect a higher prevalence of symptoms of lower respiratory tract in the population of this area.

The frequent occurrence of respiratory problems due to exposure to air pollution causes frequent visits to doctors, and often absence of work. Time and labor productivity is also affected by the fact that it comes to an active working population.

CONCLUSION

The paper showed statistically significant difference in the expression of respiratory symptoms and diseases in women exposed higher concentration of outdoor air pollutants compared to the control group. Women exposed to air pollution often use primary health care and they longer absent from work.

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THE INFLUENCE OF NUTRITION ON THE TOXICITY OF POLYCHLORINATED BIPHENYLS

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ABSTRACT

The diet is a major route of exposure to environmental contaminants, such as polychlorinated biphenyls (PCBs). However diet-derived molecules can modulate, and possibly help to prevent the toxicity of environmental contaminants. In this paper we demonstrated and analyzed published data on how diet can modulate the toxicity of PCBs.

Key words: diet, polychlorinated biphenyls.

INTRODUCTION

The fact that the human population is daily becoming more exposed to the increasingly higher concentrations of toxic compound both in the work and living environment, caused nutritionists and toxicologists to study the relationship toxic substance- nutrients in more details. (1-3). The results of recent studies point to the fact that some constituents of the nutrition can reduce or prevent adverse health effects caused by some toxic substances in the living and work environment. (4,5).

The purpose of this paper is to present the published data on the ways in which polychlorinated biphenyls (PCBs) are introduced into body through nutrition, and the compounds in the nutrition that can reduce their toxicity.

PCB GROUPS AND THEIR INFLUENCE ON HEALTH

Polychlorinated biphenyls have been classified as 209 separate congeners whose physical, chemical and biological properties depend on the position of the substituted chlorine atom in the in the biphenyl ring.

PCBs come into the environment from anthropogenic sources, but they can also be of natural origin (they have been detected in volcanic ashes). They are used in the systems for production and distribution of the electrical energy, as well as for capacitor and transformer fluids, for production of ink and in hydraulic and vacuum pumps although their use has been recently being reduced.

PCBs are divided into two large groups: coplanar PCBs ("dioxin-like PCBs") and ortho substituted isomers ("non-dioxin-like PCBs").

("Dioxin-like PCBs" congeners perform their effects through cytosolic receptor which binds aromatic hydrocarbon (AhR). Their toxic effects are seen on the immune and reproductive system, they are carcinogenic and they have adverse effect on the development of the nervous system. (6).

"Non-dioxin-like PCBs" produce their toxic effect independently from aromatic hydrocarbons (AhR). This group has a toxic effect on the nervous system, endocrine system (especially on the thyroid gland) after accidental introductions or long-term exposure (7).

Under the Stockholm convention (Serbia also being the signatory) PCBs are classified into the group of "persistent toxic compounds" (8) for which there is a prohibition or limitation of use.

Regardless of this, the research in the USA where PCBs have been discontinued from use since 1977, the serum analysis of the population still shows a significant concentration of PCBs (9). A significant part of the world's population have been exposes via nutrition to dioxin and PCBs and more frequent accidents only augment the exposure of the population to these chemicals. (e.g. from contamination of cow's milk in Germany, to citrus pulp pellets from Brazil as an ingredient in feed and etc.) (10).

NUTRITION AS RISK AND PROTECTION FACTOR AND PCBS

Due to its persistency, stability, lipophillicity, biocumulative properties, biomagnification and the possibility of being airborne, PCBs residues have been detected in almost all samples.

Although there are various routes of introduction, the human population is exposed to PCBs for the most part via nutrition (fish, shells, crustacean, meats, milk and dairy products) (6,11).

Toxic effects of dioxin and dioxin-like compounds by means of activation of aryl hydrocarbon receptor (AhR) have been the subject of many studies (12,13). At the same time many endogenous and exogenous compounds (including the compounds in diet) have been marked as agonist or antagonist thath can mediate activated AhR, without expressing toxicity (ex. flavonoids) (14). Recent studies cite several AhR-activating compounds that can influence the immune response by inhibiting the symptoms of allergy and asthma (15).

PCBs cause oxidative stress and endothelial cell inflammation, and can lead to the development of cardiovascular diseases (4), while nutrition rich in antioxidant and anti-inflammatory nutrients or bioactive compounds lead to the reduction of the inflammation, metabolic syndrome, and atherosclerosis (3,4).

Endothelial damage can be repaired by intake of omega-3 fatty acids which modify proinflammatory response (16). Some authors claim that for these fatty acids, flax oil is the better choice since sea fish which is rich in omega-3 fatty acids can also accumulate PCBs (17).

The opinions on fish intake and accumulation and exposure to POPs differ. Bergkvist C. et al. claim that although the exposure to PCBs is related to the higher risk for myocardial infraction, the protective effect is provided by fish fatty acids (eicosapentaenoic acid and docosahexaenoic acid; EPA-DHA), and advise that for this reason fish contamination by PCBs must be prevented (18).

Rylander et al. compared the level of POPs (including PCBs) in the serum of the population living in the coastal part of Norway with nutrition consisting of marine food (fatty fish, fish liver, fish liver oil, seagull eggs and halibut). The intake of fatty fish (rich in fish fatty acids) has not significantly influenced the level of POPs (19).

Different results have been obtained in France, in a research conducted in fishermen and consumers of fresh water fish. It has been confirmed that people who eat freshwater fish can have levels of PCBs in their blood, that exceed the critical concentration that presents a health risk. The French Agency for Food, Environmental and Occupational Health and Safety (Anses) recommended the limitation of consumption of fish (eel, barbel, bream, carp and catfish) which can accumulate high level of PCBs, and published recommendations on the consumption of fish products for various populations, especially for pregnant and nursing women and children under 3 years of age (20).

Fats that originate from nutrition can not only modulate the toxicity of PCBs, but are also included in the metabolism of fats in the organism thus enabling the elimination of PCBs.

Redgrave et al. (21) presented a case report of person with high PCBs concentration (Arochlor 1254), in the fatty tissue (3200mg/kg), suffering for dyslipidemia and diabetes which required daily doses of insulin. After consuming the food with addition of olestra (esters of fatty acids and saccharose; around 16 g/daily through potato chips) for 2 years, the concentration of PCBs in the patient's fatty tissue dropped considerably (56mg/kg). At the same time, the elimination of PCBs from fatty acids was in the direct correlation with the disappearance of the clinical picture of the diabetes and normalization of the serum lipids. These results were confirmed on animals (22).

The efficiency of olestra in the elimination of PCBs has been proven in the inhabitants of Anniston, USA, who had increased levels of PCBs in serum (23).

Polyphenols (especially from green tea) can affect the fat absorption and fat soluble compounds (24). By consuming green tea, the level of lipids in plasma is reduced while lipid and fat soluble compound excretion is increased, including PCBs (25,26).
An experimental study showed that mice fed on green tea had better antioxidative defense, during the exposure to coplanar PCBs, which substantiate the claim that healthy nutrition can protect from the toxicities of environmental pollutants (27).
Caffeic acid is the most common acid in most fruits (the content depend on the ripeness and the size of the fruit), but is also present in wine, potatoes, honey, pollens etc. Li et al. established that caffeic acid has protective effect by reducing liver damage in mice exposed to PCBs 169 (28).

In a study conducted in the University of Kentucky, it was established that the intake of carotenoids from fruits and vegetables can reduce the risk for dioxin induced diabetes type 2 (29).

The design of the future research should be directed to the research of the substances that can facilitate the elimination of PCBs, but also nutrients such as plant polyphenols that can reduce the toxicity of PCBs.

Further research is needed to confirm whether the consumption of green tea is recommended in order to eliminate the fats and fat soluble "persistent, toxic, organic compounds".

CONCLUSION

All mentioned results support the claim that nutrition (some components of it) can affect the toxicity of PCBs. Unfortunately, there are presently few studies so further research is needed. The result obtained could lead to the application of proper nutrition that could prevent the diseases induced by exposure of the population to polychlorinated biphenyls in the living and work environment.

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THE MEDICAL-GEOGRAPHICAL ASPECTS OF ENDEMIC NEPHROPATHY IN THE MUNICIPALITY OF LAZAREVAC

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ABSTRACT

Endemic nephropathy is a chronic non-communicable disease related to the Balkans. Therefore, the aim of the paper is to emphasise the notion of endemic nephritis with special reference to the municipality of Lazarevac by the use of medical-geographical methods. Conditionally, the paper can be divided into five segments: the first, related to the concept and causes of the disease, the second, to the specifics of the municipality of Lazarevac in relation to nephritis, the third, to the results of clinical studies of endemic nephropathy, the fourth, to the function of the special hospital, and the conclusion, which sublimates previous findings.

Key words: endemic nephropathy, Lazarevac, focal points, factors, treatment.

INTRODUCTION

The Balkan endemic nephropathy (BEN) is a hereditary, tubulointerstitial and chronic kidney disease unique only to limited parts of the rural population of Southeast Europe. It is a non-inflammatory disease which eventually leads to the deterioration of kidney tissue and its gradual function failure in terms of chronic renal insufficiency (weakness). Bearing the prefix "Balkan" in mind, the conclusion is that it occurs in Serbia, but it also occurs in the territory of Bosnia and Herzegovina (Semberija, Bosanski Šamac, Brčko and Modriča), as well as Croatia (Slavonski Brod and Županja). Apart from the countries of former Yugoslavia, the focal points have been detected in 44 settlements in the Republic of Bulgaria (areas of Vraca and Mihajlovgrad), as well as in 41 settlements in the Republic of Romania [1]. As one of the major geographic disciplines, medical geography, using numerous methods, deals with the study of various communicable and non-communicable diseases, and therefore endemic as a particular and specific segment of the population morbidity. It sublimates all data obtained from the field or clinical studies in the form of cartographic and statistical models, as well as in the form of a spreadsheet of medical and demographic statistics [2]. Bearing in mind the fact that this is a problem which is “domesticating” in specific population and spatial framework, nozogeography approaches its study very thoroughly. Based on this, the Municipality of Lazarevac is a focal point of endemic nephropathy on the territory of Serbia [3].

ETIOLOGY OF ENDEMIC NEPHROPATHY

Endemic nephropathy, also known as "the mystery of the Balkan kidney", still has an unknown etiology. Despite the fact that there has been more than a few decades of various research in this part of Europe, the results are not particularly favourable, since they are based on assumptions. As it is the case with these diseases and all others, most authors take genetic factors as a general guideline for endemic nephropathy. It may have been the first assumption of the science of the old 1960s when it was named "a hereditary and chronic disease." But the claim that this is a hereditary disease has not been proved, thus forcing the conclusion that the factors of heredity do not play a key role in its exposure. For this reason, a completely different thesis has been considered, according to which the disease occurs due to numerous animate and inanimate environmental factors. Systematic research led to the relevant proof that protozoa, bacteria and rickettsia do not affect the occurrence of the Balkan nephritis. Little is known about the importance of viruses as another biotic agent in addition to bacteria and fungi, but there used to be unconfirmed claims that the "West Nile Virus", which is transmitted by birds, could be associated with endemic nephropathy. Another possible stronghold cited was also the impact of "Ochratoxin A" (OTA), a product of fungi which pollutes cattle food, and is indirectly found in human blood and tissues, which is why it is thought to be responsible for nephropathy and closely associated urinary tract tumors [4]. The research went in different directions, which is testified by the thesis that the occurrence of the Balkan nephritis is due to numerous agents of the inanimate environment, especially lead as an extremely carcinogenic element which could be found in water, mill stones and flour for human consumption. Special attention was also paid to cadmium, which is up to ten times more toxic than arsenic, causes kidney and muscle damage, and has an emphasized carcinogenic effect as well. Unfortunately, none of these hypotheses have been scientifically justified or confirmed. Bearing in mind the prior knowledge that endemic nephropathy occurs exclusively in rural areas of river basins, major efforts have been directed to assess the hydrogeological environmental factors and their impact on the incidence of the disease. In terms of hydrogeology, endemic settlements are more often found on alluvial sediments which cover the old tertiary sediments, and less often on river and lake terraces which rise above the river plains. The approach was taken in this direction to thorough checks of physical and chemical composition of host rocks where drinking water was found. It was concluded that it was mostly areas below 200 m, and further efforts were directed at the analysis of household well waters. The analysis covered their temperature, Ph value, the content of silicon dioxide, nitrates, numerous chemical elements and ions, yet unfortunately it did not lead to any particular crucial evidence. Evidence has shown, however, that during the course of summer the well waters mix with the contaminated underground waters in villages that use them, when the well waters are at a very low level, which consequently makes such households the focal points of endemic nephropathy. If we consider that the municipality of Lazarevac and Lajkovac are among the most vulnerable areas, the connection between surface coal mining and the incidence of the disease has been sought for a longer period of time. The effort was made to determine the effect of lignite and its impact in terms of coal deposits and by-roducts resulting from washing the coal before dry separation [5]. This is the way the aromatic hydrocarbons and amines soluble in water were created, whose effects are highly malignant and therefore considered responsible for the higher incidence of urothelial cancer. Many oligoelements whose lack or excess could cause this disease were also taken into consideration. Special attention was focused on selenium which is known for its anti-cancer effect, strengthening of the immune system and resistance, and the fact that its deficiency leads to the inability of cells to defend themselves against the impact of toxic substances and organic carcinogens from the environment. When it comes to endemic areas, zinc deficiency was discovered alongside selenium (outstanding defensive element, important for the immune system), but on the other hand, high concentrations of iron and magnesium (up to 13 times higher than in non-endemic settlements).

LAZAREVAC – STATE OF THE ENVIRONMENT AND NEPHROPATHY

Lazarevac, one of the 17 municipalities with an area of 3,825 square kilometers, is located 55 kilometers southwest of Belgrade. This rather small municipality with 58,224 inhabitants (population census in 2011) attracted enormous public attention 90 years ago due to the discovery and progressive development of one of the endemic diseases – endemic nephropathy. Back in 1921/22 professor Danilović noted the presence of a curious nephrological disease hitherto insufficiently defined and poorly substantiated in literature. In the years after the war, namely 1956/57, the first thorough medical biochemical and other studies were done which confirmed the presence of nephropathy and led to the proclamation of the municipality of Lazarevac endemic. Extensive research on endemic nephritis had been started in the aforementioned area on the bank of Kolubara. Only in the period from 1972 to 1982 the far-reaching investigations on the ground revealed that out of 34 municipality settlements there was as many as 14 rural settlements where the disease was present, with particular emphasis placed on hyperendemic focal points – Šopić, Vreoci, Petka, Medoševac, Arapovac, Veliki Crljeni, Županjac, Dudovica, Junkovac, Čibutkovica, Sokolovo, Stepojevac and Cvetovac [5]. There had not been registered a single case of indigenous disease occurrence in the urban settlement of Lazarevac and the remaining 20 settlements. The location of the aforementioned rural communities indicates that it generally occurs in the areas affected by the work on surface exploitation of lignite. This fact has precisely what influenced the first analyses of the water, soil and air in the aforementioned settlements and the connection of these media with the households. By examining the literature we can see that the average annual concentration of basic pollutants (sulfur dioxide, nitrogen dioxide and soot) falls within the permissible limits, but what concerns is the data which show that among the specific pollutants benzo(a)pyrene significantly exceeds the limits. It is a polycyclic aromatic hydrocarbon which is produced by coal burning and has an extremely carcinogenic and toxic effects especially on people in the vicinity of a plant for processing and burning of coal. Maximum annual concentration allowed for $C_{20}H_{12}$ amounts (1.0 ng / m^3), while the deviations from the limit values have increased by 19.5% in 2009, by 55.2% in 2010 and by 55% in 2012. In the village of Vreoci (measuring stations "Toplana" and "Sušara") the increased concentration of nitrogen and sulfur oxides has not been registered, but the concentration of soot has (0.54 to 2.2% above the threshold) as well as suspended particles of PM10 (26.2 to 93% above the limit values) for the period from 2011 to 2013 [6]. The quality control of the surface waters is carried out on the river of Peštan (right tributary of Kolubara) by the reference laboratory four times a year. The measuring station at Peštan shows that the water falls under class III in terms of the representation of suspended solids, dissolved O2 values, and the percentage of O2 saturation of water. In certain intervals the increased value of dissolved (Mn) was also registered. Saprobiological tests show that the watercourse is loaded with moderate organic pollution, in other words, that water quality corresponds to class II. The enormous amounts of waste water from households and industrial facilities also have negative implications for human health and the occurrence of nephritis. The villages in which primary and secondary sewerage networks lead to central septic tanks due to mining colonies, as well as direct discharge to the recipients: the rivers Onjeg (Dudovica and Čibutkovica), Peštan (Baroševac, Mali Crljeni and Rudovci) and the channel of Crna Bara (Veliki Crljeni). Industrial waste waters produced by the plants of the Electric Power Industry of Serbia ("Kolubara" mining basin, the branches of "Prerada", "Metal", thermal power plant "Kolubara A", "Površinski kopovi") in Vreoci, Veliki Crljeni, Baroševac, Rudovci and Cvetovac are purified, channeled and transported to the filtering plants, then discharged to the nearest streams. The waters are transported from the wastewater filtering plant to the river Kolubara via a 7 km long channel. During the course of 2011, 2012 and 2013, the amounts of filtered water discharged have been 504,000, 328,072 and 1,262,786 cubic metres respectively [7].

RESULTS OF RESEARCH AND DISCUSSION

The cross-section study performed from 1971 to 1992 noted that, unlike other endemic areas, the municipality of Lazarevac was the only one that showed stability and even a relative increase in the incidence of the disease (approximately 80% of those in the chronic hemodialysis programme has got EN, and originates from the focal points). Realising the importance of new cases of the disease, the earlier field tests gave way to the more thorough clinical ones. Thus, the study conducted from 1993 to 2000 which involved 518 patients revealed high presence of endemic nephritis. As many as 218 patients were probably diagnosed with the disease, 49 of them surely had it, while 251 of them had all other kidney diseases. Looking at it individually, it was noted, however, that EN was the most common disease in the region [5].

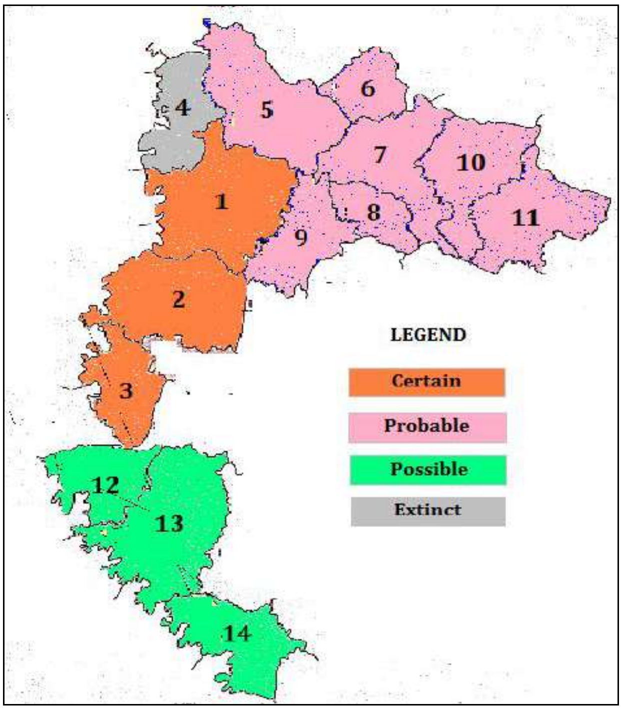

Figure 1. Focal points of endemic nephropathy in Municipality of Lazarevac
Settlements: 1–Vreoci, 2–Šopić, 3–Petka, 4–Cvetovac, 5–Veliki Crljeni, 6–Sokolovo, 7– Junkovac, 8–Sakule, 9–Medoševac, 10–Arapovac, 11–Mirosaljci, 12–Županjac, 13– Čibutkovica, 14 –Dudovica

When it comes to some of the key characteristics of the patients in the municipality of Lazarevac, their monitoring revealed the following parameters [5,8]:

Age of patients – in the past, most patients were in the fifth and sixth decades, but since 1990 the threshold has extended, so the majority of them are in the group of patients in the seventh decade. The lowest incidence of the disease is in patients in the third decade of life, although one patient was younger than this limit (he was 21 and in an early clinical stage). On the other hand, the oldest patient was 80, but based on the consolidated data it was concluded that that the average age for all of the diseased was around 56.61 ± 14.7 years. In the last 40 years this period had prolonged, thus in 1970 it was (51.6 years); from 1982 to 1991 (59.2 years), and from 1992 to 2001 (65 years). Years of experience led to the conclusion that EN has not been detected in a single child or adolescent, which only confirmed the professional literature theses dealing with this very curious phenomenon.

Sex of patients – in terms of gender representation, it can be said that EN equally affects men and women, and this relation is, in the majority of cases, 1.2:1 in favor of men.

Mortality of patients – the mortality rate used to be higher, as evidenced by the fact that in the period from 1966 to 1971 8.2 per 1,000 people died in the municipality of Lazarevac, while in the focal points that rate was even higher (Šopić – 9.3), (Petka – 8.2) and (Cvetovac – 10.8). The percentage of endemic nephropathy in the general mortality rate was even more pronounced, amounting from 30% in Cvetovac up to 41% in Šopić and Petka. Further progress of the treatment methods and less exposure to environmental influences caused the mortality rate to drop to 1.92 per 1,000 inhabitants.

Bearing in mind that the upper urothelial tumors (referring to the renal pelvis and ureter) and bladder tumors are more common in areas with endemic nephropathy (100 times as much in Serbia as in the endemic areas of Bulgaria and Romania), this disease was thoroughly researched in the region of Kolubara. Based on the monitoring, it was found that this group of malignant tumors were present in the municipalities of Lazarevac and Lajkovac, and its presence was at the highest level in the villages of Petka, Šopić and Cvetovac. It was then concluded that the risk for the population in endemic areas was as much as 95 times higher than for the residents of the other abovementioned municipalities [9]. It was found that the incidence is very high and amounts to 20.8 diseased per 1,000 inhabitants, while the rates themselves varied from 0.2 in Veliki Crljeni up to 18.7 in Petka, both belonging to the municipality of Lazarevac. One of the most complex study was carried out in the period from 1992 to 1994 within the Institute of Endemic Nephropathy, which included 73 patients diagnosed with urothelial tumors, while an identical number of diseased and treated from other kidney diseases was presented as a control group. The poll was conducted based on various categories (gender, age, marital status, family anamnesis, occupation, habits, etc.), which presented the basic postulates of patients who have been treated for the disease. Certain preliminary results of the conducted study were then presented: 67 percent of the patients suffering from endemic nephritis organizational had the presence of malignant TGU, 26.7 percent of the patients on dialysis at the Institute showed the presence of urothelial tumors, they occur in women more often than in men (1.4:1), age of the patients ranged from 50 to 80, but the largest number of affected was around 70 years old. All of them named farming as their primary or secondary occupation, smokers were affected 3 times more often than non-smokers and genetic factors are highlighted in the sense that in the first degree of consanguinity the risk of the emergence of TGU is as many as 21.8 times as higher [5].

THE ROLE OF TREATMENT IN ENDEMIC NEPHROPATHY

After the confirmation of the disease most patients are included in the chronic hemodialysis programme. The inclusion of such patients in the chronic treatment programme started significantly later compared to other renal patients (63 ± 8.0 in relation to 53 ± 13.2 years). However, the rehabilitation itself was much slower compared to other patients with CRF (chronic renal failure). The patients themselves were more often faced with the problem of anemia where the need for transfusions and additional iron was more common than in other patients. On the other hand, the most common and most dangerous complication of dialysis was gastrointestinal bleeding as a frequent cause of morbidity and mortality in the terminal stage of CRF, which resulted from peptic ulcer disease (gastric and duodenal ulcers), erosive gastritis (damage to the stomach lining) or the use of non-steroidal anti-inflammatory drugs. The number of patients on hemodialysis is above 120 per year. Bearing in mind that the programme of hemodialysis includes mainly older people, the average number of years of this treatment was usually from 1 to 5, although there were also those who were exposed to this therapy over a period of 14-16 years [10]. Today, the implementer of this treatment is the Special Hospital for Endemic Nephropathy in Lazarevac founded in 1972, whose activity is directed to: the detection, prevention, suppression, treatment and rehabilitation of people suffering from endemic nephropathy, organization and improvement of the services which fight against endemic nephropathy, and scientific research in the area of endemic nephropathy. It is an institution of secondary character which performs activities to provide preventive, diagnostic, therapeutic and rehabilitative health methods in the fields of: internal medicine, nephrology, urology, endocrinology, nuclear medicine, medical biochemistry, interventional radiology and medical statistics. In order to perform all the activities, the institution employs 103 persons, of which 68.9 percent are medical staff, while 16.5 percent are medical doctors of various specialties. In order to address the thematic of endemic nephritis, the institution co-operates with numerous scientific research and health institutions in the country, as well as numerous professional associations [8].

' CONCLUSION

Based on all of the above, we can conclude that endemic nephropathy represents a major problem in the municipality of Lazarevac, which requires systematic analysis with the implementation of appropriate measures. We need to continue with further monitoring of environmental parameters and their association with the disease. In organizational terms, we should build a communal and wastewater filtering plant and work more on the prevention as much as possible. Therefore, we should strengthen the role of the Special Hospital for Endemic Nephropathy with the aim of early detection and treatment of the disease.

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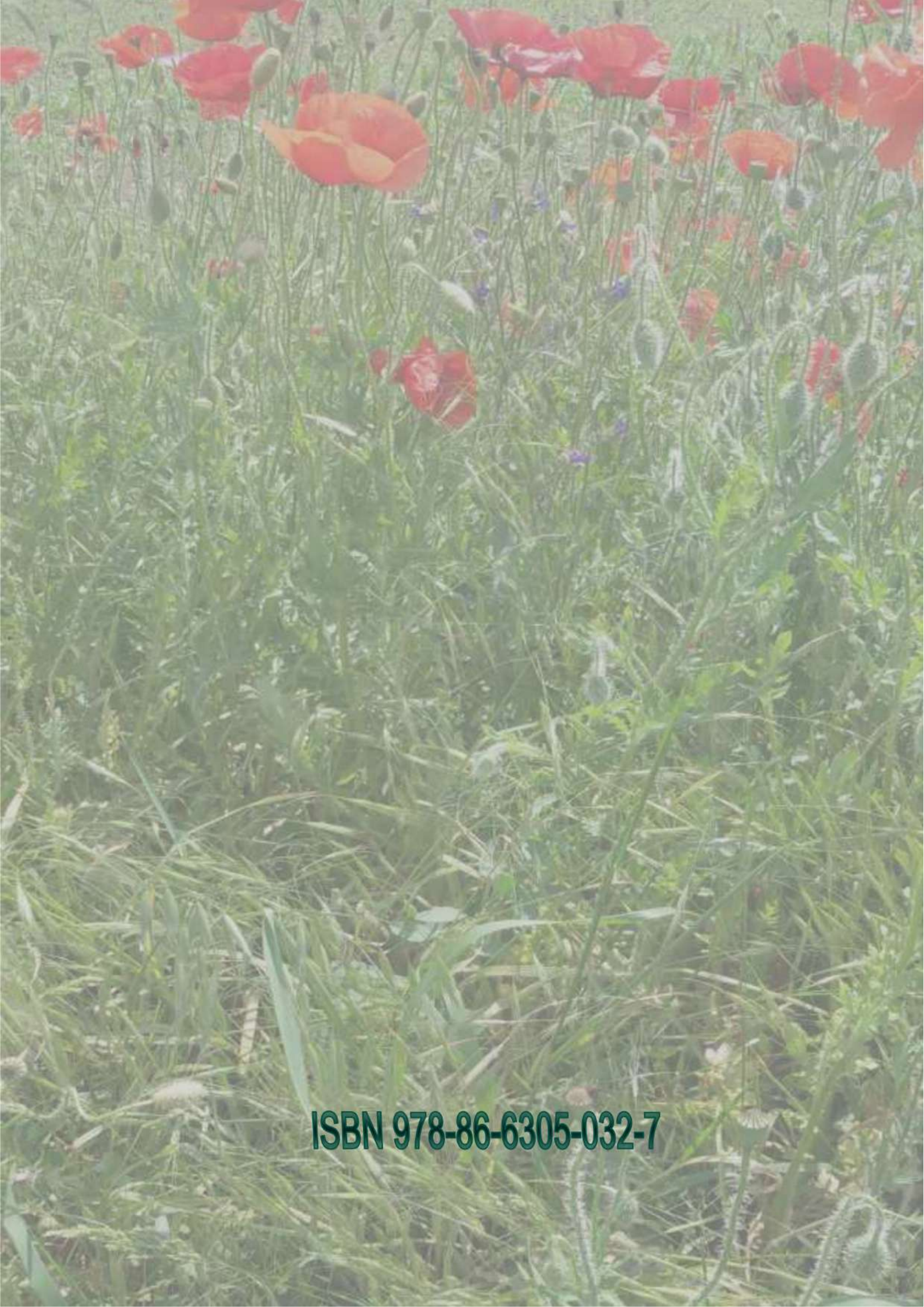

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