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TECHNICAL FACULTY IN BOR

PROCEEDINGS

XXII INTERNATIONAL CONFERENCE
ECOLOGICAL TRUTH

EcoIst '14

Edited by
R. V. PANTOVIC
and
Z. S. MARKOVIC

Hotel "Jezero", Bor Lake, Bor, SERBIA
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UNIVERSITY OF BELGRADE
TECHNICAL FACULTY IN BOR

XXII International Conference

"ECOLOGICAL TRUTH"

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XXII International Conference
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ENVIRONEMNTAL MANAGEMENT MODEL

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ABSTRACT

Environment is an area within which an organization conducts its operations, including air, water, soil, natural resources, flora, fauna, people and their interpersonal relations.

The term environment is closely related to environmental protection, i.e. protection of the basic elements of life : air, water and soil.

This paper clarifies a general idea of the environmental protection and basic management system models. The model should help an organization develop an efficient system with the objective to improve environmental protection.

Key words: environmental protection, management.

INTRODUCTION

The meaning of the word management is to take you to your goal and in this case it is the realization of environmental protection goals. In order to achieve the objectives with minimal resources, an organization needs to create a program for achieving environmental objectives, or the environmental management program. This program should include:

- Action plans
- Resources and
- Responsibility

to achieve the aims and objectives of environmental protection. Specifically, for each defined general or specific goal, it is necessary to define an action plan.

The structure of the program of the environmental management largely depends on:

- Environmental policy,
- Aspects of environmental protection, and
- Laws and regulations relevant to the organization.

The importance of the environmental protection program is to help the organization achieve its objectives, and improve the performance of environmental protection. Environmental protection programs should be dynamic and periodically reviewed and revised in order to maintain changes in the organization's objectives.

Three main components of the environmental management plan are as follows[1]:
- Environmental policy,
- Objectives (general and specific)
- Environmental protection program.

The policy answers the question regarding which way to go, the general objective of what you need to reach in this way, the specific objective regarding the time to achieve it, and the program of how to achieve it?

Each organization may have a unique method of managing the organization, which generally includes the finance, human resources, quality of products and services, relations with customers, health and safety, and among others, environmental protection. For this reason, the system of environmental management may not be unique but the organization should develop it according to its business needs.

THE MODEL OF THE ENVIRONMENTAL MANAGEMENT SYSTEM

The main purpose of the model is to assist organizations in developing effective systems to improve their performance in the field of environmental protection.

In this model of environmental management, shown in Figure 2, we can see that this system is based on the following six key elements[2]:

- Establishing the strategic position
- Defining the vision and environmental policy
- Developing a plan to implement the policy
- Implementing the policy
- Monitoring and measuring the performance
- Reviewing and improving environmental protection systems (EMS)

[1] Radojevic Radoslav, quality management and environmental protection, Operational Researchers Associations, Yugoslavia, Belgrade 2000
[2] Aćamović Nichola M., Development of an environmental management system, Novi Sad: Institute of Veterinary Medicine, 2001

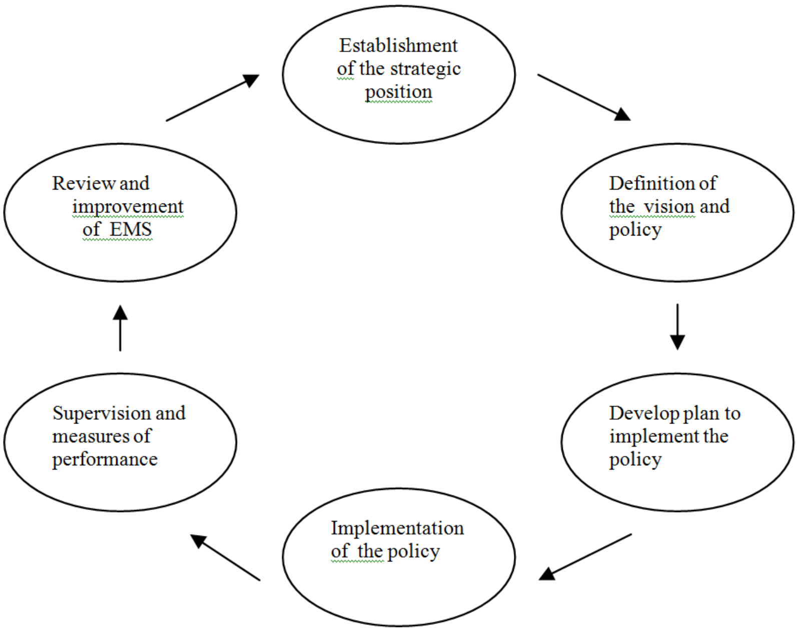

Figure 2. The model of the environmental management system[3]

ESTABLISHING A STRATEGIC POSITION

The current position of the organization with regards to the internal side of environment is determined on the basis of the initial review. The initial review basically consists of collected data and the use of data for identification of the following elements[4]:

- Applicable legal and other requirements,
- Applicable financial requirements,
- Environmental aspects and impact of existing products, activities and services of the organization,
- Customers' understanding of the characteristics of products, activities and services of the organization related to the environment,
- Current performance of the organization against the internal criteria, external standards, codes, principles and recommendations
- Prior information on investigation of incidents and non-conformities,
- Benefits of technology
- Understanding the environment of the community and others.

[3] Development of an environmental management system, Aćamović Nichola M., Novi Sad, 2001
[4] Aćamović Nichola M., Development of an environmental management system, Novi Sad: Institute of Veterinary Medicine, 2001

All this information is to be collected, systematized and used as an input for an analysis of the position of an organization so it can show potential areas for improvement.

DEFINING THE VISION AND POLICY

The vision of the organization to be attached to the protection of the environment is determined by the views, perceptions and demands of interested groups, and is defined by results of the initial review, determination of the guiding principles and values an organization should provide.

Top management then determines their commitment to the environmental protection and value of the documented policy. Environmental policy should be relevant to the products, activities and services of the organization. The management should ensure that the policy is available to all interested groups so that they understand the organization's commitment to environmental protection.

DEVELOPMENT OF A PLAN TO IMPLEMENT THE POLICY

When defining an environmental policy, the management should define the required actions. Information about these activities is obtained on the basis of the initial review. The plan is also based on fundamental drivers for such an environmental change, which is the understanding that the organization can keep under control all the influences. These drivers of change and their relevant impact on the environment, as well as appropriate priorities are identified on the basis of the initial review.

The management needs to develop a number of general and specific objectives and a program that will serve as a reference point against which all effects of protecting the environment can be measured.

IMPLEMENTATION OF THE PLAN

This element of the Environmental Management System (hereinafter EMS) essentially consists of the following two sub-elements:

- to secure capabilities of the organization by providing appropriate resources (people, equipment, finance, etc.) for the implementation of an environmental protection plan, and
- to develop support mechanisms, such as communication, reporting, document control, information management and records management, control of operations, response in emergency situations and the like.

The main activities of this element are related to the realization of general and specific objectives and environmental protection programs.

The management defines responsibilities for specific actions within the EMS and provides resources that need to be implemented. EMS requires reports on the performance of the management and interested groups. The management creates awareness of the environmental commitment for all employees and should ensure their motivation to satisfy all interested. Along with the awareness of the environment, a training program related to the priorities of the environmental impact will also be carried out. Every person in the organization needs to know their role and responsibility in the implementation of the environmental policy in order to meet interested parties.

In establishing the EMS, it is important to have good communication with both external and internal interested parties. Communication system provides for active monitoring of requests and understanding of interested parties thus giving the management an opportunity to positively influence expectations of interested groups.

What is important to the EMS is that the organization clearly understands the environmental risks regarding their products and activities. In this element of the EMS, it is important for the organization to increase the utilization of its resources and reduce all types of waste materials, which can be achieved by using documented procedures and appropriate process control. Documented procedures and control of operations allow, on one hand, obtaining accurate information about the relative performance and on the other, full management control of operations and the knowledge of what will exactly happen when organization deviates from its core line.

MONITORING AND PERFORMANCE MEASURING

This element of the EMS contains a variety of activities that are carried out in order to make a facts based-decision. This kind of decision-making enables the management to avoid the possibility of making decisions based on inaccurate perceptions of what will happen in the organization.

The core activity of this element of the EMS is to establish a system of records management. Based on validated partial reports, usually made is an annual report on the performance of environmental protection activities. This report provides integrity to reporting and communication activities.

In addition, a technique used in this element is the internal control of the EMS performance. Reports on internal control provide the management with a clear picture of the functioning of the EMS, as to how to manage the interests of involved groups and provide an early warning of potential problems.

REVIEW AND IMPROVEMENT OF THE SYSTEM

Reviewing the performance of the EMS by the management at defined intervals is the last element in the EMS loop. Review of the EMS means consideration of the strength and weakness of the EMS, as well as opportunities and threats posed by requests for changes and understanding of interested groups.

Review may result in a complete revision of data of interested parties based on the information obtained from the EMS. The strategic position of the organization can be redefined. Also possible is the revision of the environmental policy, development of new plans and continuous improvement of environmental protection.

CONCLUSION

Environmental problems are comprehensive, global and require international attention. However, we ourselves have caused environmental problems by the way we live, political elections, spending priorities of the industrial world, the twisted values of life. What we do as individuals is crucial, because in the end it all depends on us and those around us. With our way of life we have become a threat to our own survival.

The aim of this paper is the application of the project management to environmental projects and the impact of man and his activities as well as ways to protect the environment.

Because of their complexity and other characteristics, the projects require the use of the project management in order to meet the set goals. The main objective, in addition to minimizing the wasted time, resources and costs, is the completion of the project in the required and necessary quality. In order to effectively manage the project, certain methods and techniques of the project management need to be implemented. Example of a possible environmental management is described in this paper.

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IDENTIFICATION AND LANDSCAPE CHARACTER ASSESSMENT OF VALJEVO KARST

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ABSTRACT

Valjevo karst with its landscapes, is one of the most valuable placeses in Republic of Serbia and if timely protection does not happening, it will be irreversibly degradated. Aim of this paper among other things, is to emphasizes importance cultural landscape, and to analyse, evaluate and to propose guidelines for future development and clearly contribute to Valjevo karst conservation. The entire paper is based and relies on the model of the method that estimates the landscape character, and it is called landscape character assessment, which passes through the methodical process assessments of Valjevo karst landscapes and as a result provides guidance in the form of guidelines for the management of the estimated character of Valjevo karst landscapes.

Key words: culture, landscape, assesment, karst, Valjevo.

INTRODUCTION

Cultural landscapes are a reflection of the evidence of the holder of intangible human values and meanings that nourishes our existence. For us, the most important expression of culture, which at this point are not monuments, could be relics and art in the past, but an expression of cultural activities that have become invisible, but can become the basis for further human development. What makes the cultural landscape is a unique identity, and it is manifested through physical activity of components + symbolism / meaning flow regions [1]. Cultural landscape needs to be recognized as a value and it has been previously described and validated, in order to be enacted guidelines for its further development and therefore requires assesment of the character of particular landscapes. Environmental Protection Act Law of the Republic of Serbia cultural landscape describe as the category of cultural landscapes of outstanding features: "The cultural landscape of exceptional quality the area of significant landscape, aesthetic, cultural and historical values that are developed over time as a result of the interaction of nature, natural resources of the area and the traditional lifestyle of the local population." [2]. This paper declares Valjevo karst landscape as a potentially very valuable area from the standpoint of a correlation of nature and man in centuries.

MATERIALS AND METHODS

The methodology is applied in two-phase: The first phase is a characterization of the Valjevo karst landscape and the second stage is making judgments. Characterization of the landscape-takes place in five steps:

1. Definition of covers-deals with objectives of the research, the scale and level of detail, the necessary resources and the participation of the user space (stakeholders) whose participation as possible at all stages.
2. Studio work-deals with study of natural and cultural factors with the making of the landscape character drafts.
3. Terain work-deals with the perception of the observational aspects and trends prevailing.
4. Classification and description-includes the creation of a final map landscapes, description of landscape types and character areas with identification of key characteristics.
5. Decision on the method of assessment - involves defining the criteria, study other phenomena and other field observations. Judgmental phase-deals with evaluating the results obtained by this procedure include the proposals in the form of guidelines for the improvement of the landscape, the information for strategic policy planning, proposals and instructions for their location on regional level (spatial distribution).

RESULTS

After a comprehensive analysis of both literary sources and fieldwork, it can be extracted next applicable results related to the character of Valjevo karst. As identification based on Valjevo karst cultural landscapes provides a description of the wider context, which can be seen in Figure 1.

Valjevo karst is situated in region of Podrinje and Kolubara. Region of Podrinje and Kolubara covers the northwestern part of the Republic of Serbia without provinces. Kolubara District occupies the central part of western Serbia. Its seat is the city of Valjevo. Determinant factor for the definition of Valjevo karst is and depends on lithological composition. Karbonatnik rocks in our climate is appearance of karst geomorphological processes, and the karst hydrography. It follows that "Valjevo karst covers all areas between city of Valjevo, Valjevo mountains and basins that were constructed of limestone and dolomite rocks and Neogene sediments from the Kolubara basin and diabase-chert series of Valjevo mountain [3]. Valjevo karst covers an area of approximately 319.30 km^2. Basically this area is constant in karst process. Karst geomorphological process is a process that occurs the action of water on soluble rock mass. The most widespread are the limestone rock mass. Besides them there are dolomite, gypsum, anhydrite, salt. As a result of karst processes in Valjevo karst forms appear extraordinary and highly recognizable identity surface and underground forms value. Typical surface karst forms of Valjevo karst are cracks, hollows and valleys. While the underground forms are occurring pits, sinkholes, karst springs, caves, dry valleys and blind. Basically tectonic structure of shapes, series and origin of the Kolubara basin is very typical for the area of Valjevo karst [4].

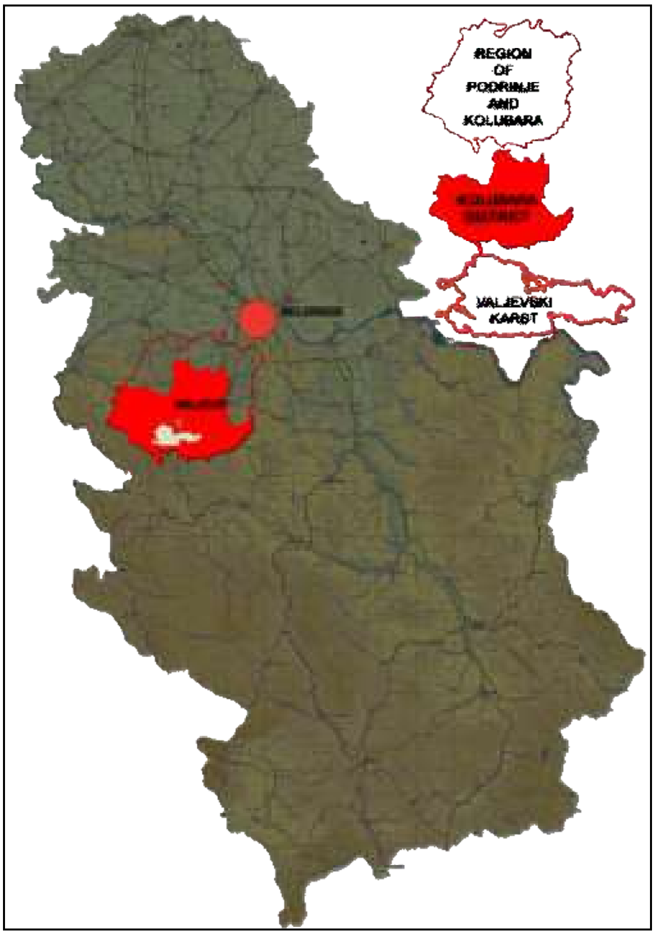

Figure 1. The border area of Valjevo karst in relation to the Republic of Serbia

Information on natural factors, social and cultural and historical events that have occurred and are occurring in this area are collected via the accessible literary sources, thematic maps (used for the overlay method-a method of overlapping thematic maps), oral history. As a result of these studies (overlay maps and study data) is map of landscape types and landscape character areas. Each character of this landscape type and character of the landscape area varies according to their own of character identity that occurs and it is a mosaic of natural features and elements; physical components (which are separated and reliably measured by the criteria (historical significance, rarity, uniqueness, value of sensual dimension, value for use, the sustainability of natural resources) and indicators of positive and negative correlation on regional level) contribution to the state and the development of a certain type character areas and / or areas characters) from various historical periods resulting from human activity and modification of natural features and schemes (forms) created in the region over time as layers or the landscape. As a result of this study is suggestions of liberalization and protection and management of landscape types and landscape character areas Valjevo karst through conservation, restauration, preservation of existing character, improvement of existing character and combination of each.

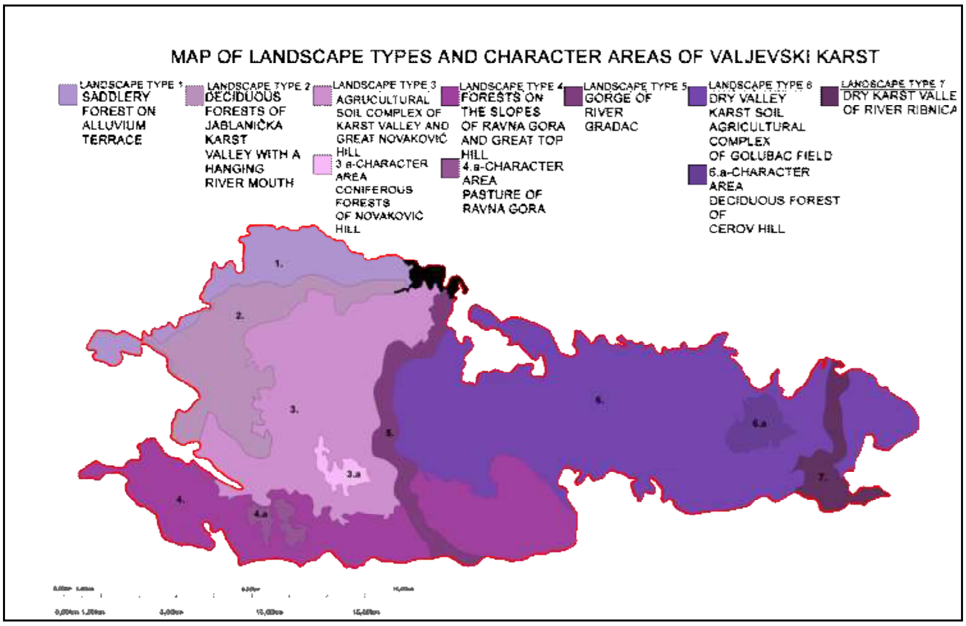

Figure 2. Map of landscape types and character areas of Valjevo karst

DISCUSSION

Guidelines for the improvement of the landscape, the information for strategic policy planning, proposals and instructions for their location (spatial distribution) that can be directed at the Valjevo karst on regional level, for each type of landscape type and landscape character areas:

LANDSCAPE TYPE 1-SADDLERY FOREST ON ALLUVIUM TERRACE

- management regime-preservation of state through:

- Preservation of existing forest and associated vegetation [5];
- Preservation of forest habitat;
- Monitoring, control of number and distribution of forest stands;
- Monitoring and networking of rural households on the map of tourist offer of Serbia and beyond (ENRD network, etc.);
- Translation coppice forest types in high production type thar are necessary for forest management measures;

- Reconstruction of devastated stands;
- Preventive and repressive measures of deforestation (mostly fertilizing cut) work in the traditional manner;
- Restoring mature stands;
- Strengthening cooperation "Srbijašume" with the local community.

LANDSCAPE TYPE 2 - DECIDUOUS FORESTS OF JABLANIČKA KARST VALLEY WITH A HANGING RIVER MOUTH - management regyme-conservation with improving the state through:

- Recultivation of reservoirs "Rovni" quarry "pillars" - open pit "pillars." (Nepotebnih demolition of buildings, forming the finished floor and the slope of the pit, removing invasive species, bringing fertile land, the application of indigenous vegetation (plants, herbs-have be under the protection of trade and commerce);
- Tourism development in the vicinity of the reservoir "Rovni"-as an opportunity for further development of hotel tourism, hunting, fishing and recreation;
- Capacity-building for the development of geotourism (IAGT-International Association for geotourism);
- Forestation or cropping the area affected by the leaching and soil filling of Jablanica river and watercourses affected by erosion processes [5].

LANDSCAPE TYPE 3-AGRUCULTURAL SOIL COMPLEX OF KARST VALLEY AND GREAT NOVAKOVIĆ HILL - management regyme - conservation of landscape elements through:

- Preservation of boundary forms of extensive agricultural areas (conservation network of dirt roads, control);
- Raise of rural tourism, agro-tourism agriculturally Tourism (ECEAT - European Centre for Ecological and Agricultural Tourism-European Centre for Ecological and Agricultural Tourism);
- Protection and strict conservation of surface geological forms (for static fields and preserving image, beauty of landscapes).

3.a-CHARACTER AREA CONIFEROUS FORESTS OF NOVAKOVIĆ HILL - management regyme - preserving the state through:

- Protection from exploitation and harvesting [5];
- Preservation of ground-vegetation;
- Periodically rejuvenate the surface conifer species;
- Protection phytopathological and entomological damages;
- Prohibition of hunting of wild animals.

LANDSCAPE TYPE 4-FORESTS ON THE SLOPES OF RAVNA GORA AND GREAT TOP HILL - management regyme: preservation of improving the state through:

- Sustainable use and exploitation of mineral resources;
- Development of scientific-research and educational capacity;
- Monitoring status of threatened and rare forest species [5];

- Prohibition of grazing cattle browse, pasture, acorn in the forest;
- Establishment of feeding (fertilising, watering,) animal (game and wild game);
- Managing of tourist routes for dealing with different types of tourism and other events.

4.a-CHARACTER AREA PASTURE OF RAVNA GORA - management regyme - conservation of the state through:

- Conservation of pasture borders;
- Limit the use of pastures for intensively grazing;
- Ban fertilization, mowing technical measures;
- Control-flow and timing fits with the number of heads;
- Monitoring of floristic diversity and grazing.

LANDSCAPE TYPE 5-GORGE OF RIVER GRADAC-management regyme -preservation of the state through:

- Preventing the exploitation of stone, gravel protection geomorphological characteristics gorges;
- High-quality protection of the river Gradac protection of the entire basin and groundwater basin with the preservation of the river flow;
- Replacement of conifer-cultures and native acacia species [5];
- Prohibition of waste disposal;
- Prohibition of construction of buildings weekend;
- Prohibition of harassment, destruction, collection of animal and plant species.

LANDSCAPE TYPE 6-DRY VALLEY KARST SOIL AGRICULTURAL COMPLEX OF GOLUBAC FIELD - management regyme - conservation and improving the state through:

- Preservation of borders forms of intensive farming of agricultural land / crops (corn, oats, barley, wheat, millet), (conservation network of dirt roads, irrigation canals, control condition);
- Raise of rural tourism, agro-tourism agriculturally Tourism (ECEAT - European Centre for Ecological and Agricultural Tourism);
- Strict protection and strict conservation of surface geological shape;
- Raise ekoagricultural approach and cooperation with all stakeholders, strengthening local initiatives.

6.a-CHARACTER AREA-DECIDUOUS FOREST OF CEROV HILL - management regyme-conservation of the state through:

- Restoring vegetative phitocenosis means;
- Protection from exploitation and harvesting;
- Preservation and ground-vegetation;
- Surface periodically rejuvenate of native species [5];
- The possibility of development of the area as a tourist point (nature lovers).

LANDSCAPE TYPE 7-DRY KARST VALLEY OF RIVER RIBNICA - management regyme-preservation of the state through:

- Preservation and forms of healing and prevention of wet river meadows and the prohibition of exploitation, usurpation (change in the composition of plant species);
- Prohibition of construction of any nature on the coast, and the nearby environment;
- Preserving water quality of the river Ribnica;
- Preserving of coastal vegetation (prohibition of exploitation, collection, arson) and the surrounding Ribnica river that usually occur and those are the types: Agrostis vulgaris, Festuca valesiacae; Rhamnus frangula, Rubus caesius, Lytrum salicaria and Mentha longifolia; Quercus conferta, Q.petraea, Q. farnetto [5],
- Preserving of architectural heritage.

CONCLUSION

On the basis of the methodology which relies on landscape character assessment, there are seven landscape types and three areas of the Valjevo karst landscape.

There is great biological, floristic diversity of Valjevo karst, which completes the karst geomorphological forms, which are very rare in the territory of the Republic of Serbia. The richness of pastures, meadows, orchards, vineyards, gardens confirm that the man in this area promptly answered all the conditions that existed and shaped karst and with it the human values. The wealth of cultural, archaeological, creative and architectural heritage and integrity is present, it is evident and reflect the status and changes in cultural and civilizational development, ranging from prehistoric times to the present day. The population is pretty much managed to maintain and preserve the tradition of their previous homeland and settle in them forever in Valjevo karst. Will it work in a moment of globalization and will it resist or will be blind and naive to track and reconcile with him, it is still hard to tell? If we give up our own culture we give up everything that makes us human, as well as its landscapes. What is the landscape, if not a reflection of the love and respect for themselves and others. How much time should pass in order to undertake measures for the protection, preservation of these same regions or even themselves? Goal in this stage of this paper is to point out that all this wealth is very great, not at all harmless and to draw attention to errors and to provide preliminary measures for the rehabilitation and management regymes for Valjevo karst landscape.

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EUROPEAN BEAVER (*Castor fiber* L. 1758) VALUE, HISTORICAL CHANGES AND THE RESULTS OF MONITORING DURING THE FIRST 10 YEARS (2004. TO 2014.) ITS REINTRODUCTION IN ZASAVICA

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ABSTRACT

The European beaver (Castor fiber) is the largest semi-aquatic rodent in the northern hemisphere. Of the presence of the beaver in Serbia there is plenty of proof in paleonto-logical and archeological findings.The reason for its extinction is over-hunting until its total exit-nction at the begining of the 20th century.The beaver had been reintroduced from Bavaria, Germany a total of 35 beavers were reintroduced in 2004. They've captured so far a total of 13 territories, and madea total of eight dams on the reservation and the wider environment. Outside of the Reservation they can now be found in the villages of Glusci, Salas Nocajski, Jadar and on the Sava River close to Martinac and Brcko.The overall population of beavers in the Reservation is around 60 animals. Their food consists mostly of *Salix*, *Fraxinus* and *Populus*. The reintroduction of the beaver is the first type of activity in Serbia where a previously extinct species had been returned to these regions.

Key words: beaver, reintroduction, Zasavica, extinct species.

INTRODUCTION

European beaver (*Castor fiber* L. 1758) is a semiaquatic animals and is the largest rodent of the northern hemisphere. Stocky dark brown body, the beaver is an excellent swimmer and diver, active at night, grows up to 1 m length. This monogamous herbivors sexually mature at 2-3 years. The money is from February to March, a female carries for 107 days and give birth to 1-5 young a life expectancy up to 20 years. The shelter is water hummock of branches or burrow into the shore. (Ćirović, et.al., 2007)

The presence of European beaver in Serbia and former Yugoslavia witnessed numerous findings. Data from the paleontological and archaeological excavations indicate the presence of relatives today beaver *Trogontherium cuvieri* during the Middle Pleistocens (Mindel/ Riss) 300000-200000 years ago, and the continued presence of recent beaver (*Castor fiber*) from prehistoric times (interglacial Riss/ Würm (120000-80000 year.) to its complete disappearance at the beginning of the twentieth century. It is a turbulent period of climate change, which had a great influence on the change of flora and fauna, and in a successive exchange of thermophilic animals with animal species that prefer colder climates. In some sites may be based on the number of skeletal remains of some animals statistically calculated that were main hunting animals. Thus, for example in Krapina half-cave in the sediments of the interglacial Riss/Würm dominated by the ruins *Dicerorhinus kirchbegensis* and *Castor fiber* and then follow *Dama dama* and *Bos primigenius*. In the early Holocene in this region still graze herds *Alces alces, Megaceros giganteus* and *Bison priscus* and rivers there were many colonies of beavers. The "man the hunter" gradual transition from nomadic to permanent settlements began "adjusting the" nature to his demands, which leads to a permanent disruption of relationships in nature (Malez,M.,1979). During the first half of the nineteenth century, the beaver was still relatively widespread along rivers and wetlands, although even then was sparse and scarce. According to the notes of the researchers recognize that the time is still present along our great rivers (Danube, Sava, Morava).

The last living specimens were registered in 1878. in the area of the Danube from the entrance to the Đerdap gorge Belgrade, and they are also the last surviving specimen of the whole Danube basin. To the beginning of the twentieth century was the shot last copy beaver, which this species disappeared from the territory of Serbia. Historical areal encompassed almost the entire Holarctic, excluding zone deserts and semi-deserts of Central Asia. Stretched from the British Isles to the eastern parts of Siberia. He lived along the wooded banks of watercourses within the zone to deciduous, and coniferous forests. Biomic speaking, the area was inhabited by the tundra in the north and the steppe zone and the Mediterranean to the south of the area of Europe there are only five autochthonous isolated populations with a very small number of species: the river Roni in France, on the River Elbe in Germany in southern Norway, on the river Njemen and the surrounding swamp Pripyat in Belarus and tell Vorornjež in Russia. In Asia there are only three populations (two in one of the China-Mongolia border) are also a small number of individuals (Ćirović, et.al., 2007).

The populations of these areas were used as a population reservoir for a large number of projects of reintroduction and translocation across the European continent. With the return of beavers in Europe began in 1922. years in Scandinavia, and to date has completed over 90 projects, settlement of which were last made right in our own neighborhood (Croatia, Hungary and Romania). The reasons that led to the almost complete disappearance of the European beaver in the whole area are identical. The primary cause of failure was excessive hunting, dating back to the Paleolithic era, until the early twentieth century. Paleolithic hunters in the area of ex Yugoslavia belong to *Homo sapiens neanderthalensis* and fossils after-*sapiens* a group whose main hunting animals in the early wirm were: *Lepus timidus*, *Castor fiber*, *Marmota marmota*, *Alopex lagopus*, etc. (Malez,M.,1979). There are several reasons for the exposure type constant hunting pressure: the belief in the miraculous healing properties of certain body parts (primarily steam gland castoreum) for high-quality fur and Beaver meat, which is the church allowed to be consumed during Lent. Excessive hunting was followed by the destruction of habitats, which led to a reduction of the territory and therefore the number of population. It is interesting that they are flooded and swampy areas in Serbia decreased by 10 times compared to the period when beaver were present in large numbers (in the nineteenth century).

The most important laws which classify vulnerability beavers are the Berne Convention, Appendix III, EU Habitats and Species Directive Annex II and IV IUCN categorization threat. The European population in recent decades, continual growth of recent population but the species remains highly sensitive to any changes within the ecosystem inhabited. Protecting species in the extent significant for unevenly distributed population. The European range is very disjoint, where there are still no popalation along major river basins (such as for example the Danube), between which there is a direct communication and exchange of genetic material.

MATERIALS AND METHODS

Reintroduction of beavers to Zasavica prior to the survey site conditions, then prepare the viewpoint that involve the use of artificial mounds in the family. Mounds are wicker, take the form of an igloo with two entrances, and were placed in after-selected locations. Mounds are then plastered with mud and covered with branches to make them look as closely as possible the natural. Implementation of the reintroduction project was carried out in spring 2004. On this occasion the Bavarian the area of the reserve at a few selected locations released a total of four families + singles or total 35 individuals beavers. Each specimen before releasing it under the skin of a microchip embedded in the dorsal part of the cervical region, in order to follow. So that each individual received the individual markings, which provides further telemetric monitoring the fate of each marked individual. The monitoring that is usledino after settlement, followed by the beginning of their deployment, and then the number and dynamics of the population of beavers in Zasavici, as well as their subsequent migration.

RESULTS WITH A DISCUSSION

Historical changes: The first data on the hunt beaver in Posavina found in Neolithic primitive man what show us found the jaw with molars Pleistocene *Castor fiber fossilis* around Surčina and Belgrade (Pribić,B.L,1961) Further gradual transition from nomadic to permanent settlements along the river usually increases and the presence of the remains of a beaver in the locality. Over the next several thousand years (the ancient Roman period) remains of beavers are increasingly appearing in the discovered archaeo-zoological material. During the decades of archaeological excavations in the territory of Sirmium, today Sremska Mitrovica, among many collected archaeozoological materials were present, and the bones of European beaver. So during the construction of the highway Belgrade-Zagreb, the section near Sremska Mitrovica from found materials archaeozoological total of 7,22% of residues of wild animals. From a total of 7,22% dominated *Cervus elaphus* from 4.2%, while the subdominant was *Castor fiber* with a 2,0% share of the locality (Božić,S.1995). Such a high percentage of beaver on the site can be linked with the fact that the territory of Sirmium was surrounded by a large wetland complex and the present channel Čikas who at the time of Fruska gora dug up to the confluence of the Sava River and the part he walked through Sirmium. More recent archaeological excavations Sirmiuma in 2005. and 2007. brought new data on the presence of beavers in the area of Sirmium. On 09.09 2005., the site of

85 square No.4, Sector - A layer of black soil (a mixture of ancient and medieval pottery) among many archaeozoological material was also one bone (*femur sin.*) of juvenile beavers. The same day 05.03 2007., at the site of 1a Imperial palace in the western part of the northern escarpment of the room 3 (residues hypocaust XII O.S) was found in bone (*femur dext.*) As the young beaver, and two days earlier (03.03 2007.) in one room only in the shallower layer of XI O.S found another femur sin of the young beaver (Archaeological excavation diary, 2005. and 2007.). All these archaeological evidence suggests that the beaver was present in the diet of people Sirmiuma especially finding the location of the Imperial Palace is a confirmation that the Beaver meat was present at the royal table.

In 1777. Taube F.V says: "You'd think they Slavonia and Srem full of beavers, because the terrain is sparsely populated, full of ponds and swamps, but not so. They'd be gone and upset and the ponds they are afraid because pigs snout digging up land so that they can really reduce the number. I mostly keep the banks of the Sava, where creep along the narrow backwaters among the many islets. Hunters from them, and network live love not so much for their fur, as for meat or live in Vienna and carry large amounts of money selling. More over another 1776 years has been found on the Turkish coast a mile below Mitrovica, their "cottage "with a family of eight beavers." (Brehm,A.,1956) from the records that gave Taube accurately described the situation and the impact of beavers in Posavini. At the same this is the official data on the presence of beavers in the area of present day reserve.

The current situation: At The Special Nature Reserve Zasavica reintroduced with a wider area of Bavaria (Germany) a total of 35 individuals, which was caught just before transport to Serbia and were released on a total of 12 locations that were previously singled out as the most suitable. On Zasavica inhabited three families with 4, 5, and 7 members, and numerous singles.

Shortly after settling beavers spotted intensive building activity which has been in operation taking territory and building permanent dwellings. So far there total at 13 territories and 13 families settled on the reserve, which can be considered also the approximate capacity. Most of the territory is on the main stream Zasavica, while one is on a tributary of the Batar and Prekopac. If we accept the expert estimates that a family of beavers on Zasavici has an average of 5 members, then the beaver population is estimated at around 60 individuals. For most of the occupied territories beavers have built their dwellings in the form of mounds, while the dens present only in Modran.

Picture 1. Beaver (*Castor fiber*)

For most families recorded only one mound, while the maximum registered three mounds per family. Population European beaver (*Castor fiber*) in Zasavici is one of the two populations reintroduced in Serbia. During the evaluation of natural resources for a new study on the reserve estimated population of beavers in Zasavica is more than 15 % at the national level. The beaver in the area Zasavica has a good conservation status. (Dobretić,et.al.,2012)

In addition to the mounds in coastal forests in the entire territory beavers notice the smaller and larger transport channels of up to 60-80 cm and 30-50 cm depths, whose function is to facilitate transport material from a distance of major building mounds or dam. A not uncommon to encounter the beaten track through the woods or brush where beavers go. After capturing territories, beavers were immediately moved into a strong building activity, which is reflected in the construction of dams.

Picture 2. Transport channel

So far, beavers in the area of the reserve with its surroundings built seven dams, and 4 of the tributary Batra and one dam is on the Zasavici (about 50 m upstream from the mouth of Batara), the Bitvanski channel in Glušac and to channel part of the circuit Batve in the village Ravnje.

Number of settlements individuals (35), and the fact that the actual number is estimated at about 60 individuals beavers, which is the approximate estimate of the reserve capacity (Stamenkovic et.al,2003). After ten years of observation we see that the beavers relatively quickly establish stable populations that are able to survive for a long time. There fore, Zasavica today represent a population reservoir for further spread of this species, especially Posavina (Ćirović, 2006) It is assumed that if the present pace continued dynamic expansion of beavers could be expected in the near future and linking these with neighboring populations in the region (Grubešić,et.al.,2006) in support of this going and previous data from the field, where they recorded two territories outside the current reserve (Glušci and Salaš Noćajski) and a large number of individual recording the presence of beavers (the Sava River near Martinci and Brčko) as in many ameliorative channels in the protection zone of the reserve and beyond.

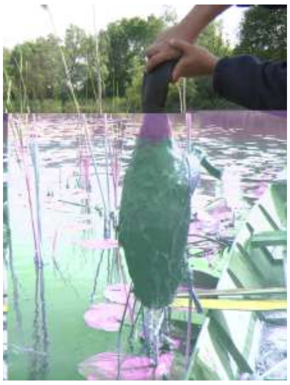
Picture 3. Beaver dams

Territory in Glušac is located on a large Bitvanski channel about 1 km from the bridge upstream beaver dam in a channel with a small dam forming a constant upstream water level depth of about 1 m. The canal bank is high and steep. Part of the canal passes very close to the forest or the tree line resting on the canal bank. The second area is located on one of the channels belonging to the canal network Stojsic Bogaz in the village of Salas Noćajski. Until now, the channel to attribute traces milling branches and bark of the trees above taxacion border. Since the dwellings are found only pit which is to be expected because the bank is very steep and high, and it is very hard and difficult to build mounds.

When it comes to the forest with Zasavica, the largest surface area (21,7%) occupied by mixed oak forests (*Quercus robur)* and ash (*Fraxinus angustifolia*) (91F0). These forests are present in the form of isolated fragments of forest stands so prohibition surrounded by arable land, resulting in a pronounced effect edge ("edge effect"), and about 70% of the habitat shows the average preserved structure (B4). Forest fragments in an insignificant percentage regenerate after harvest. Beaver are much more important alluvial floodplain forests (91E0) that occupy lower positions along watercourses (*Salix alba*, *S. fragilis*, *Alnus glutinosa*). Predominantly occur in the lower and middle Zasavica and its tributaries. Covering 9,6 % of the reserve. The largest stands are on site Vrbovac. Habitats include 91E0 Alluvial forests with alder (*Alnus glutinosa*) and ash (*Fraxinus excelsior*) (fresh *Alno - Padion*, *Alnion incanae*, *Salicion alba*) and classified in the category of endangered habitats and habitat types 91F0 that include lowland forest oak (*Quercus robur*) connection (*Ulmus laevis*), field elm (*Ulmus minor*), white ash (*Fraxinus excelsior*) and ash (*Fraxinus angustifolia*) near large rivers fresh (*Ulmenion minoris*) are classified in the category of less endangered habitats. (Dobretić,et.al.,2012). Generally beavers diet consists of tree, shrub and herbaceous species. The highest percentage in the diet are of the genus Salix which in turn depends on the percentage of the bushes (*Salix cinerea*, *S.frafilis*, *S.purpurea*) or woody (*Salix alba*, *S.petranda)* species locality. Elsewhere on the representation of the *Fraxinus angustifolia*, and then type in the genus Populus. In areas where the forest belt is very narrow and it is the continuation of arable land with corn, it is observed that taking the entire above-ground portion of corn and worn in mounds or used for coating permeable parts of the dam.

Picture 4. Castor felling trees

Since the beginning of the reintroduction has on Zasavici registered a total of 17 dead beavers. The main factor necrosis beavers were disease (29 %) , while traffic accidents (18 %) and drowning in fishing nets (12 %) were less common in the mortality rate. When the disease in question have interesting finding any parasites. In fact during the autopsy of one adult female (found dead in 2006.) found the parasite *Stichorchis subtriquetrus* in the stomach and it is the first record of this particular parasite beaver in Serbia. Decoding chip was found that the individual with Obedska bara. This fact suggests that the parasite reintroduced into Serbia along with beavers from Bavaria, and it is an example of how you can enter the reintroduction and narrowly specialized parasites that can be later and spread. (Ćirović,et.al.,2009) For 7 individuals are not able to accurately determine the cause of death. In relation to the seasonal aspect of most dead beaver was registered during the spring (41 %) and fall (29 %). In relation to the age distribution of the largest number of dead beaver was subadult for all animals (8). In the category of adult individuals is registered are 5 dead bird makes a stake of 31 % in mortality. The minimum number of dead beavers (3) is registered in the juvenile age group (19 %). (Ćirović,D.,Kureljeušić,B.,2012)



Picture 5. Dead specimen

Disturbing factors: After mapping and analysis of selected habitat types, defines the basic disturbing factors identified Natura 2000 habitats and species, based on the "reference list of factors threatening" the Habitats Directive. (Dobretić,et.al.,2012)

endangered species: the very species is threatened by predators, disease, and people. The first two are natural factors and they can not so much affect until the last of anthropogenic origin. Anthropogenic factors are manifested through hunting-killing animals, harassment of family (demolition mound or dam, digging holes in river banks, etc). Measures that are prescribed to address the threats to the species are the prohibition of the removal of the dam from the river bed, the ban breaches morphology coast, and education of the local population.

vulnerability of habitats: a lot slower but more numerous and more dangerous for the entire population are the processes that lead to the partial or complete destruction of habitats. Factors threatening the habitat as agriculture and the use of pesticides, road construction where there is suffering beavers during their migration, the second pollution of water courses (the discharge of wastewater, landfill, etc.), Harvesting (without replanting), the inversion of forest species and the spread of invasive species, uncontrolled management of the water regime and the eutrophication of water. Since these factors forest habitats suffer most under threat and that is why we analyze them in more detail. In analyzing the vulnerability of habitats to retain riparian forests (91E0), which are the best habitat for them. The main factor threatening the habitat 91E0 is the timber harvesting (without replanting) and the spread of invasive species, especially indigo (*Amorpha fruticosa*), and drainage that, loss of surface and ground water for a longer period. These habitats should be protected as soon as possible, because each of them about 40 % of the area has been reduced conservation status. Requirements habitat 91E0 (fresh *Alno - Padion*, *Alnion incanae*, *Salicion alba*) are gradually increasing the level of water in the spring and the decline in water levels in the late summer of no extreme variation, water management regime should correspond to the natural process of flooding and high groundwater levels throughout the on the habitat. According to these habitat requirements are set out measures to achieve favorable conservation status of habitats and to the prohibition of clear-cutting forests, removal of invasive species, especially indigo (*Amorpha fruticosa*), replacement of plantation poplar Vrbovac with native forest species and restoration of natural forest vegetation.

CONCLUSION

Reintroduction of the European beaver, for the first time on the territory of Serbia returned an organic species disappeared from this area. The implementation of the settlement in full respect of international standards that have been recommended and are used around the world, lays a good foundation for the future reintroduction projects to protect and preserve rare and endangered species in this country. Estimated actual number of relatively small number of registered deaths and non dispersion beavers with Zasavica clearly indicate the great importance of this population in the further expansion of species with us, but also in the wider area of the region in which we find ourselves. Therefore it can be considered that the reintroduction of the European beaver to the Zasavica managed, and that sort after a long absence returned in aquatic ecosystems Serbia.

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SPELEOLOGICAL EXPLORATION OF THE LAZAREVA CAVE, IN ADDITION (2007. – 2014.)

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ABSTRACT

This paper summarizes speleological explorations of the Lazareva cave since 2007 to 2014. The cave was already in 2006 considered the longest speleological object in Serbia with the 6793m of surveyed channels. The paper focuses on the newly explored channels as separate morphological parts of the cave: Cat's channel, High galleries, International channel T.86, Channel of the shells, Dry riverbed channel galleries and the Flooded spring channels (5). The survey measured 12 035m and proved the connection between the spring in front of the cave entrance and the lake in the tourist part of the cave by cave diving.

Key words: speleological explorations, morphological parts, galleries.

INTRODUCTION

Lazareva cave researches last more than 130 years, from the Jovan Cvijić's days. New researches of the cave have been coordinated by the SEK "Rock & Ice" Bor since 2001 (1). The survey is conducted under the natural monument "Lazar's Canyon" management rules and are supported by the decisions of the compenent ministry. The new plan of the cave that comes after the last studies and researches, with about 100.000m^{2}underground area is presented in Figure 1.

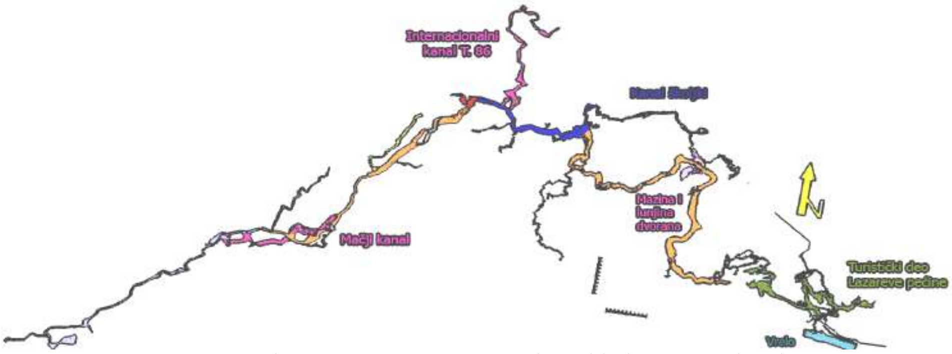

Figure 1. The New "Lazareva Cave" plan with the new explored parts

CAT`S CHANNEL

Channel was discovered after the exact plan of part of the cave of T.131 to T.199 (4) was made, after the lack of fragment 3rd levels have been noticed, continuing the High channel T.159–156–149. There aren't traces of the recent water flows in the "Cat`s channel", but it is evident that it was created by the work of the rivers that ranged from the Upper Channel over feline to High channel forming the third floor of the cave. After descending the river in the lower horizon, the Cat`s Channel is apparently disconnected by the collapsing of the T.131 i.e. the output section of the canal. Also, in places T.145 and T.149, where the contact with the lower 2ndfloor difference in height of 10m noticeable. The total length of the channel is feline 212.3m, while it's surface is about 210 m². The channel has an average height of 15 m, while the width of the channel in the preserved sections is up to 20m. Only one filling channel is noticedat T. Mk.5, which reaches from the ceiling and is visible up to 50m in height. Channel is characterized by the fallen boulders that fell from the ceiling with more than speleothem deposited in a lower horizon. The genesis of the channel undoubtedly indicates that it is now the fossil channel, which lost the hydrological function that had the T 149 to T.131.By the further river work, channel below the floor carved a south path and dips to below 10m, while leaving the departments at the contacts with the Cat channel.

THIRD LEVELOF THE HIGHER HORIZON

Italian way

This is the first in a seria of 3rdHigher horizon segments. It is a channel that is connected to the Hall of the Red Crystal (3).The Channel only seems to get upward character to T.I2, because there is a bigcalcite sedimentation. The channel has a length of 42m and is covered by the carbonate formations so that its present volume is reduced more than 30%. There is a section of 14m, when leaving the channel to T.98 in the lower level, which come by the collapsing the merger of the the 2th and 3th floors.

Hall of Camelot

Hall of Camelot is the last of the investigated because it was 14m above the T.95 and T.97 inlet to the outlet section. Only due to the fact that the other recessed and leans on the north wall, the other is preserved over a length of 37m. The Former River Terrace doesn't exist from the remains of a floor of the hall to the Italian way and Hawaii way.

Hawaii way

Hawaii's way following preserved segment of the same levels, which differs only in polluted form of the original floor, which is broken into 3 blocks. The channel can be monitored and follower 65m from T.96 to T. 93.

RMD way and Magical channel

This is the longest preserved segment of the same floors that after collapsed blocks with T.93 to T.88 covers the first floor. The channel also has contact with T.89 in the form of a vertical discharge of 19m height. The input of the channel width is more than 20m, while maintaining a ceiling height of 3th level. The huge blocks that are up to 8m in radius are making the floor. This channel, if you are looking towards the outlet part, it lost its width, which however is not less than 10m. Compared to other segments, which follow the course of the developing the channel NW-SE, RMD Way moves WE. The Magical Channel is a filling fossil channel and today drains the trickle of water from the surface. There is pillar at the entrance area is, which is almost hanging of the wall from the 2nd floor, at a height of about 10m and a radius of over 3m. Among other things, the cave jewelry, there are plenty of helictites. At the seeming end of the channel, which is already almost 20m taller than the floor of 3rd floors are covered with massive purees of the vertical cracks. Total length of the new channels in this part is 273m, out of which 66m is the length of the Magic Channel. RMD way end up at the T.88, however, the original channel and the floor was going to T.86. The evidence of this can be seen in the well preserved river terraces.

INTERNATIONALCHANEL T.86

Channel is detected and measured during the First International Camp FSUE (Federation of Cavers Europe). The channel is created by the work of the still undetermined watercourses. The first part of the channel extends to the north until the last third of the direction of the provision and the E-SE. The initial profile of the channel was 8m wide and 10m high, but the channel is ingrown in cave ornaments and its profile was reduced by half. There are twice more stalagmites, stalactites, columns and other forms of cave jewelry along the entire length of the horizontal channel (626m) then in the Resava Cave.

CHANNEL WITH CHELLS

*It is possible to enter from the Hall sinks of river channels in two ways to the downstream channel which is almost buried by the huge blocks in the entrance area at the T.68 and T.71 (2).*Channel after 15m assumes the form of a young channel with distinctive chemical and mechanical erosion along a fault line that goes in the direction of S-N. The channel apparently ends in the Lake sinking zone, but another passage was discovered on T.68r13.The Shell Channel was discovered after this passage, with the total length of over 1.2 km. Although studies have not been completed, it can be concluded that it is a double channel: lower channel, which drains less water and occasionally taller active channel. Both channels are often intertwined and moving towards the first E, and then to the SE. As the speleo-divers have already arrived at the other side to the dry zone, it is expected to connect these communications. It is estimated that there are over 500m inlength the lower channel of the river and higher channel ends in a recreation area near the falls. Validating these assumptions will change the present theory of the genesis of the whole cave.

GALLERY CHANNEL OF DRY RIVERBEDS

SAIS gallery

Present knowledgements exclude the possibility that the Galleries are the segment of the higher horizon of the Dry Riverbeds Channel. This assumptions indicate that these Filling Channels and caverns of the former Kornjetski Stream. The entrance to the hall is from the T.41 direction over collapsed blocks and after the 12m of the height difference. The hall has a direction of NW-SE, with a floor falling towards the Channel of Dry riverbeds. The total length of the channel is 202m. However, there are two side channels are raw and unexplored until their ends.

Mazina and Lunjina gallery

This hall is symmetric to the SAIS Hall. Access to it is through a vertical wall covered in drapery, at T.39. The total recorded length is 240m, an average width of 20m and height of the hall up to 30m. Floor of the both halls are covered with collapsed blocks and fine alumina applied by clay trickle water from the surface.

Darko boos

The channel is ex-filling river character with the owerall recorded total length of 140m. Its further channel exploration is disabled because of the in growth of channel ornaments.

FLOODED CHANNELS OF SPRING

The first study of submerged channels were made only in recent years and the first significant recording results are from 2013. This confirms the assumption that the Spring at the entrance to the Lazareva Cave is connected with the Lake in a recreation area by a side channel at T.3. This discovery documents another entrance to Lazareva Cave. The length of these submerged channels is 148m and they are positioned almost below the current tourist routes. Filling Channel flows from the NW-SE direction to the Lake and it is recorded in details with a total length of submerged channel of 230m. Subsequent research revealed a further extension that keeps the direction of the current, and that 150m after having contact with the dry zone of cave channels. It is realistic to expect finding the communication with the dry and free-flowing channels of the Shell Channel.

CONCLUSION

Lazareva cave becomes officially the first cave in Serbia which is more than 10km long by this research (Figure 2).Previous predictions made in previous works have been confirmed, but it is already clear that the research is not even close to its end as it is confirmed the existence of approximately 2.5 km more unmeasured channels. Further problems that follow further research can already been felt. Each generation of researchers came to the limit of their technological capabilities, however further researches behind T.199 are limited, because of the need to be in a cave and to spend more than 24 hours. This is beyond speleologist and researchers physical capabilities.

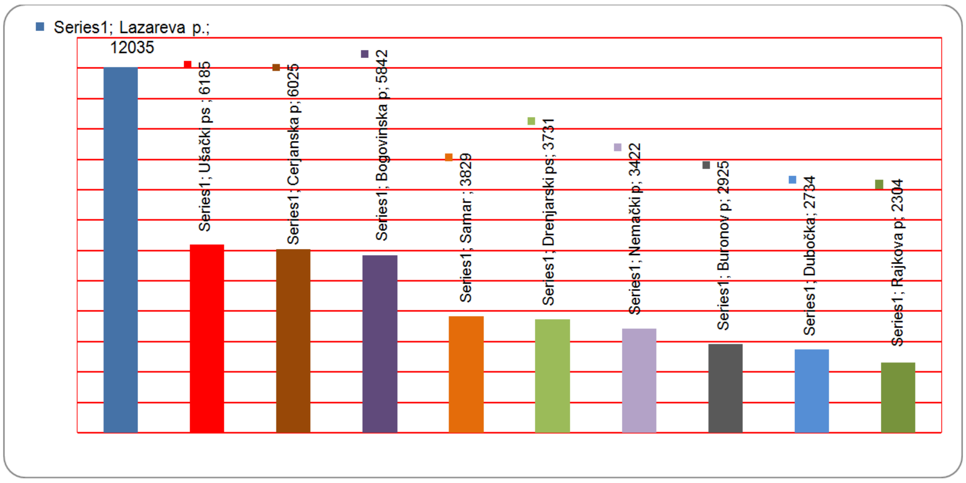

Figure 2. Graph of the longest speleological objects of Serbia.

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EFFECTS OF AIR POLLUTION ON MEDICAL PLANTS

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ABSTRACT

The aim of this paper was to analyze relationship between ambient air pollution and effects on medical plants. Important physiological processes, photosynthesis, respiration, carbon allocation and stomatal function are known to be affected by air pollutants. A wide range in sensitivity of photosynthesis both within and between species is evident from the literature. Exposure of plants to mixtures of pollutants generally reduced the threshold at which effects were first detected and increased the level of inhibitory responses. There are reasons for concerns with regards to the quality of medicinal plants and more stringent quality control seem to be necessary.

Key words: air pollution, medical plants, effects, toxic metals.

INTRODUCTION

During the past decade, there has been increasing public interest and acceptance of natural therapies in both developing and developed countries. Due to poverty and limited access to modern medicine, about 80% of the world's population, especially in the developing countries uses herbal medicine as their source of primary healthcare (1). Although herbal products are generally considered safe, significant side effects have been reported for many herbal products. The contamination of medicinal plants is considered as one of the primary reasons for the side effects (2). Less is known about the association between air pollution and the quality of medicina plants, as an important source of active principles of various phyto-pharmaceutical products (3,4).

The aim of this paper was to analyze relationship between ambient air pollution and effects on medical plants.

MATERIALS AND METHODS

Two electronic databases were searched to identify all relevant references.

RESULTS AND DISCUSSION

Medical plants represent a large group of plants used in medicine or veterinary practice for therapeutic or prophylactic purposes (5). The therapeutic properties of medicinal plants are conditioned by the presence in their organs of active substances, such as alkaloids, flavonoids, glycosides, vitamins, tannins, and coumarin compounds, which physiologically affect the bodies of humans and animals or which are biologically active in relation to the causative agents of various diseases.

There are a lot of factors that affect the quality of medical plant products, including incorrect identification, contamination and falsification of products. All of these can cause serious health problems in patients. Plants that grow in highly polluted environment have altered metabolism and in any case not suitable for human consumption (6-8).

Toxic substances from the air settle in organs of herbs or penetrate the leaves and other organs, and in both of these ways distort the structure and functional activity of medical plants. The initial changes in physiological activity and structure of organs usually are not great. Injuries herbs toxic substances may be hidden, chronic or acute. Hidden injuries are determined visually on the basis of reduced productivity and intensity of growth, a relatively short time and the intensity of photosynthesis productivity. Chronic injury of plants resulting from continuous or periodic penetration medium-high concentrations of gases in the leaves or other plant organs. In this case, reduces the number and size of leaves, branches and weight gain, and the leaf curl occurs. In the second half of the vegetation period, there are peaks and peripheral necrosis, reduced fruiting and leads to premature leaf fall. Acute injuries herbs occur after brief application of high concentrations of gases or the operation of medium-high concentration, but of long duration. As a result of such activity over the entire surface of leaves creates necrotic spots, the amount of water in the leaves is reduced and the leaves are falling rapidly.

For visual assessment of the effects of air pollutants in plants most often accompany changes in sheets, such as chlorosis, necrosis or curl. At the same time, it can be evaluated, and the degree of injured organs, abundance of fruiting, the number of seeds and their germinate, as well as plant productivity (9).

Many plant species show similar sensitivity to different gases (Table 1.), but it can be identified the most sensitive (species as indicators). According to the degree of sensitivity to the effects of gases herbs can be divided into the following groups: sensitive (I), intermediate sensitive (II), slightly sensitive (III) and resistant species (IV). According to the available data, the classification was made of some plant species according to the degree of sensitivity to gases. In determining the level of sensitivity of species in specific area, attached classification can be used.

Table 1. Classification of herbs by the degree of sensitivity (10)

Sensitive species (I)	Secondary sensitive species (II)	A little sensitive species (III)	Resistant strain (insensitive) (IV)
Betula pendula- White Birch	Pinus nigra- pine	Tilia tomentosa- silver linden	Gingko biloba- ginkgo
Papaver glaucum- ponceau	Betula pubescens- North Birch	Juniperus communis- juniper	Crataegus oxyacantha- red hawthorn
Pinus strobus- American pine	Juglans regia- nut	Taxus baccata- yew	Salix alba- white willow
Pinus silvestris- white pine	Juniperis virginiana- Virginia juniper	Sambucus nigra- elder	Achillea millefolium- milfoil
Picea orientalis- Caucasian spruce	Aesculus hippocastaneum- horse chestnut	Quercus robur- oak	Hibiscus syriacus- mallow
Beberis vulgaris- barberry	Tilia cordata- small-leaved lime	Vitis vinifera- Vonn vine	Crataegus monogyna- white thorn

Different plant species may differ in sensitivity to air pollutants. These variations occur due to differences in geographical location, stage of growth and maturation.

In the areas where the air is mainly polluted by sulfur-dioxide, chlorine, nitrogen oxides and ammonia , the plant species listed in the table 2. will not be found.

Table 2. Medicinal plants sensitive to certain pollutants (10)

Herbs sensitive to suplpur dioxide	Herbs sensitive to chlorine gas	Herbs sensitive to ammonia
Matricaria chamomilla- chamomile	Quercus robur-oak	Ribes rubrum- currant
Trifolium repens- white clover	Tilia cordata-lime	Fraxinus pennsilvanica-ash
	Salix alba- white willow	Sambucus nigra-elder

Correct sample preparation of medical plants for investigations about air pollution effects, is very important for obtaining accurate data and reliable interpretation of the results. The plant material must be clean and without the presence of substances, including soil and dust particles, which may affect the analytical results. Decontamination processes involving washing and rinsing with deionized water, and 0.2% detergent solution (nonphosphate), should be used only for fresh samples of plants.After the decontamination of the water is removed from the plant tissue to a temperature below 60 Co, in order to stop the enzymatic reaction and to stabilize the samples (11).

The most common contaminants are present in the plant material or plant products are heavy metals (12), pesticides, microbes, mycotoxins.

The most commonly detected toxic metals are lead, mercury, cadmium, arsenium, cooper, and thallium. Plants are an important link in the way in which excessive amounts of heavy metals are coming to feed and to a variety of biological cycles. Contamination of medicinal plants to heavy metals varies in some plant species, although they grow in the same environment. The contents of heavy metals in the same plant is different from one to another of the collection. On bioaccumulation also be influenced by genetic predisposition given species, the period of collection, and other geoclimatic factors.

Plants represent a bioindicators of environmental pollution and herbs need careful monitoring for certain types accumulate incredible amounts of heavy metals. It is known that about half of the amount of lead and zinc to be inserted into the human body comes from foods of plant origin. For herbs that are used for internal use in powder form or in the form of extracts, it is recommended to avoid picking in areas affected by pollution. A sure way to prevent the high accumulation of heavy metals in the human body is the quality control of herbal raw materials.

Many heavy metals are essential and are important components of pigments and enzymes of plants, and these are mainly zinc and nickel. High levels of heavy metals can cause morphological abnormalities of cells and induce hereditary mutageene effects in humans.

Control of heavy metals in medicinal aromatic plants is one of the methods evaluating their quality. Depending on the point at which the growth, there is a big difference in the quality and concentration of heavy metals in plant tissues. Limit values for heavy metals in herbal medicines do not exist except in the individual monograph Kelp for: As (90 mg//kg), Pb (5mg/kg), Cd (4mg/kg), Hg (0,1mg/kg). European Pharmacopoeia provides a limit for the Pb (5mg/kg), Cd (0,5mg/kg), Hg (0,1mg/kg), unless otherwise permitted and justified. The World Health Organization recommended limit values for a variety of medicinal plants is not more than 10mg/kg material. Annex to the regulations of the European Commission includes threshold Hg (0.02 mg / kg) in plant and spice infusion.

Moreover, the function of plants is one of the most important factors in maintaining the purity of air.

The most resistant medicinal plants to the wind blow are: the sessile oak *(Quercus sesilis*), the English oak (*Quercus robur*), the downy oak (*Quercus pubescens*), the Turkey oak (*Quercus cerris*), sweet chestnut (*Castanea sativa*), yew (*Taxus baccata*) etc. Of the above mentioned species the most resistant to the air pollution are: horse chestnut (*Aesculus hypocastanum*), acacia (*Robinia pseudoacacia*), and some types of roses, for example *Rosa rugosa*, etc. Resistant to the low temperatures are: green ash (*Fraxinus pensylvanica*), eastern white pine (*Pinus strobus*), the spruce (*Picea axcelsa, P. Canadensis, P. Pungens),* the Eurpoean barberry (*Berberis vulgaris*), etc.

Some important vegetation has a biotic environmental factor that modifies some other environmental conditions other than air flow, and conducive to the making and maintaining of various pollutants. Especially important conditions for the emergence of various pollutants are temperature and humidity.

The biochemical effect of vegetation in the direction of reducing pollutants in the atmosphere is insignificant to be of greater practical importance.

There is great importance of vegetation, that is, medicinal plants as an indicator of the type and intensity of environmental pollution. It is based on the special sensitivity of certain plant species to specific pollutants in the atmosphere, thus the ascertainment certain changes or damage to particular organs of certain plants is not only a sure sign of the presence and action of pollutant but it is also a sign of intensity, ie. concentration.

Herbs that are sensitive to the presence of sulphur oxides are: primrose (*Mirabilis Jalpa*), walnut (*Juglans regia*), mallow *(Malva sp*), common soapwort (*Saponaria officinalis*), chestnut (*Castanea sativa*), etc.

Herb that is sensitive to the presence of fluorine and halogen compounds is St. John's wort (*Hypericaceae sp.*).

Herbs that are sensitive to the presence of smog are: walnut (*Juglans regia*), beans (*Phaseolus vulgaris*), celery (*Apium graveoleus*), onion (*Allium cepa*), etc.

CONCLUSION

Air pollution is mainly due to anthropogenic activities and the negative impact of air pollution manifested in human health, animal and plant life. Effects of air pollution on medicinal plants is a consequence of the accumulation of greenhouse gases and toxic metals. The air pollution greatly reduces the therapeutic efficacy of medicinal plants. The attention has been focused on the collection of medicinal plants from polluted areas and their eventual decontamination and cleaning of unwanted agents.

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„MALI VRSACKI RIT“ - HABITAT AND SPECIES MANAGEMENT AREA

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ABSTRACT

Wetland ecosystems have special conditions for a vast diversity of habitats and species. „Mali vršački rit“ providing food, shelter and nesting place for many birds. It is also important for other fauna species, such as dragonflies and amphibians. This area is characterized by wet and dry meadows, ponds and reed beds, with typical representatives of the living world. Despite its importance and status of protection, „Mali vršački rit“ is being endangered by wildfires caused by arson, deforestation and conversion to farmland.

Key words: Wetland, Mali vršački rit, diversity

INTRODUCTION

Since Vojvodina is the largest European area of confluence, it was often heavily flooded till XIX century. Over the last century, the number and size of its wetlands have decreased progressively, almost one-third of its area.[1] „Mali vršački rit“ is small marsh area, 11 km long and 2 km wide, at an altitude between 80 and 90 m. Despite extensive drainage in the past, it has not been converted to farmland and its vast diversity of phytoplankton, plants, insects, reptiles, amphibians, birds and mammals has preserved.

MATERIAL AND METHODS

The methodology of the survey was data analysis from conducted studies of visual monitoring, explorations of daily counts of flights, observations of bird nests, monitoring of behaviour of turtles, amphibians, reptiles and other animals in this area.

RESULTS AND DISCUSSION

An area of “Mali vršački rit” which is protected, comprises 931,20 ha. It provide habitat for many of species of aquatic and terrestrial plants and animals. It was found a total of

24 taxa of phytoplankton which were classified taxonomically in four major groups: Cyanophyta (Cyanobacteria), Bacillariophyta (diatoms), Euglenophyta and Chlorophyta[1].

In this area it was determined 139 taxa of plants in 98 orders. Two of them are strictly protected Aster sedifolius L. subsp. canus (Waldst. & Kit.) Merxm. and Peucedanum officinale L. Aster sedifolius subsp. canus is a plant growing in wet thickets, salty marshes (Soó, 1970). It belongs to Pontic-Pannonian floristic element (Stevanović,!) and is an edificator of the alliance Festucion rupicolae Soó (29) 40 corr. Soó 64 (Soó, 1970). According to Gajić, in Serbia, this plant grows only in Vojvodina, where it is often found on salty habitats (G a j i ć, 1975).[2]

Hog's fennel (Peucedanum officinale L.) is rare native plant of meadows and pastures. It prefers moist soil, so it can be find on clayey banks near the water.

According to the prevailing type of vegetation and influence of ground water, it can be distinguished two main groups of phytocoenoses and one characteristic alliance: Phragmitetum communis Schmale 1939, Peucedano-Asteretum punctati Soó 1947 and Festucion rupicolae Soó 1940. The community of reed is the most widespread of the rush communities which grow along the banks of channels.[3] The phytocoenoses with the domination of Phragmites communis are covering northern and north-western parts of "Mali vršački rit". In the zones of varying supplies of waters on salt marshes grows phytocoenose of Peucedano-Asteretum punctati Soó 1947. Alliance of Festucion rupicolae, are characteristic of steppe region of Serbia.[4] The most widespread plant of this alliance are Festuca rupicola Heuffel, Alyssum alyssoides (L.), Potentilla argentea L.) and Galium verum L.[1]

Figure 1. Phytocoenoses of "Mali vršački rit" (photo: Vučanović, M. 2010)

In the framework of valuation of natural resources for protection in 2008[th] for the first time research of insects of this area was performed. Species from 18 families have been recorded: Coenagrionidae, Lestidae, Corduliidae, Aeshnidae, Libellulidae, Gomphidae, Acrididae, Tettigonidae, Pentatomidae, Scarabaeidae, Cetoniidae, Coccinellidae, Cerambycidae, Carabidae, Chrysomelidae, Nymphalidae, Pieridae and Papilionidae. Dominant species of insects in "Mali vršački rit" are those that are characteristic of agricultural land, such as Moroccan locust (Dociostaurus maroccanus (Thunberg, 1815)) and short-horned grasshopper (Calliptamus italicus (Linnaeus, 1758)). Small water bodies in this area, though typically lacking riparian vegetation, may potentially to provide habitat for several Odonata species within the rural landscape. There is no doubt that the insect order Odonata has a great potential for use in efficiently indicating the quality of water in respect to its effects on biota, at least on a local scale.[5]

According to morphological data, 11 species of amphibians and reptiles are present in this area. The most common among amphibians are pool frog (Pelophylax lessonae (Camerano, 1882)), edible frog (Pelophylax ridibundus (Pallas, 1771)) and Eurasian marsh frog (Pelophylax ridibundus (Pallas, 1771)). Pool frog is threatened by habitat loss through agricultural intensification and urbanization, channelization of water bodies, drainage and pollution of wetlands, and the introduction of predatory fishes to breeding sites.[6] Eurasian marsh frog and pool frog are incorporated into the IUCN Red List of Threatened Species as Least Concern category (LC).

European pond turtle (Emys orbicularis (Linnaeus, 1758)) is qualified as near threatened, which means that is not dependent on conservation but is very close for qualification as vulnerable.[7] It requires aquatic and terrestrial habitat and feeds on invertebrates, amphibians and their larvae and on plants.

The reptiles that mainly inhabit or feed in "Mali vršački rit" are grass snake (Natrix natrix ((Linnaeus, 1758)), Aesculapean snake (Zamenis longissimus (Laurenti, 1768)), Balkan wall lizard (Podarcis tauricus (Pallas, 1814)) and the common wall lizard (Podarcis muralis (Laurenti, 1768)). Aesculapean snake and Balkan wall lizard are is listed on Annex II of the Bern Convention, and on Annex IV of the European Union Habitats Directive, and are protected by national legislation.

Figure 2. European pond turtle (photo: Vučanović M.2011)

More of 150 birds are partially dependent on this area, e.g. for breeding or feeding. One of them is still on the IUCN Red List: Ferruginous duck (Aythya nyroca (Güldenstädt, 1770)). Main known threats to the Ferruginous duck are habitat loss and degradation, climate change/drought, and over-hunting.[8] "Mali vršački rit" is breeding habitat for corncrakes (Crex crex (Linnaeus, 1758)), a globally threatened species, too. The species is listed on Annex I of the EU Wild Birds Directive, Appendix II of the Bern and Bonn Convention (Convention on the Conservation of Migratory Species of Wild Animals).[9] White and Black stork (Ciconia ciconia and Ciconia nigra (Linnaeus, 1758) are listed as SPEC 2 (Birdlife International 2004). Storks using "Mali vršački rit" for feeding and surrounding area for selection of nest sites. Great bittern (Botaurus stellaris (Linnaeus, 1758)) and common grasshopper-warbler (Locustella naevia (Boddaert, 1783) show a strong preference for quiet lowland marshes with extensive dense young reedbeds of Phragmites spp. Some species, such as European roller (Coracias garrulus (Linnaeus, 1758)) prefers drier pastures, till whiskered tern (Chlidonias hybridus (Pallas, 1811)) and black-necked grebe (Podiceps nigricollis (Brehm, 1831)) require ponds and open water.[1] There were recorded occasional nesting of Montagu's harrier (Circus pygargus (Linnaeus, 1758)), short-eared owl (Asio flammeus (Pontoppidan, 1763)) and common snipe (Gallinago gallinago (Linnaeus, 1758)) as well as wintering of common redpoll (Carduelis flammea (Linnaeus, 1758)). Lesser spotted eagle (Aquila pomarina (Brehm, 1831)) and Ural owl (Strix uralensis (Pallas, 1771)) build nests in trees on Vršac Mountains, but feed on a wide variety of vertebrates which live in "Mali vršački rit". Ornithofauna of this area involves a number of species which are due to its importance in the national and international levels included in the relevant lists, regulations and conventions.[1]

Figure 3. Nests of black-winged stilt on the ground (photo: Vučanović M.2012)

Although mammals in "Mali vršački rit" don't represent its fundamental value, they are an extremely important factor in the diversity of habitats. Meadows and pastures are inhabited by Poland vole (Microtus arvalis (Pallas, 1778)), European pine voles

(Pitymys subterraneus (McMurtrie, 1831) and Eurasian harvest mouse (Micromys minutus (Pallas, 1771)). Water vole (Arvicola amphibius (Linnaeus, 1758)) occurs around irrigation ditches, with a preference for slow flowing or still waters. The common hamster (Cricetus cricetus (Linnaeus, 1758)) is a mammal characteristic of an open, steppe-like and cultivated landscape. [10] For arable land is also characteristic hillock mouse (Mus hortulanus (Nordmann, 1840), and because of the proximity of human settlement in "Mali vršački rit" can be found synantropic species of rodents such as house mouse (Mus musculus (Linnaeus, 1758)) and common rat (Rattus norvegicus (Berkenhout, 1769)).

Figure 4. Rare winter guest - common redpoll (photo: Vučanović M.2009)

CONCLUSION

Wetlands are considered valuable because they clean the water, reduce flood risks and provide wildlife habitat and recreational opportunities. They are the focus of many recovery efforts because over the past 200 years the area and health of wetlands have declined significantly.[11] There are numerous threats to the natural values of "Mali vršački rit", the most important are: habitat destruction and change of land use, unsustainable farming, uncontrolled hunting, road which cuts corridors for animals and lack of awareness of citizens and decision-makers about the importance of this little marsh.. Therefore, on the August 1st of 2013 this place is protected as Habitat and species management area according the classification of IUCN and as protected habitat under national classification.

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KARST PLATEAU DUBASNICA AS GEOPARK - CONTEMPORARY MODEL FOR GEOHERITAGE PROTECTION IN SERBIA

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ABSTRACT

Further development of the nature resources protection system in Serbia involves activities related to the protection of geodiversity as an integral part of nature, and the introduction of geoparks as new, contemporary models of conservation and sustainable management of geoheritage. So far, geoheritage in Serbia was considered and protected through individual natural phenomena and forms, being a part of the common preserved natural environment and biodiversity protection. The paper discusses an initiative to designate the Dubašnica Karst Plateau as geopark, within the existing natural resources of Nature park "Kučaj-Beljanica" and Natural monument "Lazar river canyon", as a potential model for sustainable use and promotion of geoheritage and geodiversity of Serbia.

Key words: geopark, geoheritage, geodiversity, geomorphology, karst, Dubašnica Plateau.

INTRODUCTION

Public attention to the geodiversity issue for the purpose of conservation, protection and sustainable use of natural resources in Serbia has been increased during recent years. The legislation relating to the protection of nature, including the protection of geodiversity as its integral part as well as the procedure for the designation of protected objects of geoheritage, have often been changed. By the adoption of the Law on Environment in 1991. objects of geoheritage were protected as a "natural monuments" or "nature reserves", being treated as habitats of scpecific flora and fauna. From 1991. they can be protected as other types of protected natural assets (6). The Declaration of II Scientific Meeting on the Serbian Geoheritage in 2004. (1) has highlighted the following main objectives: the inclusion of new type of protected natural resource - geopark in corresponding legislation, establishment proposal for the first geopark in Serbia, the initiation of mandatory technical processing and presentation of geoheritage, launch of educational programs on geoheritage etc. These objectives were later elaborated in the National Strategy for the Sustainable Use of Natural Resources in 2012. (10), which in addition to proposed increase in the number of protected objects of geoheritage and establishment of geoparks, also initiates their integration into the European Geoparks Network. However, the legal framework for comprehensive models of protection and the promotion of geoheritage has not yet been defined. Although the Institute for Nature Conservation of Serbia in cooperation with experts from a variety of geosciences has done an inventory of the geoheritage of Serbia (1) that includes about 650 objects, only small share of them has been protected within the existing system of nature evaluation and protection.

STUDY AREA

Dubašnica Karst Plateau is located in eastern Serbia, in the area of South Kučaj. Dubašnica Plateau occupies an area of about 160 square kilometers. It is karst surface placed at 800 -1000 m above sea level (7), slightly wavy, sharply bordered by the deep canyon valleys. Boundaries of Dubašnica (8) are morphohydrological and are following the watersheds - the basin of Lazar canyon and right side of the River Beljevina basin. Two main geomorphological units can generally be distinguished: wide karst surface in the northeastern half of Lazar canyon and the wellspring part of the canyon in its south-western half, named Mikulja Plateau. Area of Dubašnica is bounded from the east side by Beljevina river, on the southeast side by the range Malinik, on the west side with the peaks Omaniš, Oštri kamen, Kiseli vrh and Tresta, on the north with steep limestone hill Velika Kršiora and on the northeast by river Tisnica basin (figure1). The river basin is disorganized and occasional flows occur in spring (7). Carved in the south side of Dubašnica karst Plateau is Lazar canyon, currently protected as a natural monument.

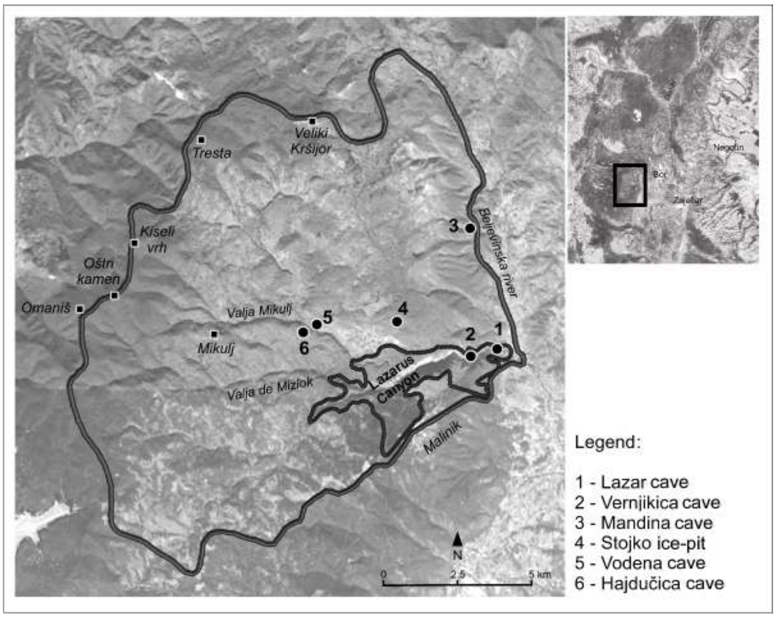

Figure1. Location and boundaries of the karst plateau and potential geopark Dubašnica

The idea of protecting natural heritage of Dubašnica dates back to the early 20th century. The first proposal to protect its natural values dates back from 1924. when a geologist and academician Petar Pavlović, the first director of the Natural History Museum in Belgrade, suggested the protection of Lazar Cave (6). Serious steps have been made after the establishment of the Institute for the Protection and Research of Natural Rarities of the Republic of Serbia (now the Institute for Nature Protection of Serbia). On the basis of the former Act on the Protection of Cultural Monuments and Natural Rarities natural monument Lazar Cave was protected in 1949., and in 1957. rainforest and beech stands in Malinik were placed under protection as Reserve of mixed stands of fir, beech, yew, Turkish hazel and black ash. Although these were significant steps to protect nature of Dubašnica, only a small part of Dubašnica gain officiall status of protection. At the end of the 20th century investigations of Dubašnica area by experts of various professions were intensified. Results of these studies showed that Dubašnica, as well as the canyon valley of the Lazar river, river Mikulja, Demizlok and stream Vej present exceptionaly valuable areas for their geological, geomorphological and hydrological characteristics, and also a remarkable floristic and faunistic centers of Serbia and Europe. After the Lazar river canyon was designated to be a natural monument in 2000. (covering the area of natural monument "Lazar cave" and Nature reserve "Malinik", where the previous solutions for protection of these facilities ceased to exist) and the adoption of the Act on the Protection of Nature Park "Kučaj Beljanica" (this study is currently in the process of adoption for the Protection Act) which is expected in the future, Dubašnica and it`s immediate surrounding will be state protected on a much larger territory (over 5500 ha).

Dubašnica landscape has great natural resources. In addition to its biological values, this area has been recognized by many experts in the field of geosciences as geodiversity center of both national and international importance. Eastern Serbia karst was originally studied by Jovan Cvijić. Modern researches of its geomorphological phenomena were mainly done by R. Lazarević, with the assistance of young researchers organizations and speleologists, who investigated a large number of caves, underground hydrographic network, assesed the need for protection of the caves as well as their potential for tourism (2). On the basis of these results Lazar and Vernjikica caves have been adapted for tourist use and existing wells were capped for water supply. The first initiatives for complex protection of Dubašnica were launched by developing special expertise of Institute for the Conservation of Nature in 1993. (8), that has been made upon the request of the Municipality of Bor. Particular importance is given to the latest researches of Speleology Club "Bradan" and Research Center of the Lazar cave, who showed that according to the hitherto explored cave channels Lazar Cave is considered to be a longest cave in Serbia (12,13,14).

The inventory of the geoheritage of Serbia (Institute for Nature Protection, 2005) so far has recognised and listed following phenomena: geomorphological karst relief park South Kučaj – Beljanica, Lazar river canyon, stone bridge Samar at a river Perast, Lazar, Vernjikica and Hajdučica Cave, pit Dubasnica, geomagnetic field anomaly and others (1). Among numerous geomorphological phenomena of Dubašnica there are over 130 explored caves, karst springs, sinkholes and underground streams, plateaus terraces, valleys, canyons, dry valleys and other features (2).

Serbian Spatial Plans (11) initiate protection of the preserved geoheritage, so one of the basic preferences in Spatial plan of Special Purpose Area "Kučaj - Beljanica" (which is in the process of adoption) is the conservation and sustainable use of the geoheritage and landscape in a way that provides public interest in the protection and conservation of natural resources, development of local communities and education of visitors and stakeholders. For this reason, a potential of Dubašnica Karst Plateau as Geopark within the Nature park "Kučaj - Beljanica" was recognized. At the state level, acknowledgment of the importance of Dubašnica`s natural resources is protection of natural monument "Lazar river canyon" due to the "maze of limestone canyon valleys of impressive dimensions and distinctive morphological traits, with many significant caves" and " interesting phenomena and processes of karst water circulation " (15).

The Regional Plan of Bor emphasizes that the most important natural values in the municipality are remains of rich geological history through numerous exclusive karst phenomena and forms, as well as the biogeographic karst phenomena. The most prominent and richest karst is present in the eastern part of Kučaj within the geomorphological units of: Dubašnica karst plateau, Zlotska river gorges, Lazar river canyon (with the canyons of Mikulj, Demizlok and Pojenska River), Malinik mountain, numerous caves and pits (among which the most important are Lazareva and Vernjikica cave that are arranged for visitors), Vodena, Hajdučka i Mandina caves, Stojko ice-pit etc. (picture 1). This Plan initiates the status of Dubašnica`s protection as a karst geopark, with a number of natural phenomena important for the conservation of geodiversity and geoheritage, scientific research and education, the geological, ecological, speleological and other specific forms of tourism, in accordance with the National Strategy for the Sustainable Use of Natural Resources (10,11).

Based on these facts the Association of Young Researchers of Bor, along with other environmental NGOs, launched the initiative, that is continously being renewed, to promote the protection and sustainable use of Dubašnica`s geoheritage. This initiative has so far been recognized and adopted in the spatial plans of Bor and natural resource Kučaj - Beljanica, as well as in the strategic documents of Bor municipality - Local Environmental Action Plan and Local Sustainable Development Strategy.

DUBAŠNICA - POTENTIAL GEOPARK OF KARST RELIEF

Dubašnica is identified as an area of great potential for the formation of karst geopark as a special form of geovalues promotion, due to its exceptional geological and geomorphological phenomena. Geopark presents an area where geoheritage is managed according to the principles of sustainable development and it has to:

- contain one or more objects of scientific importance for geology, geomorphology and archeology, ecology, history, etc.
- have a management plan that will encourage sustainable development and socio -economic development of the area
- provide education in different geosciences and on the importance of environmental protection
- be part of a global effort to protect the natural resources in accordance with the concept of sustainable development (4,5,6).

Based on criteria of Global Geoparks Network geopark "is **not** an area of exceptionall, but a single object of geoheritage, or individual sites of geological importance, or an area that is limited to scientists or geological thematic park, nor is an area where local communities are not involved, or where there is no strategy for sustainable economic development" (9). Geopark size may vary but it is important to be large enough to support implementation of a plan for its sustainable development. Also, the territory of geopark must be clearly defined and managed by an organized structure.

The idea of protecting the individual objects of geoheritage (caves, canyons, springs etc.), as well as the protection of entire areas (e.g. Reserve Géologique de Haute Provence in France that was established in 1984.) appeared in the 90s of the last century in response to an increasing threat to the exsistance of these values and the potential dangers of their permanent destruction. This is why UNESCO initiated activities related to geoparks, the territories where geoheritage is going to be adequatly protected, in late 1990s. To put this model of geoheritage protection in practice, it needs to become understandable to the general public by means of promotion through targeted activities, where one of the main roles belongs to a geotourism. The term geotourism refers to a specific kind of tourism which promotes the values and social benefits of geoheritage, and ensures their protection and sustainable use by different interested parties.

Increasing the total area under the protection and promotion of sustainable management of natural resources in Serbia can be achieved through specific protection models and sustainable use of geoheritage. There are objects of geoheritage or their complexes in Serbia that have already been explored and evaluated by experts and local communities, such as Dubašnica is, so that the launching and implementation of the initiatives for their establishment as a geopark protection model can be commenced.

For coming to life as karst geopark it is necessary for Dubašnica to envise the activities at the national level (such as effective implementation of national strategies for sustainable use of natural resources and goods, the legal regulation of geoheritage protection and the formation of geoparks, to comply with the relevant international evaluation criteria, to define the national criteria for the allocation of geoparks and to form a National geoparks network, as well as to raise awareness of the importance, protection and sustainable use of geoheritage). Beside those, it is also necessary to develop a range of activities at the local level to ensure the involvement of local communities and other stakeholders in the implementation of protection and sustainable use of geoheritage. Municipality of Bor has recognized the potential of this area, but it is required to carry out additional investments in infrastructure development so that Dubašnica may become accessible to a wider range of users. Only when the designated geopark area starts to function sustainably, an initiative for the European Geoparks Network membership can be launched. Until then, organizational structures must be well defined, business and marketing plan needs to be developed, and projects that may contribute to the sustainability of geopark should be promoted and supported. Additional educational activities in primary and secondary schools are of great importance, and it is of particulary importance to encourage and enable students of geosciences to conduct their excercises, researches, master 's and doctoral theses within this area (3). Some of the most important activities at the local level that should predate and contribute to the designation of the geopark Dubašnica would be:

- to intensify cooperation between diverse stakeholders at local and national level
- to support the extension and intensification of geomorphological and geological phenomena in the proposed karst Geopark Dubašnica by the local and national scientific, educational and professional institutions and non-governmental organizations
- to present and promote current and future results of Dubašnica geoheritage researches to the professional and scientific national and international public
- to develop a program for the presentation of current natural monument "Lazar Canyon" and all the other so far recorded and investigated geoheritage objects of Dubašnica in order to inform and raise awerness of the general public
- it is very important to prepare and implement the programs to raise awareness, educate and inform the local population, as well as all other potential users of geopark from the very beginning of the realization of this idea. The role of NGOs, schools and the media is of a particular importance for this process.
- to regulate the access to the canyons of Lazar, Mikulj, Demizlok and Pojenska rivers and Vernjikica cave (that should be re-open for the public), to restore hiking trails, lookouts and to label geoheritage objects in Dubašnica
- to develop a program for touristic valorization of Dubašnica that would include a development of geotourism.

CONCLUSIONS

In the following period, Serbia should expand the percentage of protected areas and improve the quality of their protection in accordance with the principles of sustainable development. At the same time, this process should be based on initiatives for the protection of valuable areas of preserved nature, previous researches and valorisation of natural resources and new directions in field of nature protection, such as the protection and sustainable use of geoheritage.

Dubašnica Karst Plateau in eastern Serbia is prominent example of such area, since the existance of long-lasting survey of its natural resources and continual, ongoing initiatives for the protection of the area. Certain parts of Dubašnica are already protected ("Lazar river canyon") or have been in the previous protection status, and the whole area of Dubašnica will soon become integral part of the Nature Park "Kučaj - Beljanica". Contemporary models of geoheritage protection provide unique opportunity to raise the quality of Dubašnica Karst Plateau protection to a higher level and ensure its sustainability.

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MIGRANT LEPIDOPTERA SPECIES OF NATIONAL PARK FRUSKA GORA

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ABSTRACT

Entomological survey on Fruška Gora revealed total of 61 species of Lepidoptera (6.53% of the total number of species on Fruška Gora) from a group of migratory species. There are 7 seasonal migratory species of 1st order, 1 seasonal migratory species of 2nd order, 36 emmigrant species (local migrants of 1st and 2nd order), 10 occasional migrants (temporary migratory species), 2 dismigratory species (species that expand their areal), while there are 5 possible migratory species recorded so far. Inventory of migratory Lepidoptera species is the first phase of a consistent approach to its conservation. Area of migratory species distribution and determination of population dynamics should also be established, as well as subsequent monitoring of species ability for long term living and development within the associated ecosystem.

Key words: Lepidoptera, migratory species, Fruška Gora.

INTRODUCTION

Available research knowledge about insect fauna in Serbia is scarced for the actual needs of science-based evaluation of their populations characteristics and conditions, necessary for design of the appropriate protection measures. The Republic of Serbia is a signatory to a number of important international documents that are of particular importance for nature conservation activities and management of protected areas. In order to implement them, Republic of Serbia has passed the laws on their ratification and took responsibility and obligation to implement the signed documents. In this way, institutional respond to the threat of rapid degradation and destruction of natural habitats and ecosystems has been provided.

The most important international agreements relevant to the management of protected areas (and also relevant to the management of entomological research within this complex) are: the UN Declaration on Environment and Development - UN Rio Declaration, UNCED, Rio de Janeiro, 1992 ("Official Gazette of FRY - International Agreements" no. 11/ 01), known as Rio Declaration, Convention on Biological

Diversity (CBD), Rio de Janeiro 1992 ("Official Gazette of FRY - International agreements", no. 11/ 01), Convention on the Conservation of European Wildlife and Natural Habitats, Bern, 1979 ("Official Gazette of RS - International agreements", no. 102/ 07), known as the Bern Convention, Convention on the Conversation of Migratory Species of Wild Animals (CMS), Bonn, 1979 ("Official Gazette of RS - International agreements", no. 102/ 07), known as the Bonn Convention.

Migratory species, both their entire population and geographically separate parts, belong to a significant group of wild animals whose members cyclically and predictably cross one or more national jurisdiction boundaries. Migratory species of butterflies are an integral part of the insect fauna of Fruška Gora National Park, but they were insuficiently investigated so far. Data on research of this group are scarce (Eitschberger et al., 199; Beshkov, 1994a, 1994b, 1996a, 1996b; Vajgand 2000; Zečević, 1995, 2002; Stojanović, 2009a , 2009b , 2012; Stojanović et al., 2010, 2011, 2011, 2013 and 2013b).

Inventory of Lepidoptera faunal diversity is the first stage of a consistent approach to its conservation. Here presented data on the diversity of migratory species are direct result of such stage. The conservation status of migratory species of butterflies, which depend on a set of influences that may affect their long-term distribution and abundance, is so far unknown. Favorable conservation status of migratory species of butterflies should be assessed throught evaluation of the species ability for living and development within the associated ecosystem and within a long-term period. Such investigations and subsequent monitoring of migratory Lepidoptera species should detect possible changes in the distribution areas of migratory species in the long-term period, foresee if they are going to be expected in future, and recognize adequate habitats for the maintenance of these populations.

MATERIALS AND METHODS

During the period 2009–2012 we collected lepidoptera by light trap (250 W TEŽ VTFE high-pressure mercury discharge lamp; 100 W, 160 W, 250 W, and 400 W Philips ML lamp; Petromax lamp) with a cotton panel at the back. The lepidoptera specimens were gathered by entomological net in the vicinity of light source, as well as directly at the lamp. Specimens were killed by modified killing jars with diethyl ether, which was used for narcosis and neutralization. The collecting of lepidoptera in forest and meadow habitats was done mostly at dusk and at night (photophilous species), but by day as well. The collected lepidoptera were afterwards stored as dry specimens in entomological boxes in the private collection of the first author. Permanent slides of the genital structures are deposited in the collection of permanent slides of the first author as well.

The analysis of chitinized genital structures was performed according to the standard method (Fibiger et al. 2009), which was improved, optimalized and adapted to laboratory conditions. The posterior part of the abdomen was carefully removed by a forceps from fresh or dry specimens, then macerated and stored in a vial filled with 10% KOH. The material was subsequently boiled in a boiling water bath. Finally, the permanent microscope slides were made. The most important morphological features of the specimens were photographed by a special digital photo accessory on a Carl Zeiss Stemi 2000 stereomicroscope.

RESULTS

The entomological studies of Fruška Gora, revealed the presence of 61 species of Lepidoptera that belong to a group of migratory species. The division of a migratory Lepidoptera has been given according to Zečević (1996). Principally, migratory Lepidoptera are divided into seasonal migratory species of 1st order, seasonal migratory species of 2nd order, emmigrant species (local migratory species of 1st and 2nd order), occasional migrants (casual migratory species), dismigratory species (subgroup species extend their distribution area) and possible migratory species.

1. The Seasonal migrants 1st order, recorded on Fruška Gora are:
Pyralidae
1. *Nomophila noctuella* (Denis & Schiffermüller, 1775)
Sphingidae
2. *Agrius convolvuli* (Linnaeus, 1758)
3. *Acherontia atropos* (Linnaeus, 1758)
Nymphalidae
4. *Vanessa atalanta* (Linnaeus, 1758)
5. *Vanessa cardui* (Linnaeus, 1758)
Noctuidae
6. *Autographa gamma* (Linnaeus, 1758)
7. *Agrotis ipsilon* (Hufnagel, 1766)

2. Seasonal migratory species of 2nd order that has been recorded on Fruška Gora is:
Arctiidae
1. *Euplagia quadripunctaria* (Poda, 1761)

3.Emmigrant species - local migrants 1st and 2st order recorded on Fruška Gora are:
Pyralidae
1. *Ostrinia nubilalis* (Hübner, 1796)
Sphingidae
2. *Macroglossum stellatarum* (Linnaeus, 1758)
3. *Hyles euphorbiae* (Linnaeus, 1758)
4. *Hyles livornica* (Esper, 1779)
Pieridae
5. *Aporia crataegi* (Linnaeus, 1758)
6. *Pieris brassicae* (Linnaeus, 1758)
7. *Pieris rapae* (Linnaeus, 1758)
8. *Pieris napi* (Linnaeus, 1758)
9. *Pontia daplidice* (Linnaeus, 1758)
10. *Colias erate* (Esper, 1805)
11. *Colias croceus* (Fourcroy, 1785)
12. *Colias hyale* (Linnaeus, 1758)
13. *Gonepteryx rhamni* (Linnaeus, 1758)
Lycaenidae

14. *Lycaena phlaeas* (Linnaeus, 1761)
15. *Leptotes pirithous* (Linnaeus, 1767)
16. *Everes argiades* (Pallas, 1771)

Nymphalidae

17. *Issoria lathonia* (Linnaeus, 1758)
18. *Inachis io* (Linnaeus, 1758)
19. *Aglais urticae* (Linnaeus, 1758)

Geometridae

20. *Rhodometra sacraria* (Linnaeus, 1758)
21. *Orthonama obstipata* (Fabricius, 1794)

Noctuidae

22. *Tyta luctuosa* (Denis & Schiffermüller, 1775)
23. *Macdunnoughia confusa* (Stephens, 1850)
24. *Trichoplusia ni* (Hübner, 1803)
25. *Acontia lucida* (Hufnagel, 1766)
26. *Schinia scutosa* (Denis & Schiffermüller, 1775)
27. *Heliothis viriplaca* (Hufnagel, 1766)
28. *Heliothis peltigera* (Denis & Schiffermüller, 1775)
29. *Helicoverpa armigera* (Hübner, 1808)
30. *Spodoptera exigua* (Hübner, 1808)
31. *Phlogophora meticulosa* (Linnaeus, 1758)
32. *Mythimna vitellina* (Hübner, 1808)
33. *Noctua pronuba* (Linnaeus, 1758)
34. *Noctua fimbriata* (Schreber, 1759)
35. *Peridroma saucia* (Hübner, 1803)

Nolidae

36. *Nycteola asiatica* (Krulikovsky, 1904)

4. Occasional species recorded on Fruška Gora are:

Sphingidae

1. *Hyloicus pinastri* (Linnaeus, 1758)

Papilionidae

2. *Papilio machaon* Linnaeus, 1758

Pieridae

3. *Colias alfacariensis* Ribbe, 1905

Nymphalidae

4. *Nymphalis polychloros* (Linnaeus, 1758)
5. *Nymphalis xanthomelas* (Esper, 1781)

Noctuidae

6. *Mythimna albipuncta* (Denis & Schiffermüller, 1775)
7. *Mythimna l-album* (Linnaeus, 1767)
8. *Xestia c-nigrum* (Linnaeus, 1758)
9. *Agrotis exclamationis* (Linnaeus, 1758)
10. *Agrotis segetum* (Denis & Schiffermüller, 1775)

5. Dismigratory species (expanding their areal) recorded on Fruška Gora are:
Lycaenidae
1. *Polyommatus amandus* (Schneider, 1792)
Nymphalidae
2. *Polygonia c-album* (Linnaeus, 1758)

6. Possible migratory species recorded on Fruška Gora are:
Papilionidae
1. *Iphiclides podalirius* (Linnaeus, 1758)
Noctuidae
2. *Amphipyra pyramidea* (Linnaeus, 1758)
3. *Amphipyra berbera* Rungs, 1949
4. *Hoplodrina blanda* (Denis & Schiffermüller, 1775)
5. *Mamestra brassicae* (Linnaeus, 1758)

CONCLUSION

Entomological survey on Fruška Gora recorded 61 species of Lepidoptera (6.53% of the total number of species on Fruška Gora) from a group of the migratory species. Among them, there are 7 seasonal migratory species of 1st order, 1 seasonal migratory species of 2nd order, 36 emmigrant species, 10 occasional migrants, 2 dismigratory species and 5 possible migratory species. However, list of migratory Lepidoptera species of Fruška Gora is not closed. The following research may show that the increasing number of Lepidoptera species recorded on Fruška gora could lead to an increase in the number of species belonging to this specific bihevioral group.

Results of inventory research on migratory species of Fruška Gora National Park indicate a strong need to extend similar studies to other representative protected areas in Serbia, in order to establish the area of migratory Lepidoptera species distribution and determine their population dynamic, and to subsequently monitor the sustainability of defined habitats on which they were recorded. All these are necessary steps toward the future comprehensive habitat valorization and protection.

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EVALUATION OF RADIATION LOAD IN MOSS FROM EASTERN SERBIA IN 2000-2013

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ABSTRACT

Moss samples were randomly collected on the territory of Eastern Serbia in the period 2000-2013. Average yearly values of absorbed dose strength for ^{137}Cs in moss from the territory of Eastern Serbia were from 0.035 mGy/year (2012) to 5.033 mGy/year (2003). Minimal absorbed dose strengths for ^{137}Cs (mGy/year) were from 0.002-0.216, while maximal values were from 0.120-13.99. Absorbed dose strengths for ^{137}Cs (mGy/year) in 2011 were from 0.030 to 0.534. In 2013 they were from 0.004 to 0.682. Absorbed dose strengths in mosses from the territory of E. Serbia were lower than doses that cause changes in the reproductive cycle of flora and fauna and lethal doses.

Key words: moss, Eastern Serbia, absorbed dose strengths.

INTRODUCTION

Exposure to ionizing radiation is an event or conditions during which an organism is irradiated with ionizing radiation that can be both useful and harmful. Ionizing radiation can cause functional, morphological and genetic mutations in an organism. If the exposure doses are high they can cause death.

Accidents in nuclear facilities or nuclear testing release large amounts of polluting radioactive material into the atmosphere. The leading radionuclide, from the viewpoint of formation of tissue doses and radiobiological consequences is ^{137}Cs, the chemical and biochemical homologue of potassium, following its metabolism in an organism. The physical and biological half-life of ^{137}Cs is long. The retention time of ^{137}Cs in an organism is linked to the physical damage of the organism it is polluting. Radiocezium-137 built into an organism becomes a source of internal radiation and also a radiation source for other organisms immediately linked in the food chain[1-3].

The Chernobyl accident (26.4.1986, Ukraine) released a large amount of polluting radionuclides – 10^{18} Bq into the atmosphere, of which $3.7x10^{16}$ Bq ^{137}Cs. Total contamination levels of former Yugoslavia from radioactive fallout were 0.08-6.40 μGy/L, Eastern Serbia 1.41–2.56 μGy/L, Southern Serbia 0.45-1.40 μGy/L and Central Serbia 0.08–0.44 μGy/L[4].

Moss (old, primitive group of organisms with a specific construction and specific ecology compared to higher flora) can be used to collect information on the spatial and time distribution of pollution and pollution trends of air and the environment with polluting substances[5,6]. Adoption of polluting substances by moss depends on many factors: moss species and age, their morphological and physiological characteristics, location position and substrate, and altitude. Research of the diversity of moss in Serbia has shown that 444 moss species grow classified into 169 genuses and 53 families[7].

Evaluation of the radiation load of organisms in the environment using moss is complex. Dose calculation requires information on the internal and external distribution of radionuclides and their behavior in the environment. This data is rarely available, especially for individual species and this is why data is simplified and generalized[8,9].

MATERIAL AND METHODS

Moss samples (275) were collected in the period 2000-2013 in the region of Eastern Serbia. Moss samples were dried in air, homogenized, and the activities were measured gammaspectrometrically. Radioactivity measurements were performed using an HPGe gamma-ray spectrometer (ORTEC-AMETEK, with 8192 channels, resolution of 1.65 keV and relative efficiency of 34% at 1.33 MeV for ^{60}Co). Samples were measured in Marinelli vessels. Sample weight was about 0.1 kg. The counting time for each sample was 60000s. The relative error for sample preparation and measurement was 10%. Gamma Vision 32 MCA emulation software was used to analyze gamma-ray spectra[10]. The specific activity of the artificially produced radionuclide ^{137}Cs was measured via the γ-line at the energy of 661.6 keV. Nuclides were identified using a library driven search routine and quantitative analyses were carried out using the appropriate detector calibration. Measured activity was converted into doses with the assumption that all emitted particles (gamma and beta) were absorbed in the tissue that accumulated ^{137}Cs.

RESULTS AND DISCUSSION

Diverse mosses grow on the territory of Eastern Serbia and they are good models for calculating the absorbed dose strength. Table 1 shows the absorbed dose strength for ^{137}Cs (mGy/year) in moss from the territory of Eastern Serbia: Djerdap national park (NP), Sokobanja (SB), Banja Jošanica (BJ), Gamzigradska banja (GB), collected in the period 2000-2013, standard deviation, and also minimal and maximal dose strength values.

From Table 1 follows that the average values of the absorbed dose strength for ^{137}Cs (mGy/year) in moss from Eastern Serbia were from 0.035 (2012) to 5.033 (2003). The minimal absorbed dose strength (mGy/year) in moss was from 0.002 (2010) to 0.216 (2003), while the maximal values was from 0.120 (2012) to 14.10 (2003). The average values of the absorbed dose strength for ^{137}Cs were the highest in moss collected on the territory of the Djerdap national park

Table 1. Absorbed dose strength for ^{137}Cs (mGy/year) in moss from the territory of Eastern Serbia, minimal and maximal value of dose strength, absorbed dose strength for ^{137}Cs (mGy/year) in moss from: Djerdap national park (NP), Sokobanja (SB), Banja Jošanica (BJ), Gamzigradska banja (GB), collected in the period from 2000 to 2013, standard deviation.

	Dose for ^{137}Cs (mGy/year)			
YEAR (sample number)	**av. value (E. Serbia) ± st. dev.**	**min**	**max**	**av. value (parts of E. Serbia) ± st. dev.**
2000. (1)	0.503*	---	---	SB
2001. (6)	0.249 ± 0.160	0.071	0.503	SB
2002. (5)	0.290 ± 0.154	0.071	0.500	SB 0.250 ± 0.159
2003. (11)	5.033 ± 4.963	0.216	14.10	NP 4.330 ± 4.300
2006. (54)	0.963 ± 1.867	0.008	9.840	NP 2.080 ± 2.640 SB 0.099 ± 0.090 GB 0.329 ± 0.170
2008. (52)	0.242 ± 0.307	0.008	1.597	NP 0.290 ± 0.390 SB 0.063 ± 0.051 BJ 0.296 ± 0.183
2009. (28)	0.181 ± 0.282	0.007	1.276	NP 0.100 ± 0.120 SB 0.035 ± 0.036 BJ 0.461 ± 0.093 GB 0.457 ± 0.112
2010. (28)	0.104 ± 0.114	0.002	0.421	NP 0.710 ± 0.890 SB 0.055 ± 0.042 BJ 0.300 ± 0.080
2011. (21)	0.147 ± 0.131	0.011	0.534	NP
2012. (34)	0.035 ± 0.032	0.006	0.120	SB 0.034 ± 0.031 BJ 0.255 ± 0.026
2013. (35)	0.161 ± 0.171	0.003	0.682	NP

*only one sample

In this work the absorbed dose strength for ^{137}Cs was investigated in the following moss species: *Amblystegium serpens (Hedw.) Schimp. (1), Grimmia trichophylla Grev. (2), Oxyrrhynchium hians (Hedw.) Loeske (3), Brachytheciastrum velutinum (Hedw.) Ignatov&Huttunen (4), Leucodon sciuroides (Hedw.) Schwaegr. (5), Hypnum cupressiforme Hedw. (6), Orthorichum anomalum Hedw. (7), Ceratodon purpureus (Hedw.) Brid (8), Homalothecium sericeum (Hedw.) Schimp. (9), Kindbergia praelonga (Hedw.) Ochyra (10), Brachythecium salebrosum (F. Weber&D. Mohr) Schimp. (11), Plagiomnium undilatum (Hedw.) T.J. Kop(12), Anomodon viticulosus (Hedw.) Hook&Tayl. (13), Neckera complanata (Hedw.) Hueb. (14), Anomodon attenuatus (Hedw.) Hueb. (15), Grimmia pulvinata (Hedw.) Sm.(16), Bryum capillare Hedw. (17), Abietinella abietina (Hedw.) Fleisch. (18), Syntrichia ruralis (Hedw.) F. Weber & D. Mohr (19), Polytrichum juniperinum Hedw. (20), Pogonatum urnigerum (Hedw.) (21), Dicranella heteromalla (Hedw.) Schimp.(22),* collected in 2011 and 2013.

Table 2. Absorbed dose strength for ^{137}Cs (mGy/year) in moss from the territory of Eastern Serbia collected in 2011, moss locality and species.

2011			
No	**Locality**	**Species**	**Dose for ^{137}Cs (mGy/year)**
1.	Entrance to NP Djerdap	*1*	0.011
2.	Karataš	*2*	0.367
3.	Kladovo	*3*	0.035
4.	Negotin Badnjevo	*4*	0.176
		5	0.102
			0.136
		6	0.153
5.	Negotin Bukovo	*5*	0.315
		7	0.534
		8	0.068
6.	Štubik-Klokočevac	*9*	0.082
			0.108
7.	Klokocevac	*5*	0.074
8.	Donji Milanovac	*6*	0.111
			0.088
			0.284
		9	0.128
9.	Lepenski vir	*9*	0.038
			0.213
		10	0.030
10.	Dobra	*11*	0.041

In 2011 21 moss samples (11 species) were collected on 10 localities, while in 2013 35 samples (15 species) were collected on 18 localities (Tables 2 and 3). Absorbed dose strengths for ^{137}Cs (mGy/year) in moss collected in 2011 were from 0.030 (Lepenski vir, *Kindbergia praelonga (Hedw.) Ochyra*) to 0.534 (Negotin, Bukovo, *Orthorichum anomalum Hedw.*), while in mosses collected in 2013 from 0.004 (Kamenolom PIM, Brnjica, *Homalothecium sericeum (Hedw.) Schimp.*) to 0.682 (Miroč, *Plagiomnium undilatum (Hedw.) T.J. Kop*).

Absorbed dose strengths in investigated moss samples were from 0.002 mGy/year (2010) to 14.0 mGy/year (2003). From Table 1 follows that the absorbed dose strength in moss from the investigated territories several times lower than doses that cause changes in the reproductive cycle of flora and fauna (0.4 to 1 Gy year) and lethal doses (4 Gy and 0.4 Gy year).

Table 3. Absorbed dose strength for ^{137}Cs (mGy/year) in moss from the territory of Eastern Serbia collected in 2013, moss locality and species.

2013			
No.	**Locality**	**Species**	**Dose for ^{137}Cs (mGy/year)**
1.	Golubački grad	*9*	0.122
			0.102
2.	Kamenolom, PIM, Brnjica	*9*	0.003
			0.004
3.	Brnjica	*6*	0.060
		11	0.032
4.	Miroč, base	*12*	0.682
5.	Miroč, top	*6*	0.026
		11	0.051
6.	Miroč, towards Brza Palanka	*8*	0.020
7.	Vratna canyon, Mala Kapija	*13*	0.162
			0.259
			0.315
			0.164
		14	0.247
		15	0.213
8.	Road to M. Kapija	*6*	0.088
9.	Vratna monastery	*6*	0.168
			0.134
10.	Negotin Bukovo	*9*	0.344
		16	0.665
		17	0.162
11.	Štubik-Plavna	*18*	0.042
12.	Plavna	*19*	0.015
13.	Klokočevac	*9*	0.099
14.	Gornjak monastery	*9*	0.057
			0.082
15.	Mlava source, Žagubica	*9*	0.159
			0.520
16.	Dubašnica, Crni vrh	*20*	0.009
		21	0.014
17.	Zlot (Lazar's) cave	*9*	0.055
			0.273
		19	0.139
18.	Tilva Njagra	*22*	0.131

CONCLUSION

Average values of the absorbed dose strength for ^{137}Cs (mGy/year) in moss from the territory of Eastern Serbia were 0.035-5.033. Absorbed dose strengths for ^{137}Cs (mGy/year) in 2011 were 0.030-0.534, while in 2013 they were 0.004-0.682. Minimal absorbed dose strengths for ^{137}Cs (mGy/year) were 0.002-0.216, while maximal values were 0.120-13.99.

The highest average values of absorbed dose strength for ^{137}Cs in moss were noted on the locality of the Djerdap national park.

Absorbed dose strengths in mosses from the investigated territories are much lower than doses causing changes in the reproductive cycle of flora and fauna (0.4 to 1 Gy/year) and lethal doses (4 Gy to 0.4 Gy/year).

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SOLIDIFICATION OF AIR BUBLE IN THE FROTH LAYER BY SURFACE ACTIVE ORGANIC COMPOUNDS – FROTHERS

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ABSTRACT

Substances used for the foaming process of the copper mineral and precious metal flotation, are heteropol hydrocarbon compounds, which absorb at the border of gaseous and liquid phases, with the low solubility in water. Orientation of the frother moleculs at the interface of the liquid and gaseous phases are reverse to orientation of the collector molecules at the interface solid and liquid phases.

Key words: froth flotation, Cu-Au ore, frothers

INTRODUCTION

In order to achieve higher efficiency , in particular noble metals , are applied such frother types, that provide the specific gravity of the mineral complex of grain - a bubble less than the specific gravity of the pulp.

Due to the reduction of surface tension result of oriented frother moleculs at the interface liquid/gas, based on the individual characteristics of the respondents frother, showing physical and chemical characteristics and the quantitative ratio of minerals copper and gold for certain types of frother.

Frothers characteristics were determined by the appropriate choice of different chemical groups. There are three main group of chemicals, which are used in the frothers. These are: higher alcohols, polyglycols and polyglycol ethers. Some of these groups are subdivided into subgroups. Each chemical group gives to frother specific characteristics in terms of the intensity of the mineralized foam, bubble diameter, water retention, air dispersion and kinetics of the formation of froth. These chemical groups can then be mixed in various proportions to achieve optimal performance foams for each fineness of particle size distribution of the solid phase in the flotation of copper and precious metals .

Each of chemical groupgives to frother specific characteristics. In the present study by determining the size and volume stability of the foam, in order to serve in the correct choice of frother in a variety of flotation conditions for copper minerals and precious metals .

As noted, there are three major chemical groups: higher alcohols, polyglycols and polyglycol ethers. Although these groups are not the prevailing one and only. There are other frothers that are freely associated with these groups. Thus, for example, eucalyptus oil hydrolyzed in alcohol. Furthermore, the product can be freely trietoksibutan attached to polyglycol ether groups, and the structural characteristics. Frothers are characterized by a mechanism of reducing the surface tension of the liquid stabilizes the double membrane of the bubble. This causes a structural stabilization of the membrane, the intensity of which is necessary to support the absorption of collector chemical structure on mineral particles.

During testing, the resulting strong mineralized foam bubble diameter on average 5 mm, the proof is successful collecting and sufficient quantities of frother. Quite small bubbles of less than 2 mm, shown during the experiment, as a sign that there is an excess penušača, a poor foam with large hats than 15 mm in diameter shows a lack of frother.

FROTHERS

The alcohol group

Within these there are two groups, let us call them, subgroups, namely linear aliphatic alcohols and cyclic alcohols.

Linear aliphatic alcohols

This is the general group which covers both linear and branched chain aliphatic alcohols with a carbon number of C5 - C10. In this case, there is only one bound hydroxide groups in the molecule of hydrocarbon. They are commonly expressed by the formula:

$$R - OH$$

Wherein R is - a linear or cyclic hydrocarbon series C5 - C10 of which depends on whether the alcohol islinear or cyclic aliphatic .

The basic characteristics of linear alcohols are fast kinetics, brittle foam, foam less stable and less water retention ponds, resulting in higher selectivity process.

Linear alcohols are generally sensitive to changes in pH which can sometimes be an advantage in the conduct of the technological process. The increase in pH reduces the content of H2O in mineralized foam. This feature can lead to improved quality of mineralized foams, resulting in reduced water retention. This reduced water retention caused by decreased removal of gangue, which is a prerequisite for enhanced selectivity. In this way, the foam brittle is controlled by amount of linear aliphatic alcohol frothers or by the pH value.

Linear alcohols generally have faster kinetics than the other groups. They provide a higher utilization at the beginning of the flotation process. This is of importance in terms of short time of flotation, when the content of minerals in the flotation of the entrance of the project is greater than anticipated. As a consequence of the faster kinetics of the formation of mineralized foam reduced the effect of the concentrations of useful minerals from mineral input changes, the amount of ore processed, the solid contents as well as the changes in the hydrodynamic work the cells in the flotation process. The linear alcohols are more water soluble and their solubility ranges from 0.3 to 0.9 %. It is because of these characteristics, these alcoholic frothers have faster kinetics formation ofmineralized foam and brittle foam.

Less durable foam in some circumstances may be a problem, and sometimes be advantages offrothers depending on the specific conditions of concentration. This characteristic linear alcohol is directly dependent on the chemical structure. The faster kinetics of the formation of mineralized foam is a result of the limited solubility. Frother is characterized by significantly lowering surface tension and respond quickly to the dispersion of air to the surface of the flotation cell. This causes a lower durability foam and is necessary this type of frother added in several places during the production process. This frother dosage has the advantage because in this way it controls the process of flotation kinetics and accelerates the formation of mineralized foam.

Total lower durability mineralized foam is the result of faster kinetics formation mileralized foam, and some brittle mineralized foam can be a major advantage when treating ores with high content of aluminate sludge, then when the increased processing capacity .

Disadvantages are seen using linear alcohol are obvious when the predominantly processed ore in the flotation concentration at high pH and lower fineness.

Polyglycolic ethers

The most common and more efficient are polyglycol methyl ethyl ethers. They are usually displayed by the formula :

R1 - (O - R2) n – OH

Advantages of this frother type lies in the fact that R1 can be kept constant , and (R2) n can be varied and adapted to the specific characteristics of the ore and specific features of hydrodynamizm made in operating conditions in flotation cells. Polyglycol mono alkyl ethers are completely soluble in water. This results in lower consumptions, the ability to better control the thickness of the foam, the foam durability and enhanced intensity at a constant dose. The intensity comes mainly from improved water retention and capillary phenomena in the formation of mineralized foam. Consistent mineralized foam can cause problems when transporting offlotation products. Glycolether groups are less sensitive to changes in pH of the pulp. Their stable foam reduces the sensitivity to changes in pH. Increased intensity of creating mineralized foam in relation to alcoholicfrothers and the ability to adapt the molecular weight to accommodate technological conditions allow and the increased use of coarser particles without significant changes in selectivity, ie, the quality of the concentrate .

Glycol ethers have slower kinetics than alcoholic frothers. Their use in the production process of flotation concentration make difficult transport conditions of flotation products.

Polyglycols

Features and poliglikolskih polyglycol ethers can be adjusted by selecting the molecular weight. Polyglycols such groups are based on the strongest of the chemical structure of water-soluble frothers for copper mineral flotation processes. They have a more stable foam without the dosage of a power . This feature at lower frother doses added in a wide range of pH values are extremely useful for creating the conditions for increasing the recovery of copper and precious metals in terms of flotation rougher product of grinding and classification. This is particularly important in terms of increasing the processing capacity of the grinding and flotation processes. Larger particles in the flotation need frother with features intensely mineralized foams and greater reduction in surface tension.

This is even more important in terms of when in the process of concentration applied high pH environment. Increased intensity of mineralizing foam provides enough thickness foam flotation cell, which enables the optimization process of the concentration of the level control of the pulp and the amount of air introduced.

The biggest disadvantage of polyglycolicfrothersis high content of H2O in the foam as a result of high water retention. These problems are more pronounced in terms of a shorter time of flotation. When the flotation pulp is treated with fine grinding, a high water retention in the foam, in combination with a large thickness of the mineralized foams, leads to a reduction in selectivity due to the increased weight of the concentrate greatly. Adverse effects are often congestion in the pipes and pump baskets, which creates faulty conditions in the transport of the products of flotation . This is often the reason why the polyglycols are used in combination with other frothers.

FROTHERS OPTIMIZATION IN THE FLOTATION OF COPPER MINERALS AND GOLD

In order to define the degree of concentration of certain frother of the three groups and determine their impact on the use of Cu and Au were examined for superficial changes to the minerals copper and gold.

Given that, the reduction of surface tension Gφf is result oriented frother concentration at the interface liquid - gaseous, for his determination was applied method, which simulates one of the important factors in the process of concentration - air bubbles. The value of surface tension, after a measurement, determined by the following equation :

$$\vartheta\varphi f = \frac{g \cdot r(\varphi_1 \cdot h - \varphi_2 h_1)}{2} = J \cdot cm^{-2}$$

wherein :

g - acceleration due to gravity (cm • s- 1) ;

r - the radius of the capillary testing (cm) ;

φ1 - liquid density (g • cm - 3) ;
φ2 - test penušača density (g • cm - 3) ;
h - the height difference in the manometer (cm) ;
h1 - deep immersion in liquid capillary (cm) .

In Table 1 are shown the values of surface tension for tested frothers in all three groups.

Table 1. Measured value of the surface tension of frothers from all three groups

Concentration g/l	Surface tension N/cm		
	I - group	II - group	III - group
distilled water			
0,25	69,348	69,306	69,218
0,50	69,415	69,380	69,416
0,75	69,505	69,671	69,780
1,00	69,875	69,896	70,043

Also, the measured viscosity of frother from certain groups by Hoppler's viscometer with glass beads. Table 2 shows the measured values of the tested frothers.

Table 2. The values of the viscosity of certain frothers

Concentration g/l	Surface tension N/cm		
	I - group	II - group	III - group
distilled water			
0,25	69,348	69,306	69,218
0,50	69,415	69,380	69,416
0,75	69,505	69,671	69,780
1,00	69,875	69,896	70,043

Effects of application of certain types of frotherin function of concentration of certain types of frother analyzed three groups, we show in Figures 1 and 2.

On the basis of the characteristics of certain types of tested frother follows that the total score obtained by determining the size and volume stability of the foam, as shown in Tables 1 and 2, as well as in Figures 1 and 2.

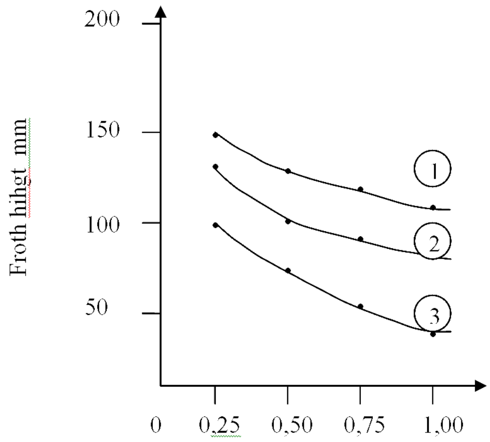

Figure 1. Froth hight in function of frother concentration

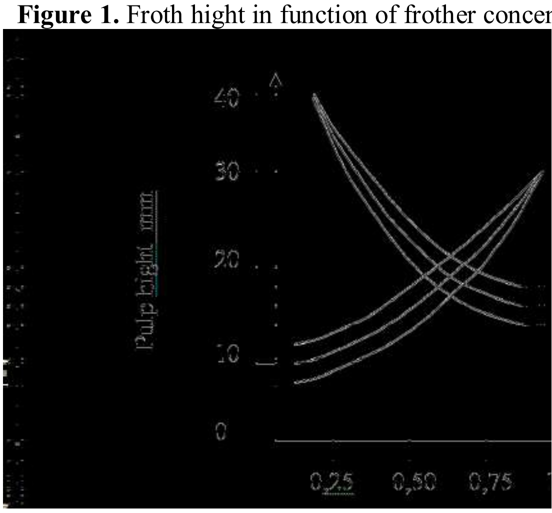

Figure 2. Structure of mineralized foam in function of frother concentration

CONCLUSION

Characteristics of the three main frother groups differ sufficiently to provide adequate opportunity for the desired characteristics of the mineralized foam optimal size in terms of volume of flotation machines and foam stability.

So, alcohol frother products selectively often with brittle mineralized foam that provides an easier process control and transport products flotation without hindered conditions. Although this is the weakest group of frothers, increasing the dose may be offset by added brittle nature of the mineralized foam that make these frothers. Increased recovery of Cu and Au , as compared to all other frothers, is obtained by applying the elastic mineralized foam with a cyclic frothers (F521 , A65 , A76) which are the best known from this group of frothers.

Glycol ether group of frothers is a medium-strong group. This group of frother gives intense foaming than the alcohol group. Add in several places in the process is rarely necessary, since this group is completely water soluble and left her reduced voltage allows operation during the entire process of concentration. Molecular weight of polyethylene glycol ether it is possible to select, and thus adjust the relationship between the optimum intensity of the mineralized foam and the selectivity as well as, the possibilities for process control .

Polyglycols are the most powerful surface active frothers in use. They are very effective, the maximum intensity of the mineralized foam and to extract the concentrate of the largest particles, as well as able to successfully focus the high mineral content in the pulp, and are active in the widest range of pH.

The test selectivity index of copper and precious metals in relation to the overburden, is higher frother application types from the first group. You evidently have higher coefficients of mineralization using frothers from first and third groups, in terms of changes in the time of flotation concentration process in the preparation of concentrates and tailings , as well as different grain size and specific gravity of the grain. Based on the characteristics of the respondents frother of these three groups, it follows that it is not enough for their optimal use in the concentrations of copper and precious metals, to know some physical and chemical constants, but it is necessary in addition to know the impact of expenditure frother the coefficient of mineralization and more the value of the specific rate of flotation of copper and precious metals.

In industrial practice, each flotation of copper with associated gold is a special problem because of the increased molecular mass of mineralized foam. Therefore, in choosing the best frother, be achieved experimentally in the laboratory.

Proper conduct experiments, as well as the proper interpretation of phenomena and interpretation of results, enabling cost-effective solution of industrial problems concentrations of copper and gold.

Been tested in this paper , will certainly facilitate practical implementation of research works for industrial purposes, the concentration of copper with associated gold.

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COMPARISON OF FLUE GAS RECIRCULATION AND REBURNING IN REDUCTION AND COMBUSTION EFFICIENCY

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ABSTRACT

Among the so-called primary methods of decrease of the NO_x emissions, the flue gas recirculation and the reburning are by far the most widely used in industry because they prevent NO_x formation in accordance with the limit level of the regulation at a lower cost acceptable to manufacturers. In this paper the implementations of flue gas recirculation and reburning were analysed on the test combustion facilities regarding its reduction and combustion efficiency at combustion of natural gas. The flue gas recirculation was shown as a very effective method in reduction of the NO_x emissions, and the reburning has equally good efficiency in reduction and combustion.

Key words: NO_x emissions, flue gas recirculation, reburning.

INTRODUCTION

The legislation relating to the NO_x emissions is strict, with the permissible emission levels being constantly reduced. It is worth noting that NO_x, in addition to having many well-known adverse effects, is also one of the greenhouse gases listed by the Gothenburg and Kyoto Protocols. Bearing that in mind, development of the efficient and low polluting combustion systems is a major aim in the combustion research. A burner is always one of the key components of any combustion system. There are many factors related to the design of a burner that have significant impact on the emissions from its flame.

Many so-called “advanced” combustion techniques, such as the High Efficiency Combustion (HEC), are new developed combustion technologies that combine high thermal efficiencies with reduced NO_x emissions. Given their high investment costs at replacement of the existing combustion systems, the focus of this paper is given on retrofit measures using commercially available technologies for lowering NO_x emissions on the existing furnaces equipped with conventional combustion technologies.

Different strategies to reduce the amount of NO_x released into the environment from combustion devices have been developed, where the flue gas recirculation (FGR) and the reburning belong to the group of so-called primary methods used to prevent NO_x

formation in accordance with the limit level of the regulation at a lower cost [1,2]. The flue gas recirculation method is based on decreasing the temperature in the combustion zone, unlike the reburning or fuel staging, which is method based on the staged combustion technology. Due to the higher combustion efficiency, reburning is shown as one of the most efficient and attractive NO_x reduction techniques [3–5].

This paper presents the results of a series of laboratory tests to determine the emissions of nitrogen oxides from the standard conventional partially premixed gas burner, which is commonly applied in the industrial practice. Natural gas was used both as a fuel and a reburn fuel. The objective of this work was to investigate the reduction and combustion efficiency in both cases: at the flue gas recirculation adjusting the quantity of the recirculated flue gases in the combustion air, and at the reburning adjusting the quantity of the reburn fuel.

EXPERIMENTAL FACILITIES

Experimental data were obtained on the experimental facilities intended for testing and improving industrial burners. The main device of the experimental facilities is a horizontal combustion chamber with standard industrial partially premixed gas burner. The combustion chamber volume is insulated with a refractory concrete insulation. Non-preheated atmospheric air was used as an oxidizer. Scheme of the experimental facility with measuring equipment for testing the efficiency of flue gas recirculation is shown in the Fig. 1, and for testing the efficiency of reburning in the Fig. 2.

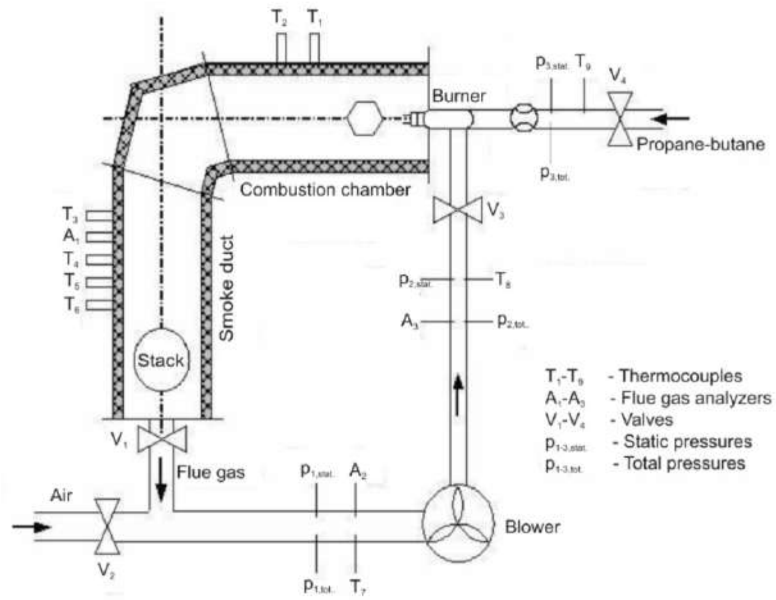


Figure 1. . Scheme (top view) of the experimental facility for testing the efficiency of flue gas recirculation

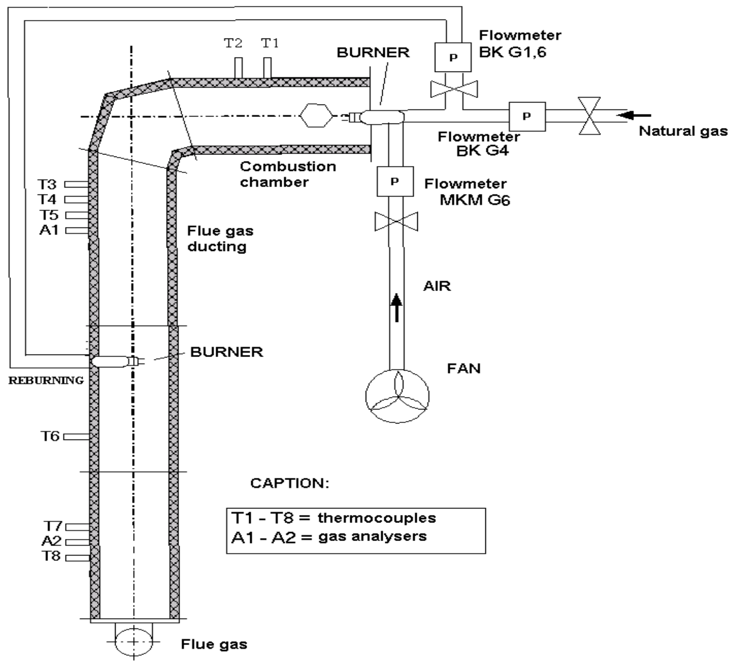


Figure 2. Scheme (top view) of the experimental facility for testing the efficiency of reburning

EXPERIMENTAL RESULTS

The efficiency of FGR depends on both the quantity and temperature of the recirculated gases. In this case, the experiments were performed with the cooled recirculated gases at temperatures less than 300 ºC. The first experimental investigations were done at the constant burner input of 16 kW. The recirculated part of flue gases in the mixture with combustion air was varied between 0 and 20 %. The value of air-fuel-ratio was $n = 1.1$. The results are shown in Fig. 3. As it can be seen, the NO_x emissions without recirculation of the flue gases reach the value of about 130 ppm. This is relatively low emission due to the high fuel flow rate and intensive mixing with the air, which reduce residence times (smaller flame) and thickness of the flame regions. If the quantity of recirculating flue gases in the combustion air increases from 0 up to 20 %, the actual NO_x values (at 3% O_2) decrease. For fire operation at the excess air of $n = 1.1$, the decrease in NO_x emissions is approximately 64%. The decrease in NO_x emissions is mainly due to the flame temperature reduction. Fig. 4 demonstrates the influence of the quantity of recirculating flue gases in the combustion air on the temperatures of flue gases measured in the combustion chamber at the excess air of $n = 1.1$.

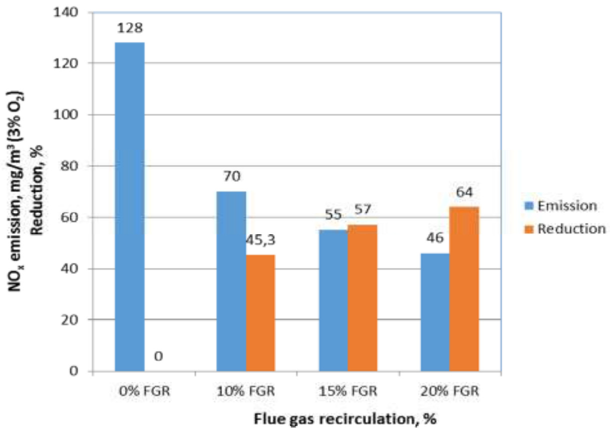
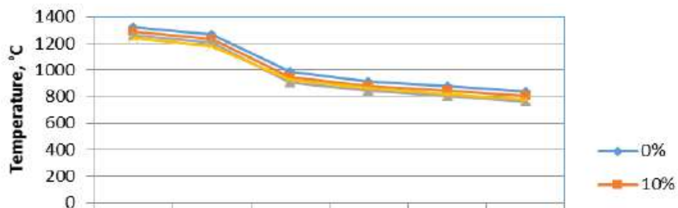


Figure 3. Influence of the flue gas recirculation on NO_x emission at the air-fuel-ratio of 1.1 and the burner input of 16 kW

The influence of the reburning process parameters on NO_x formation at the reburn fuel input of 0-10-15-20%, the air-fuel-ratio of 1.1 and the burner input of 16 kW were investigated. The results are presented in Fig. 5. The lowest emission, i.e. the maximum reduction of NO_x emission of 39.2 % was achieved at a percentage of reburn gases of 20%. Temperatures and concentrations readings were recorded over a period of approximately one hour for continuous operation at steady state conditions with regard to the set values. The influence of the percentage of reburn gases on the measured peak temperatures of combustion gases are shown in Fig. 6., demonstrating that the temperatures T1, T2 and T3 in the main combustion zone are reduced after injection of reburn fuel, thereby creating a reducing atmosphere suitable for the reduction of NO_x emissions. Above the reburn zone, the temperatures T4, T5, and T6 are increased as a result of mixing the combustion products of the reburn fuel and main fuel. The temperature at the point of injection was around 1140 °C.



	T1	T2	T3	T4	T5	T6
0%	1324	1268	985	913	875	839
10%	1289	1235	947	875	842	801
15%	1264	1208	908	841	803	762
20%	1238	1182	924	862	819	778

Thermocouples

Figure 4. Influence of the flue gas recirculation on the measured peak temperatures of flue gases at the air-fuel-ratio of 1.1 and the burner input of 16 kW

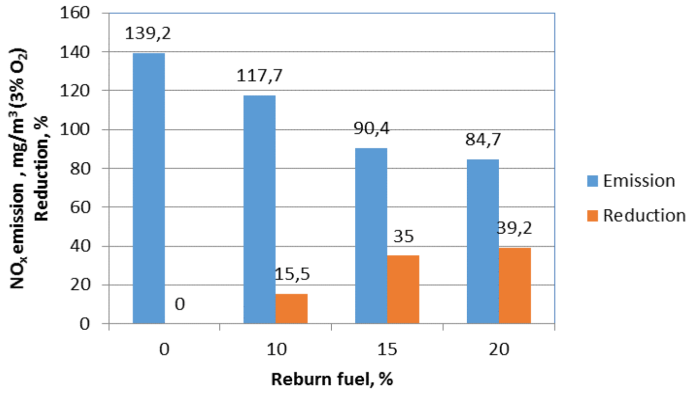
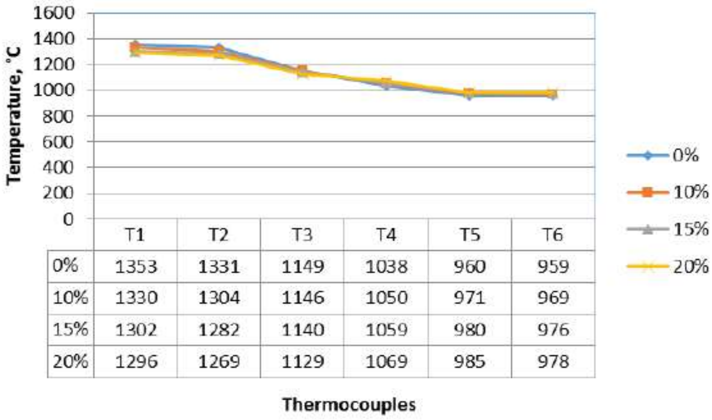


Figure 5. Effect of the percentage of reburn gases on NO_x formation at the air-fuel-ratio of 1.1 and the burner input of 16 kW



	T1	T2	T3	T4	T5	T6
0%	1353	1331	1149	1038	960	959
10%	1330	1304	1146	1050	971	969
15%	1302	1282	1140	1059	980	976
20%	1296	1269	1129	1069	985	978

Figure 6. Effect of the percentage of reburn gas on the measured peak temperatures of flue gases at the air-fuel-ratio of 1.1 and the burner input of 16 kW

In order to compare the combustion efficiency, the results of calculated values of enthalpy of the combustion products originated by combustion of the natural gas, of the lower heating value of 35 MJ/Nm^3, at the air-fuel ratio 1.1, are presented in Fig. 7.

Since the temperatures of flue gases in application of the reburning are approximately 210 °C higher compared to the temperature in application of the FGR, the enthalpy of flue gases is approximately 30% higher as well. Consequently, the so-called available heat is also higher for this value, so that there is the greater combustion efficiency at the reburning.

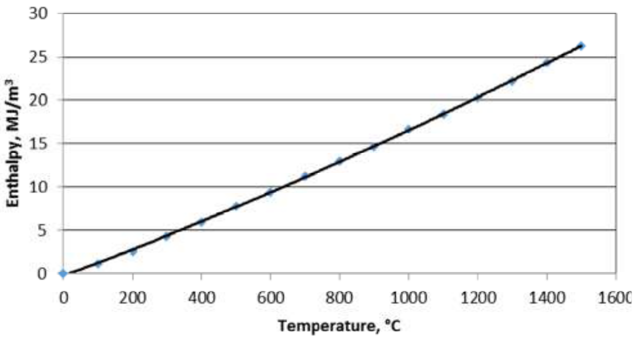


Figure 7. Enthalpy of the combustion products originated by combustion of natural gas at air-fuel ratio 1.1

CONCLUSION

Thermal NO_x is formed as a result of the oxidation of nitrogen to NO_x through a reaction path that involves oxygen, hydrogen and hydroxyl radicals. The direct reaction between nitrogen and oxygen molecules also contributes to the formation of this pollutant species via the thermal mechanism [6-8]. The rate of thermal NO_x formation is extremely sensitive to the local temperature of the flame and, to a lesser extent, to the local concentration of oxygen, as well as the time that the reagents N_2 and O_2 stay in the flame area. Accordingly, the decrease of high flame temperature, the avoidance of too much excess air and the reduction of the residence time of the reagents in the high-temperature zone can reduce thermal NO_x formation. Therefore the main problem of the reduction of nitrogen oxides formation is to eliminate the thermal nitrogen oxides formation by means of decreasing of the local peak temperature values and decreasing of local partial pressure of oxygen.

The results of this study represent the best possible reductions in the thermal NO_x emissions that are achievable by balancing the quantity of the recirculating flue gases with quantity of the combustion air. The marked reductions in the NO_x values are in the range of the amount of FGR rate from 0 up to 10 %. Taking into consideration the amounts of reductions in the emissions and, on the other hand, lowering of combustion efficiency because of the decrease of operating temperatures, the optimum value of FGR rate is between 10 and 15 %.

By applying the reburning technology, i.e. staged combustion to create a reducing zone in the second stage (reburn zone), it is possible to achieve somewhat lesser reduction in NO_x but with the enhanced combustion efficiency.

It can be concluded that, in order to achieve the greater reduction of nitrogen oxides, the flue gas recirculation is a more efficient method. In contrast, the application of reburning is a more suitable method for achieving the enhanced efficiency of the combustion process.

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ANIMAL WASTE MANAGEMENT BY INCINERATION AND COMPOSTING – A PRACTICAL SOLUTION

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ABSTRACT

According to the data from the National strategy for waste management for the period 2010-2019, the amount of by-products of animal origin in Serbia reaches about 300,000 ton annually.Only some 20% are managed in rendering plants, indicating that huge amount of waste is excluded from appropriate control system. Such waste material is classified into three categories each requiring different grades of treatment, where the first category encompasses biohazardous materials that must undergo incineration in special incinerators. Treatment of waste of the Category 2 and 3 is variable. Practical solution proposed in this paper encompasses management of all three categories of animal waste, that is, incineration of Category 1 waste and targeted composting of Category 2 and 3 waste. Installation of special incinerators and closed reactors – biovator composters for microbiological composting along with relevant infrastructure directly at waste-production sites is proposed. The process is accelerated by introducing commercially available saprophyte bacteria and lignocellulosic material(plant waste). Biotechnological procedure lasts about 20 days, resulting in the production of useful end product, i.e. compost.

The aim of the study is to present a practical solution and possibilities of application for all sources of animal waste. The procedure is safe, economically feasible and compliant with all relevant legislation on public health and environment protection.

Key words: animal waste, incineration, biovator, composting.

INTRODUCTION

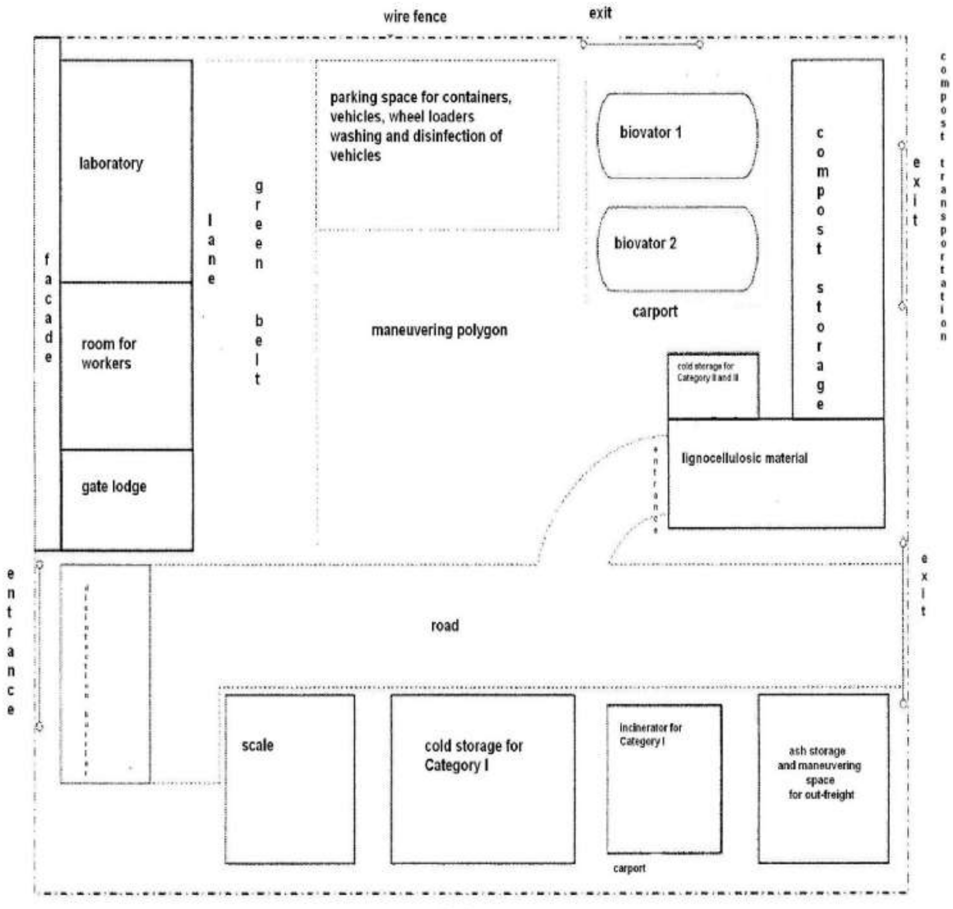
Biotechnological processes used in agricultural industry and production of food of animal origin produce tremendous amounts of by-products, i.e. animal waste. Such products adverselyinfluence the local environmentposing potential hazard for local public health as a potential reservoir of infectious and zoonotic diseases. Appropriate management and disposal of such materials is of paramount importance.So far, the system of animal waste management has not yet been implemented in Serbia (although the relevant strategy has been adopted), which negatively affects the production of safe food, environment protection and economy as a whole. National strategy for waste management for the period 2010-2019 indicates that amount of by-products of animal origin in Serbia reaches about 300,000 ton annually, and only some 20% are managed in rendering plants. These data strongly indicate that huge amount of waste is excluded from appropriate management strategy and control *endangering public health* or the environment[4].Until last year, Serbian legislation was not harmonized with European laws, thus regulation applied in animal waste management did not comply with modern and safe disposal policies. Currently, the Regulation (Official Gazette of RS 31/11)that is in line with EU-provisionsis legally effective; however, its application in practice is still questionable because of financial issues, passive administration, imprecise licensing policy, advocating expensive technologies and lack of control at the locations of origin of waste products [3].Implementation of modern and safe waste management methods is crucial, having in mind that some categories of by-products are categorized as biohazardous waste. In countries characterized by developed livestock production and application of advanced biotechnologies, waste management implicates microbiological composting procedures in closed reactors – biovators [7,8].

Taking into consideration the wide heterogeneity of waste material and their potential hazardous impact on human and animal health, the waste management requires safe methods, strictly obeying the legal provisions and relevant standards. Thus, management of by-products of animal origin is regulated by both European and national laws and bylaws. In 2002, the European Union adopted the Directive on Animal Waste Management (CONSLENG:2002R1774-01/052003) [1], which applies to all member countries. Pursuant to the aforementioned Directive, animal waste is classified into three categories each requiring different grades of treatment, where the first category encompasses biohazardous materialsthat must undergo incineration at high temperature in special incinerators [11].Treatment of other waste categories is variable, offering possibilities of recycling and manufacturing a range of new products.These issues are comprehensively laid down in the new Directive [2].Composting is the oldest-known and economically justified practice that can be performed in both closed and open space by adding heterotrophic microorganisms or enzymes or using the existing microorganisms from the waste material itself. This practice is well established and justified by experimental research [5]. This method of safe waste / by-product management is supported in recent Serbian Regulation through classifying all kinds of animal waste as „by-products of animal origin". Monitoring and control of these products are under the control and jurisdiction of Veterinary Directorate of the Ministry of Agriculture of the Republic of Serbia [3].

TECHNICAL DESIGN OF THE SAFE DISPOSAL SYSTEM - DETAILED DESCRIPTION AND CHARACTERISTICS

The draft encompasses complete safe disposal of by-products of animal origin at production sites (farms, slaughterhouses) or in specific facilities belonging to local communities. The procedure relies on strict compliance with aforementioned legal provisions, both those of the EU and national ones, laid down in the Regulation (Regulation 31/011 adopted pursuant to the Article 117 Paragraph 3 and Article 137 Paragraph 3 of the Law on Veterinary Medicine) [3]. This draft of disposal system implicates incineration of hazardous waste (Category 1) at high temperatures (800-1200 ^{o}C) in special environmentally friendly incinerators. Animal by-products of the Categories 2 and 3 are subjected to microbiological composting process in closed biovator systems. The aforementioned procedure requires appropriate area with relevant infrastructure and facilities that meet all relevant standards.By selecting the area intended for this purpose, local governments are obligated to assess the potential location in line with provisions of the Law on environment protection and with evaluation on potential environmental impacts. The proposed technical design of a disposal system including facilities and equipment is presented at Scheme 1.

The scheme on figure 1 depicts facilities and equipment enabling appropriate procedure order for each particular category of animal by-products and obtaining of final product – compost. The crucial pieces of equipment in this process are special incinerator and closed reactors -biovators (Fig.1,2,3).



Scheme 1. Tehnical solution sheme – facility location

Figure 1. Special incinerator for animal waste

SPECIAL INCINERATORS

Material from the Category 1 poses the highest risk, thus destroying byincineration is strictly prescribed. This category encompasses the following waste: animal carcasses and relevant parts, TSE (mad cow disease) infected or suspect animals, animals died or killed by implementation of programs for control, suppression and eradication of TSE, SRM (specified risk material), experimental animals, pets and circus animals, wild animals suspected for infectious diseases, by-products containing harmful residues, organochlorine and organophosphorus compounds, mycotoxines, kitchen waste in international transport as well as mixed materials from all categories. Category 1 material originates from production plants for food of animal origin, domestic animal breeding or from animal breeding for specific purposes. The main locations of origin are farms, slaughterhouses, rural households and all locations enabling free movement of domestic and wild animals, food production plants and animal feed selling points.

In accordance with the European and national regulations on mandatory incineration of such materials, Scientific Veterinary Institute has a special incinerator for that purpose - A8000, with following characteristics: large-volume of 1000 kg/h; internal chamber capacity 6.75m^3; incineration capacity 24; two-chamber structure; secondary chamber retention time 2 sec; large full size load door; electronic lid opening; automated burner start; continuous ventilation; digital temperature control; diesel fuel tank capacity 1000 L. According to cited characteristics and manufacturer's certificate, this system for combustion of animal by-products has no negative environmental effects.

CYLINDRICAL REACTORS – BIOVATORS

Biovator composters are specially designed enclosed cistern-type systems equipped with automatic devices for monitoring and regulating diverse parameters such as optimum humidity, temperature, content movement and animal component/lignocellulosic material ratio throughout the microbiological composting process. The capacity of such devices ranges around 500 kg/day and production of high-quality compost without applying commercially available microorganisms is possible within 14 days. Comprehensive research demonstrated that biovator composters meet all requirements of both users and institutions responsible for public health protection [10].

Figure 2. Biovatorcomposter on the farm

Figure 3. Compost ready for use

The installation of biovator composters on farms or specified local areas does not require any substantial investment. The disposal of animal waste is carried out at the site of its production using existing equipment (machinery) and lignocellulosic material and is possible through 365 days a year.

These systems are developed on demand of farmers, as a solution for safe disposal of dead animals at the farms. Previous disposal systems that included transportation to rendering plants were extremely expensive and inadequate in terms of environment protection.

Biovator composters are suitable for installation atdiverse locations such as the city dumps, local governments and plants for production of food of animal origin. However, ensuring a safe transportation is essential in this case.

COMPOSTING PROCESS IN BIOVATOR COMPOSTERS

Composting is a microbiological bio oxidation process, which takes place in heterogeneous organic materials where carbon dioxide, water, salts and stable organic material – compost are produced during the thermophilic stage. Decomposing of biomaterials during composting is determined by the following physicochemical factors: heat, humidity, particle size and the volume of the material being composted. The aforementioned factors are particularly important as they represent the critical points to the speed of the process, the safety of the compost as a finished product, its quality and its application in agriculture. Compost is produced in 14 days, provided thatall required conditions are met. Control of these parameters is possible in the enclosed systems such as biovator composters, which are equipped with automated instruments. Monitoring of critical points resulted in defining the optimal valuesfor the composting parameters, being: temperature in the range 45-59^{0}C; humidity 40-60%; particle size 12mm. Thetemperature is determined by microorganism activity and conditions of their replication and growth. Humidity affects the thickness of a thin liquid layer on the surface of organic particle, where the most intense microbial activity takes place. Keeping the optimum moisture humidity between min 30% and max 60% is important, as microbial activity ceases beyond these levels. Increased compost mass humidity beyond the maximum levelinducestransformation from aerobicto anaerobic composting conditions. Material rich in nitrogen are more humid than those containing carbon. Therefore, animal /lignocellulosic material ratio is of great importance [6,11].

CONCLUSION

Implementation of microbiological composting of the Category 2 and 3 animal waste materials and incineration of biohazardous material (Category 1) in special incinerators enables full management of by-products of animal origin. The advantages of this integrated process, which is carried out at the site of production of animal waste, are multifold: environment protection, economical feasibility, recycling possibilities and obtaining of useful final product.

Composting in a closed reactor is beneficial in terms of short composting period, being 10 to 14 days. The parameters such as temperature, automated mixing of composting mass, ventilation, aeration, humidity and access of diverse vectors of transmissible diseases are under control. This process enables composting proportional to the mixture ingredients, optimal composting process in regard to working temperature, humidity level, optimal rate and rotation speed of the biovator. The procedure is applicable throughout the year, i.e. in summer and winter periods. Moreover, the levels of specific bacterial and pathogenic organism are controlled at the end of composting cycle.

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SINTERED GLASS-CERAMICS PREPARED FROM WASTE GLASS AND WASTE FOUNDRY SAND

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ABSTRACT

In this study the glass-ceramics was prepared using waste glass and waste foundry sand as raw materials. The powder technology route was employed and the mixtures containing 10-50 wt% of sand were sintered at T = 750^{0}C for t =1h. The chemical durability of the resulting glass-ceramics was determined by leaching test in HCl, H_2SO_4, NaOH and distilled water at T = 95^{0}C for t =1h. It was shown that the sintering process without crystallization of glass matrix carried out. A lowest chemical durability in alkali solution of waste glass-ceramics was determined.

Key words: sintering, glass-ceramics, waste glass, waste foundry sand.

INTRODUCTION

As reported in numerous studies, the waste from different industrial processes can be utilized successfully in fabrication of new valuable materials. The recycling technologies of waste glasses provided the opportunity to prepare a new glass and glass-ceramics materials with great technological advantages. Good mechanical, chemical and thermal properties enable a wide application of these waste materials, especially in building industry [1-3]. One of most frequently employed technology for fabrication of waste glass-ceramics is the sintering of glass powder. The waste glass can be combined with other waste material to improve some of the properties of sintered material [4-7]. In typical foundry processes, sand from collapsed molds or cores can be reclaimed and reused. Spent foundry sand consists primarily of silica sand, coated with a thin film of burnt carbon, residual binder (bentonite clay, sea coal, resins) and dust and has been used as a fine aggregate substitute in construction applications and as kiln feed in the manufacture of Portland cement. Landfilling as the most common waste disposal method is not appropriate solution for this material because of negative impact on environment.

In this work, the possibility to obtain sintered glass-matrix composite using waste glass and waste foundry sand from collapsed molds for ferrous metal casting was investigated. The powder sintering route was employed for fabrication of this material. The chemical durability of as-prepared glass-matrix samples containing 10-50 wt % of waste foundry sand was determined.

EXPERIMENTAL PROCEDURE

Waste bottle glass and waste green foundry send were used as starting materials for preparation of glass-ceramics body. The waste glass was washed, dried, crushed in a jaw crusher Retsch 300 and then milled to grain size <100μm by using a laboratory vibrating mill with rings - Humbolt Wedag KHD 953/3. The waste send collected in a form of lumps was previously disintegrated and then used for preparation of the mixtures. The grain size of sand is determined by sieve analysis. The chemical compositions of starting raw materials were determined using gravimetric and spectroscopic methods (AAS Analyst 300). To prepare the pellets for sintering experiments (Ø 35 mm, h=10mm), the glass/sand mixtures containing 0, 10, 20, 30, 40 and 50 wt % of sand was homogenized and than cold pressed at 20 MPa in a laboratory hydraulic press Manfredini C95. These samples were labeled as WGS. The sintering of pellets was performed at T = 750^{0}C for t =1h in an electric furnace - Carbolite CWF1300. The phase composition of sintered samples was determined by X-ray diffractometry (XRD) and the XRD patterns were collected on a Philips PW-1710 automated diffractometer using a Cu tube operated at 40 kV and 30 mA. The instrument was equipped with a diffracted beam curved graphite monochromator and a Xe-filled proportional counter. The diffraction data were collected in the 2θ Bragg angle range from 5 to 70°, counting for 0.50. The surface textures of the resulting glass-ceramics were examined using an optical microscope EU Instruments.

To determine the chemical durability, the sintered samples were crushed and then sieved to grain size of 0,5-1mm. The leaching procedure was performed in a distilled water (pH = 6.93, conductivity (χ) = 4.91 μS/cm at T=25 °C), HCl, H_2SO_4 and NaOH solutions (20%) at T = 95^{0}C for t =1h using 2g of samples. The mass loss of samples (Δm) and ions concentration released were determined.

RESULTS AND DISCUSSION

In Table 1, the chemical compositions of waste glass and waste foundry sand is shown. The results of grain size analysis of waste foundry sand are presented in Table 2.

Table 1. Chemical compositions of waste glass and waste foundry sand

Sample	Oxide [wt %]								
	SiO_2	Al_2O_3	CaO	MgO	K_2O	Na_2O	Fe_2O_3	TiO_2	L.o.i
Waste sand	92.84	2.55	0.56	0.30	0.17	0.45	0.74	0.20	2.08
Waste glass	70.02	4.28	8.15	2.09	0.81	10.92	3.85	0.17	0.27

Table 2. Grain size analysis of waste foundry sand

(mm)	1+ 0.5	0.5+0.4	0.4+0.3	0.3+0.2	0.2+0.1	0.1+0.075	0.075+0.063	0.063
wt%	7.86	11.38	60.94	12.52	5.87	0.38	0.70	0.35

In Fig.1, the images of the grains of waste foundry sand obtained by optical microscope is shown. As seen in Fig.1, the grain size of sand is very uniform, with contribution > 90 % of the grains dimension between 0.5 and 0.1 mm (Table II). The quartz grains shape is subangular to rounded and are partly coated with burnt carbon and residual bentonite clay binder.

It was noted that during sintering the shrinkage of pellets decreases with quantity of the sand added. This indicates an influence of the rigid sand particles on the viscous behavior of glass matrix composite. The presence of quartz grains covered with bentonite clay hinders the viscous flow of the glassy phase that cause a poor densification of the samples. As shown in Fig.2, the glass matrix does not crystallize during sintering. The shape of XRD pattern revealed an amorphous structure of WGS sample.

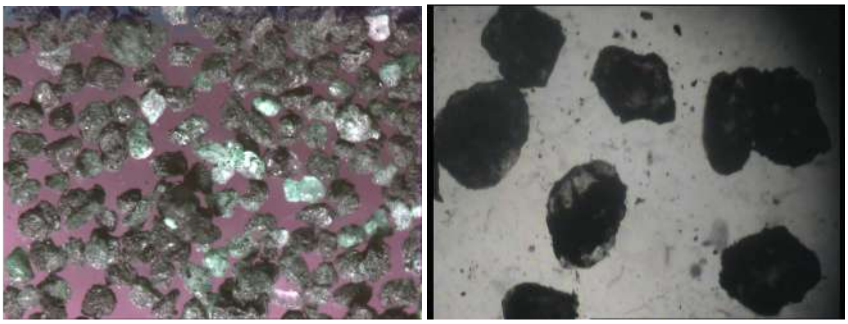


Figure 1. Waste foundry sand sample

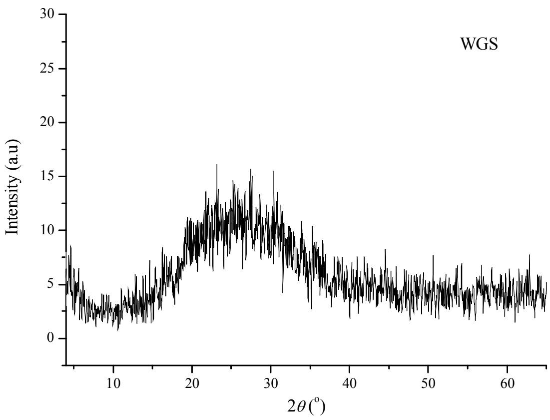
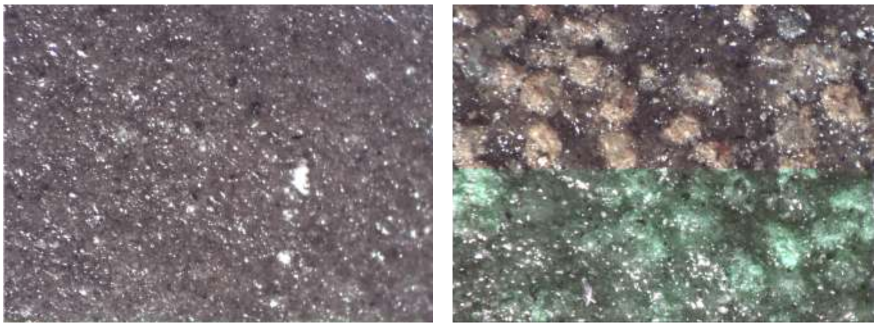


Figure 2. XRD pattern of WGS sample sintered at $T = 750^0C$ for t =1h

In Figure 3, the surface textures of sintered samples WGS and WGS 5 are shown. The sample WGS (without sand addition) revealed a numerous cavities on surface (black spots, Fig.3a), that indicates the separation of gasses during sintering. Such cavities are also visible on the samples containing 10-50 wt% of waste foundry send in glass matrix composite. In Fig. 3b, the quartz sand particles are seen to be well-distributed in glass matrix of WGS 5(50wt % of sand) sample.



a) b)

Figure 3. Surface textures of samples sintered at T = 750^{0}C for t =1h: a) WGS ; b) WGS 5

The leaching test in different media revealed a high durability in distilled water of the sintered composite, Table 3. Mass loss of samples increased during leaching in acid solutions and as may be seen in Table 3, there is not significant difference between durability in HCl and H_2SO_4. A lowest chemical durability was determined in 20 % NaOH. In all leaching media a mass loss increased with increase of the content of waste foundry send in samples.

Table 3. Mass loss of the sintered samples grain size of 0,5-1 mm leached in different media at T = 95^{0}C for t =1h

SAMPLE	Distilled H_2O		20 % HCl		20 % NaOH		20 % H_2SO_4	
	Δ m (gr)	%	Δ m (gr)	%	Δ m (gr)	%	Δ m (gr)	%
WGS	0,0012	0,060	0,0124	0,620	0,0349	1,75	0,0118	0,59
WGS 10	0,0014	0,070	0,0172	0,860	0,0568	2,84	0,0170	0,85
WGS 20	0,0014	0,070	0,0265	1,325	0,1428	7,14	0,0264	1,32
WGS 30	0,0022	0,110	0,0308	1,540	0,1460	7,30	0,0280	1,40
WGS 40	0,0024	0,120	0,0392	1,960	0,1608	8,04	0,0312	1,56
WGS 50	0,0026	0,130	0,0533	2,665	0,1622	8,11	0,0388	1,94

The dissolution of glass matrix is a complex process with several characteristic steps. In neutral and acid media the initial dissolution is characterized by ion exchange processes between protons in solution and glass network modifier cations, resulting in the formation of a hydrated layer, through which the aqueous species diffuse. At the same time, the glass network composed of network forming tetrahedral hydrolyzes, causing the release of cations into solution. As a consequence a complete destruction of polyanionic glass network occurs. In alkaline media the dissolution of the Si-glass network by which the glass dissolves directly into the solution take place. This type of chemical reaction leads to a higher weight loss as a function of time as determined for the sample leached in NaOH solution.

In Fig.4, the concentration of ions released during leaching in different media as a function of waste foundry sand in the samples is shown.

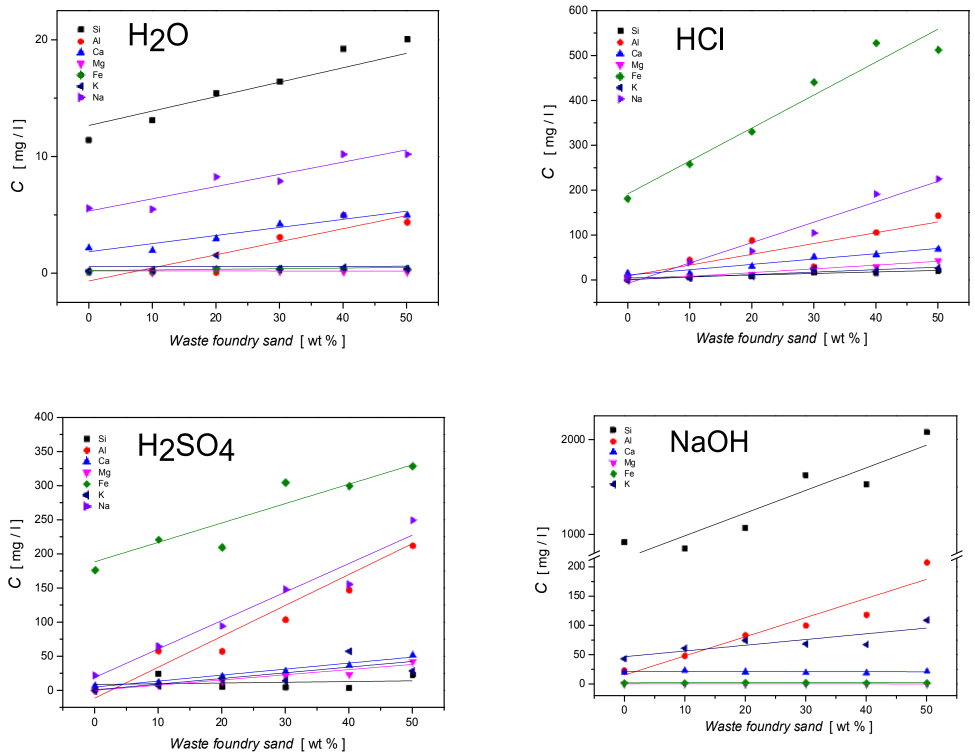


Figure 4. Concentration of ions released during leaching in different media as a function of waste foundry sand in the samples sintered at T = 750^{0}C for t =1h.

As seen in Fig 4, a high concentration of Si-ions in NaOH solution was determined that indicated an intensive destruction of Si-glass network. Otherwise, in the case of distilled water, HCl and H_2SO_4, the diffusion of alkali ions through the glass network into the solution took place as a first step of dissolution. The concentration of all ions released during leaching in different media increased by increasing the quantity of waste foundry sand in the samples.

CONCLUSIONS

The glass-matrix composites were prepared using the powdered waste glass and waste foundry sand as raw materials. It was determined that the increase of sand quantity in the composites causes a poor densification of sintered samples. As confirmed by XRD analysis the sintering process at T = 95^0C for t =1h carried out without crystallization. The results of leaching test revealed a high durability in distilled water of the sintered samples. Acid durability is lower and no significant difference of leaching in HCl and H_2SO_4 was noted. Weigh loss determined after leaching in NaOH solution confirmed a poor alkali durability of the samples. For all leaching media the durability decreased with increase of the quantity of waste sand in the glass matrix composite.

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POSSIBILITY OF REMOVAL OF IBUPROFEN FROM AQUEOUS SYSTEMS BY FERRATE(VI)

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ABSTRACT

Examined was the possibility of removing pharmaceuticals from aqueous solutions, on the example of ibuprofen oxidation, using *in situ* electrochemically synthesized ferrate(VI), a strong oxidant and coagulant, with forming of non-harmful byproducts. The solution of ibuprofen of 0.375 mg/l in 0.05 M Na_2SO_4 was treated by different amounts of ferrate(VI), whereby changes in the concentration of ibuprofen using of the UV absorbance spectrophotometer, the change of the total chemical oxygen demand (COD) and the change of total organic carbon (TOC) of test samples were monitored. Shown was that effective removal of ibuprofen from aqueous solutions can be done up to 26% by using ferrate(VI) in ratio 1:1.5 (2.2:1 as Fe). The possibility of removing ibuprofen by ferrate(VI) was confirmed by the results of the COD and TOC, which demonstrated reduction up to 50% and 38% respectively.

Key words: oxidation, ibuprofen, ferrate(VI).

INTRODUCTION

Recurrences of pharmaceuticals are present in the environment, in drinking water and wastewater in significant concentrations due to use of human and veterinary medicinal products all over the world. These compounds show the highest persistence in the environment. Many studies [1] indicate that the existing facilities for wastewater treatment are not effective enough to remove these micropollutants from wastewater and sludge. As a result of this, pharmaceuticals have found their way into the environment. When they enter the environment, the pharmaceutically active compounds can cause undesired effects on aquatic and terrestrial organisms. Although the concentration of the pharmaceuticals in an aqueous environment is low, a continuous and long-term intake of these pollutants may pose a potential risk for the terrestrial and aquatic organisms. For many compounds their potential effects on humans and aquatic ecosystems are not completely understood, especially if it is considered that they co-exist in mixtures with other chemicals forming so-called chemical "cocktails". Therefore, in recent years, they are considered as an emerging environmental problem.

Continual improvements in analytical equipment and methodologies enable the determination of pharmaceuticals at lower concentration levels in different environmental matrices. In a toxicity study, Cleuvers also found that the mixture of a few drugs could even augment the toxicity of each drug separately [2].

There are mainly three possible fates of the drugs and other xenobiotics after they enter into the aquatic environment: (a) the compound finally mineralizes into carbon dioxide and water, (b) the compound is hard to degrade because it is lipophilic and is partially retained in the sediments of the sludge, (c) the compound metabolizes into higher hydrophilic molecules, passes through the water treatment plant and ends up in the wastewater recipients (mainly rivers).

Ibuprofen (Ibu) or 2-(4-isobutyl phenyl) propionic acid, is the first of the non-steroidal anti-inflammatory drugs (NSAID) derived from propionic acid which is sold in many countries. It is important to emphasize that in 2005 this drug took 17th place on the list of the most commonly prescribed medications in the United States [3] or 2300 t/year. Studies were also performed in countries such as Germany, Spain, Switzerland, France, Italy, Sweden, Canada and Denmark, where the quantifications for Ibu in wastewater effluents varied from 60 to 3400 ng/l [4]. In numerous studies, the analysis of concentrations of pharmaceuticals found in surface waters, detected were concentrations of ibuprofen from 0.05 to 0.28 mg/l [5]. Considering all these facts, it is vital to develop a process with significant potential to remove pharmaceuticals residue.

In order to remove residues of pharmaceuticals, different methods are applied: advanced oxidation methods [6], ozone [7], activated carbon filtration [8] as well as a combination of ozone and hydrogen peroxide [9]. Despite the high efficiency of residue removal using these methods, up to 90%, detected were intermediate compounds, formed by the oxidation of the pharmaceutical products, which are more toxic than the pharmaceutical pollutants themselves [3]. Richards and Cole (2006) studied the toxic response of frog embryos to different concentrations of ibuprofen via the *Frog Embryo Teratogenesis Assay – Xenopus (FETAX)*. The results showed inhibition in embryo growth at concentrations of 30 mg/l after 96 h of exposure. Based on the results of toxicity tests [10] with *S. capricornium*, the compound released during ozonation is more toxic than the parent compound.

One of the possible methods of removal of pharmaceuticals as well as Ibu from the aqueous environment is the application of ferrate(VI), an environmentally friendly oxidant, coagulant and disinfectant. Because of the suitable physical and chemical properties of ferrate(VI), such as high oxidation potential which is 2.2 V in acidic conditions and 0.7 V in alkaline conditions, forming of the oxygen by oxidation of water, and the high capacity of coagulation of iron (III) hydroxide, a product of ferrate(VI) reduction, ferrate(VI) is proved to be a very efficient and environmentally friendly oxidant, disinfectant and coagulation agent in a variety of application areas. Current research indicates [11], based on the kinetic results of ferrate(VI) reactions with Ibu, that a high percentage of Ibu could be removed from an aqueous solution depending on the treatment conditions (pH, concentration of ferrate(VI)) by oxidation of Ibu with ferrate(VI) in a reaction of the first order or by the coagulation effect of formed Fe(III) as a product of ferrate(VI) reduction. Recent research of application of ferrate(VI), in the process of removal of micropollutants from an aqueous medium, showed efficiency of removal of more than 85%, whereas for ibuprofen the efficiency showed was 40% of removed drug[12]. Also, a non-toxicity of the intermediate, formed during the process of ibuprofen removal, to the development of living organisms in water was shown.

The purpose of this paper is to contribute to the research of possibilities of ferrate(VI) application in the process of removing the remainder of pharmaceuticals, for example ibuprofen, as a secondary or primary processes in conventional water treatment methods. The application of ferrate(VI), obtained using a useful and environmentally friendly electrochemical process of synthesis, allows *in situ* application. This paper shows information which may be useful in defining the optimum conditions of Ibu treatment by ferrate(VI) with the aim of minimizing the concentration of Ibu by monitoring changes in concentration of Ibu, total oxygen demand (COD), total organic carbon (TOC) and forming of intermediates in the process of oxidation of ibuprofen by ferrate(VI).

MATERIALS AND METHODS

Materials

The pharmaceutical certified product Ibu was of analytical grade (99.6 %) and provided by the Pharmaceutical Laboratory Galenika a.d., Beograd, Serbia. Stock solution of ibuprofen, concentration of 0.375 g/l was prepared in 0.05 M Na_2SO_4. The solution Na_2SO_4 was made by using Na_2SO_4 salt *p.a.* quality, provided by Centrohem, Stara Pazova, and demineralized water.

The Na_2FeO_4 solution, concentration of 8 g/l used for the treatment Ibu 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]. The anode is made of an iron alloy with a content of: silica of between 1.6% and 6%, carbon up to 0.1%, manganese up to 0.1%, and copper, sulfur and aluminum at the level of impurities. The cathode is made of stainless steel in the form of a sheet. The process of anodic dissolution was carried out for a period of 3 hours using an electric current of 2.5 A ($j = 85$ mA cm^{-2}) and at a temperature of 25 °C, whereby a solution of Na_2FeO_4 concentration of 8 g/l was obtained. The concentration of synthesized ferrate(VI) is controlled by the titrimetric chromite method at a temperature of 25 °C. Freshly synthesized ferrate(VI) was used for the treatment of the solution of ibuprofen.

Methods

The change in the concentration of Ibu was monitored by UV-Vis spectrophotometer (Shimadzu UV 1800) at a wavelength of 264 nm and the extension coefficient of $\varepsilon = 437 M^{-1}cm^{-1}$. Chemical Oxygen Demand (COD) determinations were made following the titrimetric method, according to standard methods [14], and measurement the Total Organic Carbon (TOC) was measured on a Shimadzu TOC-VCPH/CPN apparatus.

Procedure

The basic solution of Ibu in 0.05 M Na_2SO_4 had characteristics according to Table 1. After determination of physical and chemical characteristics of the solution, 100 ml samples of the Ibu solution were treated with freshly synthesized Na_2FeO_4 in amounts of 41.6 mg/l, 84 mg/l, 126 mg/l and 168 mg/l as Fe. The samples were treated at room temperature of 25 °C, stirred for 5 min at a speed of 400 rpm and 20 minutes at a speed of 40 rpm, and then precipitated for 60 min. The treated samples were then filtered through a ceramic vacuum filter. The pH value of the treated samples after filtration was 13 and it was adjusted to pH = 6-7 by adding 1 M H_2SO_4.

Table 1. Characteristics of Ibu initial solution

c, mg/l	pH	COD, mg O_2/l	TOC, mg C/l
375	6	930 ± 35	280

The change in concentration of Ibu treated by ferrate(VI) was determined by the analysis of treated samples using a UV/VIS spectrophotometer. For each treated sample values of COD and TOC were also determined.

RESULTS AND DISCUSSION

The solution of Ibu concentration of 375 mg/l treated by electrochemically synthesized fresh solution of Na_2FeO_4 at various concentrations Ibu : Fe (9:1, 4.5:1, 3:1, 2.2:1) showed a tendency of decreasing of Ibu concentration with an increase in the concentration of ferrate(VI).

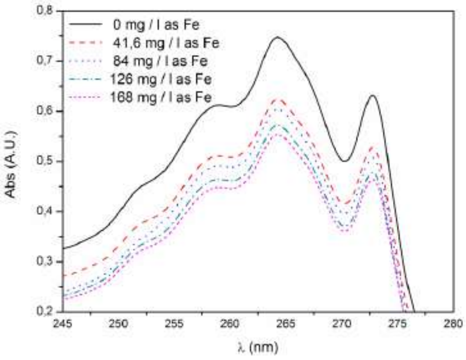

Figure 1. Change of Abs UV specter of Ibu with different doses of ferrate (VI)

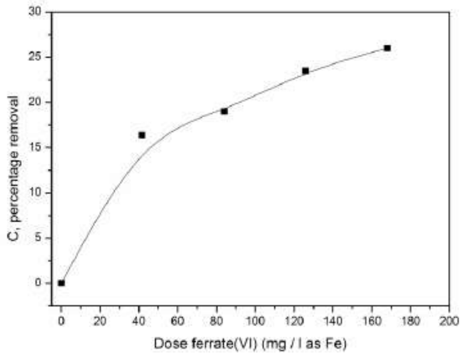

Figure 2. Correlation of reduction of Ibu concentration to the added dose of ferrate(VI)

According to the spectrophotometric results, Figure 1, Ibu solution has two peaks (264 and 272 nm). Based on literature data [20] for the determination of Ibu peak at 264 nm was selected. The concentration of Ibu present in each sample was calculated by determining the value of absorbance for each sample at peak 264 nm and by using the coefficient of extension and the calibration curve. The results of reduction of Ibu concentration in proportion to the added dose of ferrate(VI) as Fe, are shown in Figure 2. The largest reduction of the concentration of Ibu, 16.4%, is shown when adding 41.6 mg/L ferrate(VI) as Fe. Further increase of the ferrate(VI) dose shows a smaller percentage of reduction with the tendency of stagnation. The maximum achieved reduction of concentration of Ibu, compared to the initial concentration, was 26% obtained by adding 168 mg/L of ferrate(VI) as Fe.

The possibility of Ibu removal by ferrate(VI) was additionally confirmed by determining the value of COD and TOC in the Ibu solution treated by ferrate(VI), Figures 3 and 4. The obtained results showed a 50% reduction of COD and 38% of TOC compared to the solution with the initial concentration of Ibu with the addition of 168 mg/l of ferrate(VI) as Fe.

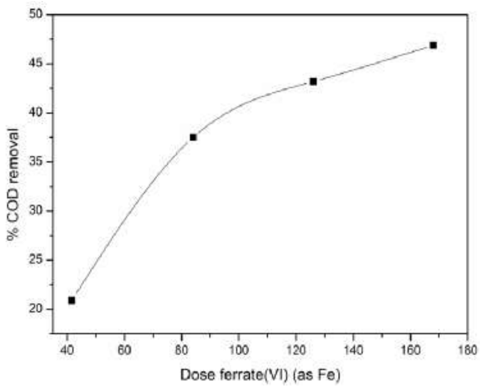

Figure 3. Percentage of COD removal during oxidation reaction of Ibu with different doses of ferrate(VI)

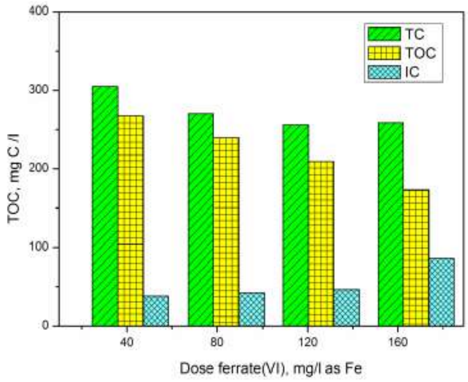

Figure 4. Change of total organic (TOC), inorganic (IC) and total carbon (TC) in the Ibu solution treated by ferrate(VI)

According to the obtained results of Ibu oxidation by ferrate(VI) observed is that ferrate(VI), as a strong oxidant, can oxidize Ibu to 26% of removal, and that the reactivity of ferrate(VI) with Ibu is low. Changes in the concentration of Ibu in the treated solution are decreasing by increasing the amount of added ferrate(VI), Figure 1.

The explanation of weak reactivity of Ibu with ferrate(VI) lies in the fact that the carboxyl group of Ibu is an electron - withdrawing functional group, which can depress the reaction of the aromatic ring with ferrate(VI) [15]. Therefore, the reactivity of ferrate(VI) with carboxylic acids is usually low, the rate constant for Ibu is only 0,09 M^{-1} s^{-1} at pH 8,0 [11]. However, the treatment of Ibu by ferrate(VI) deserves attention and further optimization due to demonstrated non-toxicity of waste intermediates and byproducts formed in the reaction of oxidation of Ibu by ferrate(VI) in contrast to the other oxidizing agents [12].

CONCLUSION

The aim of this study was to examine the possibilities of Ibu removal from aqueous solution in the reaction of oxidation by freshly synthesized ferrate(VI) due to environmentally friendly non-toxic intermediates as the final products of oxidation. It has been shown that the effective removal of Ibu by ferrate(VI) in the aqueous solutions can be possible up to 26%, in the ratio of Ibu to ferrate(VI) 1:1.5 (2.2:1 as Fe). The possibility of Ibu removal by ferrate(VI) was also confirmed by the results of COD and TOC, which have demonstrated the removal of 50% and 38% respectively. Low reactivity of Ibu with ferrate(VI) can be explained by low reactivity of ferrate(VI) with a carboxylic group, an electron-withdrawing functional group which hinders the reaction of ferrate(VI) with the aromatic ring of Ibu.

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ELECTROCHEMICAL GENERATION OF FERRATE(VI) ON DIAMOND ELECTRODE IN PERCHLORIC ACID SOLUTIONS

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ABSTRACT

Generation of ferrate(VI) by anodic oxidation of ferric salts solutions in 0.1 M $HClO_4$at a diamond electrode is explored with the aid of cyclic voltammetry. The anodic wave of ferrate(VI) generation was observed at electrode potentials >2.2 V *vs*. NHE, but not the corresponding wave of its cathodic reduction because of its instability. The conditioning of adiamond surface and atype of iron salt used in electrolysis notably influencetheferrate(VI) generation.Adsorption of iron(III) on adiamondprecedes oxidation to ferrate(VI) and would be a kind of chemisorption by chemical linking with C=O groups on oxidized diamond.

Key words: ferrate(VI), perchloric acid, diamond electrode, cyclic voltammetry.

INTRODUCTION

Ferrate(VI) ion is a strong environmentally friendly oxidizer and has already found practical applications in processes of contaminated waters reclamation [1, 2]. The red–ox potential of $FeO_4^{2-}|Fe^{3+}$ couple at higher pH values(9–10)is moderate (0.7 V*vs.*NHE) but very high(2.2 V*vs*. NHE)at lower pH values (2–5)[3, 4, 5].In acid solutions half–life of ferrate(VI) ion is very short becauseof the fastoxidation ofwater or other oxidizable species.Accordingly, direct synthesis of ferrate(VI) in acid water solutions would be a viable and effective technique for decomposition of resilient water contaminants because of very high ferrate(VI) reduction potential in such environment. Until recently the process of direct electrochemical synthesis of ferrate(VI) by oxidation of iron(II) or iron(III) ions on the conventional virtually inert anode materialsin acidic media has been considered unlikely, because of its high red–ox potential, much higher in respect of water molecule oxidation. This situation has beenfundamentally changedin the last decade with appearance of commercially available industrial boron doped diamond electrodes (BDDE)characterized by high oxygen evolution reaction (OER) potential, low electrical resistanceand acceptableprice for practical solutions.Direct electrochemical synthesis of ferrate(VI) in acid solutions by oxidation of Fe^{3+} ions on BDDE is effective because of high potential of water molecule oxidation. Electrochemical generation of ferrate(VI) in acid solutions is discussed in a few articles [4, 5]. In this paper electrochemical generation of ferrate(VI) in perchloric acidic solution is analyzed with respect tothe type of salt used as a source of iron and electrochemical parameters of iron ionanodic oxidation.

EXPERIMENTAL

Cyclic voltammetry experiments were carried out in the custom designed three–electrode system which consisted of a standard calomel reference electrode (SCE) ($Hg|Hg_2Cl_2$ in 3.5 M KCl, E = + 0.250 V *vs*. NHE at 25 °C), coiled platinum wire as a counter electrode and a highly boron-doped synthetic diamond working electrode at the cell bottom with a surface of 0.785 cm^2bounded by a chemically resistant rubber o–ring. Cyclic voltammetry (CV) experiments were performed by potentiostat – galvanostat Gamry G300 control.

The low specific resistivity (0.02 – 0.18 ohm cm)working electrode,0.6 mm thick diamondlayer,boron-dopedwith [B] > 10^{20} atoms cm^{-3},deposited by chemical vapor deposition (CVD)on a p-silicon wafer plate of 1 cm^2 area, was purchased from Element Six Ltd. UK (www.e6.com/sensors).The silicon plate was electrically connected to the copper rod current collector with conductive silver glue.

Before each CV experiment BDDE wasconditionedat potential of + 3 V*vs*. SCE in 0.1 M $HClO_4$for 5 minutes.

All solutions in experiments were prepared from bi–distilled water and chemicals of pro analysis quality.

RESULTS AND DISCUSSION

Perchloric acid,chemically stable with respect to oxidation at high anodic potential,was selected as a supporting electrolyteto eliminateinfluence of electrolyte components on generation of ferrate(VI)and because of high solubility of iron(III)perchlorate, formed in a reaction of used iron salts with it.Oxidation of sulphate or chlorideionson BDDE is possible at high anodic potentialswhich can affect ferric ion oxidation, see Table 1, while nitrate oxidation is unlikely.

Table 1. Possible electrode reactions at high anodic potentials[3]

Reaction	*E vs.* NHE /V
$OH^{\bullet} + H^+ + e^- \rightarrow H_2O$	2.80
$SO_4^{-\bullet} + e^- \rightarrow SO_4^{2-}$	2.60
$FeO_4^{2-} + 8H^+ + 3e^- \rightarrow Fe^{3+} + 4H_2O$	2.20
$O_3(g)+2H^++2e^- \rightarrow O_2(g)+H_2O$	2.075
$S_2O_8^{2-}+2e^- \rightarrow 2SO_4^{2-}$	2.01
$H_2O_2+2H^++2e^- \rightarrow 2H_2O$	1.763
$HO_2^{\bullet} +3H^++3e^- \rightarrow 2H_2O$	1.65
$Cl_2(g)+2e^- \rightarrow 2Cl^-$	1.358
$Fe^{3+} + e^- \rightarrow Fe^{2+}$	0.77

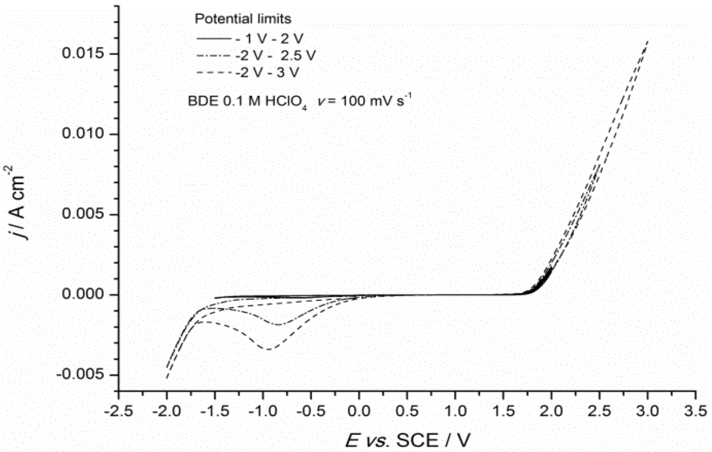

Figure 1. Behavior of BDDE in 0.1M $HClO_4$ at potential cycling with different scanning potential limits.

Fig. 1 illustrates behavior of BDDE in pure perchloric acid solution at potential cycling between various linear potential scan limits. It is obvious that the cathodic current waves are a result of reduction of species formed athigh anodic potential of the diamond electrode, because the peaks of cathodic current waves increase with changing of the anodic potential scan limit towards a more positive potential. Cathodic current waves would reflect reduction of oxygenated carbon formed on the diamond surface during anodic polarization of BDDE[2, 6, 7]. The results shown in Fig. 2 support sucha presumption, and show that addition of methanol in the solution of perchloric acid eliminates cathodic current waves on the CV. This effect would be explained by consumption of oxygen fromoxygenated carbon atomson the BDD surface in the process of methanol oxidation.

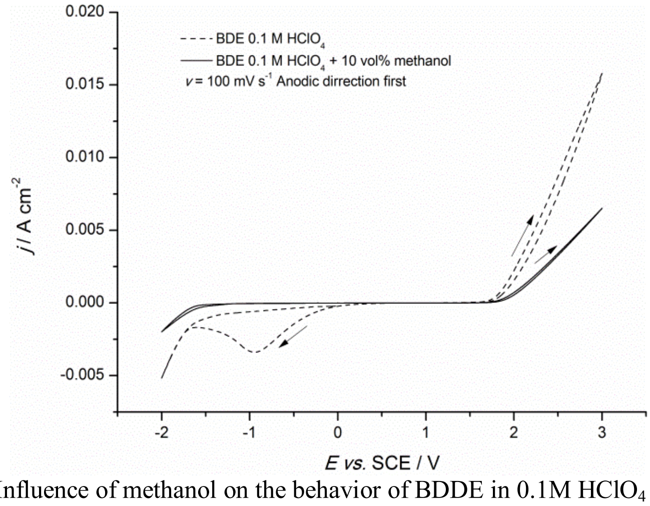

Figure 2. Influence of methanol on the behavior of BDDE in 0.1M $HClO_4$ at potential cycling between potentials of oxygen and hydrogen evolution

The behavior of BDDE in course of potential cycling in perchloric acid solutions ofselected iron salts is presented in Fig. 3. The two anodic current waves A_1 and A_2 appeared on CVs when iron saltsweredissolved in perchloric acid solution. Wave A_1 has been explained [4, 5] as a result of iron(II) to iron(III) oxidation, but it is evident that it appears in the solutions which contain iron(III) ions only.Also, wave A_1appears at the more positive potential with respect to $Fe^{3+}|Fe^{2+}$ red–ox potential. Therefore, it seems that A_1 would be the effect of Fe^{3+} ion reaction with oxygen on the surface of BDDE, formed by carbon oxygenation [2, 6, 7] in the conditioning process,and subsequently formation of a higher valence state of iron as a precursor of ferrate(VI) formation.Potential of the current wave A_2 of ferrate(VI) formation, as shown in Table 1, is the most pronounced on the voltammogram obtained in ferric nitrate solution, possibly because of the concurrent reactions of chloride and sulphate anodic oxidation in solutions containing chloride and sulphate respectively.

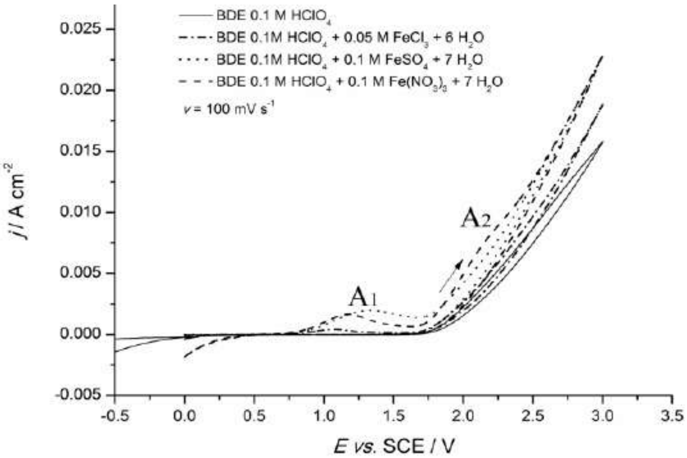

Figure 3. Influence of the iron(III) salt composition on BDDE behavior at cycling in the region of anodic polarization and appearance of a ferrate(VI) current wave.

Fig. 4 displays CVs obtained in solutions containing various concentrations of ferric nitrate, which show obvious increase of relevant anodic current wave peaks A_1 and A_2 with the increase of iron(III) concentration, which confirms ferrate(VI) generation.Before oxidation iron(III) ions should be previously adsorbed on the inert diamond surface. Therefore, it is very interestingto note on aCV in Fig. 4which electrode potential has been scanned first in the cathodic direction after conditioning, to ensure reduction of oxidized BDD surface [2, 6, 7],the absence of current waves of iron(III) oxidation (A_1) and ferrate(VI) formation (A_2). Such behavior would be the result of absence of ferric ions adsorption at non–oxidized BDD.Adsorption of iron(III) on the BDDE may be considered as a kind of its chemisorption by chemical linking between Fe^{3+} ions and C=O groups, which have been formed at the diamond surface throughout anodic conditioning [6, 7].One can conclude that conditioning of BDD electrodes by anodic polarization catalyzesthe diamond surface bycreation of C=O groups as active sites for iron(III) ion adsorption and further oxidation to ferrate(VI).

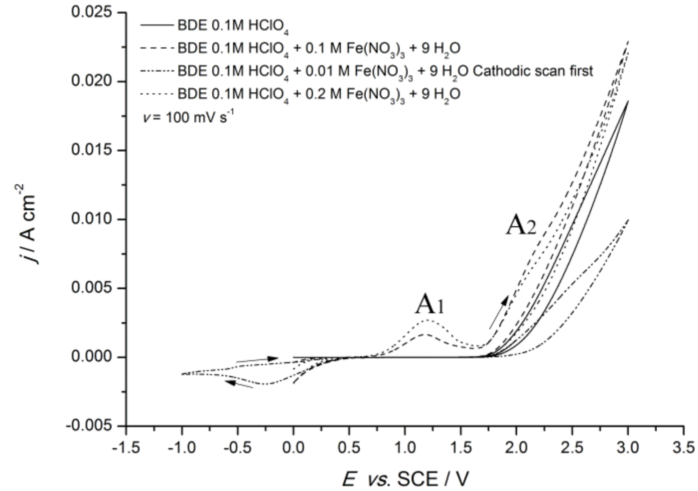

Figure 4. Influence of iron(III)nitrate concentration and direction of potential cycling of BDDE on the appearance of ferrate(VI) current wave.

Summary reaction of ferrate(VI) formation is given in eqn. (1).

$$Fe^{3+} + 4\ H_2O \rightarrow FeO_4^{2-} + 8\ H^+ + 3\ e^- \quad (1)$$

As the cathodic peak of ferrate(VI) reduction was not observed in Figs. 3 and 4 we concluded that theelectrochemically generated ferrate undergoes a rapid decompositionin reaction with water,eqn. (2),because of a great difference in reduction potential between ferrate(VI)(2.20 V *vs*. NHE) and water(1.23 V *vs*. NHE).

$$2\ FeO_4^{2-} + 5\ H_2O \rightarrow 2\ Fe^{3+} + 6½\ O_2 + 10\ H^+ \quad (2)$$

Finally, the authors expect that ferrate(VI)electrochemically formed directly in acid solutions, having one of the most positive reduction potentials according to Table 1, would successfully decompose very stable poisonous compounds present in wastewater or a raw potable water, which cannot be neutralized by conventional techniques.

CONCLUSION

Ferrate(VI) is generated in acidic media at high anodic potentials (> 2.2 V vs. NHE) on the BDD electrode by oxidation of iron salts.

Ferrate(VI), because of high reduction potential in perchloric acid solution,rapidly decomposesin the process of water oxidation, which would explain absence of the ferrate(VI) reduction peak on the cyclic voltammograms.

Surface oxidation of the diamond lattice in the pretreatment process notably influence the process of ferrate(VI) generation, which means that ferric ions interact with oxidized diamond surface before oxidation to ferrate(VI).

It is obvious from Table 1 that the high anodic potential electrolysis of acidic solutions of ferrous or ferric sulphate or chloride on BDDE produces, besides ferrate(VI) ion (FeO_4^{2-}),a lot of very strong oxidants such as hydroxyl radical ($OH^\bullet$), sulphate radical ion ($SO_4^{-\bullet}$),ozone, peroxodisulphate ($S_2O_8^{2-}$), hydrogen peroxide, hydroperoxyl radical ($HO_2^\bullet$) and chlorine. Such an oxidative ambient, obtained with technically simple procedure, should effectively decompose even very stable toxic chemical compounds in wastewaters and raw water intended for production of potable water.

Acknowledgment

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ELECTRO-COAGULATION AS ADVANCED TECHNOLOGY IN WASTEWATER TREATMENTS

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ABSTRACT

In this work are given some theoretical and practical knowledge of electro-coagulation as an advanced and alternative technology in wastewater treatment. The electrochemical reactions of Al and Fe anodes as generators of Al and Fe cations which break dawn the colloidal stability and initializes the process of coagulation, are presented. The reactor design and operations, depending of specific need, are also shortly explained.

Key words: electro-coagulation, wastewater treatment.

INTRODUCTION

Water is the source of all life in the world but it is very limited natural resource. With development of industry and human standard rapidly grows water pollution. Natural and wastewater very often contain dissolved and small solid particles. These particles can be dispersed upon several forms depending of their size: solution, colloids and suspensions. The colloidal pollutants in wastewater contain: organic materials, metal oxides, insoluble toxic compounds, stable emulsions, biotic material, including viruses, bacteria and algae. The colloids are the type of mixtures that appear to be a solution but it is actually a mechanical mixture. Each colloid system consists of two separate phases: a dispersed phase and a continuous phase. The dispersed phase is made of tiny particles or droplets that are distributed evenly throughout the continuous phase. The size of the dispersed-phase particles are between 1 nm and 100 nm in at least one dimension. The colloids particles consists atoms and molecules. They have the surface charges which can be positive or negative. Such a charge comes from: ionisable groups (amino or hydroxyl groups), lattice imperfections at the crystal due to the replacement of some atom by another ion that has a different amount of electrons This results in a charged surface and ionic species that can become adsorbed on the surface of the colloids. Examples of colloidal systems include: milk (liquid fat droplets emulsified in water), paints (small pigment particles dispersed in a carrier fluid), aerosols (liquid droplets dispersed in air), blood (the cells that flow through our veins are colloidal particles)

METHODS

Coagulation

In wastewater, the colloids generally have the negative charges and they are stable. The charged colloidal particles affects the ions in the surrounding media and the ions of opposite charge are attracted towards the surface, whereas the ions of the same charge are repelled from the surface. When the colloidal particles are surrounded with enough counter ions they become electrically neutral. This point is called izoelectric point and in izoelectric point zeta potential is zero. A classic example in colloid chemistry is to measure zeta potential vs. pH to determine the conditions where the zeta potential reaches zero. Stable colloids are those that remain fully dispersed over time, with no degradation or sedimentation. The stability of colloids become from electrostatic repulsion between the particles, prevents the aggregation between them as well as other particles, fig.1. The stability of colloids is due to the existing charge which attracts other ionic species present in water, resulting formation of an electrically charged layer around the colloidal particles. If these charge layers are removed, the particles become thermodynamically unstable and tend to agglomerate spontaneously. To remove the colloids from wastewater, repulsion must be broken down and they become unstable.

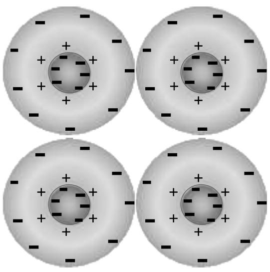


Figure 1. Stable colloid

Coagulation is destabilization of colloids by neutralizing the forces that keep them apart with introduction of an opposite charge. It is a phenomenon in which the existing charged particles in colloidal suspension are neutralized by mutual collision with counter ions added in the solution and promote contact between them. Once the charge is neutralized the colloidal particles are capable of sticking together. For achieving good coagulation, the rapid mix to properly disperse the coagulant and promote particle collisions is needed. There are three main types of coagulants that are used to neutralize the repulsive forces of particles and allow them to come closer together, i.e. to aggregate. These three main types are: inorganic electrolytes (alumina, lime, ferric chloride, ferric sulphate etc.), organic polymers and synthetic polyelectrolyte with cationic and anionic functional groups. Cationic coagulants provide positive electric charges to reduce the negative charge (zeta potential) of the colloids.

There are four main mechanisms for destabilization of colloids which provoked coagulation: compression of electrical double layer, adsorption, inter particle bridging an precipitation. Traditionally the most used counter ions in waste and drinking water treatment, which result from dissociation of added chemicals are: aluminium sulphate $Al_2(SO_4)_3 18H_2O$, ferric sulphate $Fe_2(SO_4)_3$, ferrous sulphate $FeSO_2 7H_2O$ and ferric chloride $FeCl_3$. These chemicals are called coagulants and produced the positive charges. The coagulation occurs when the net surface charge is reduced to some critical point where the colloidal particles previously stabilized by electrostatic repulsion can approach closely enough for Van der Waal's forces, to hold them together and allow aggregation.

Electro-coagulation

Electro-coagulation was originally developed and patented in 1906 from A.E. Dietrich to treat bilge water from ships [1]. But this process was never adopted at time due the lack of legislation. The treatment of wastewater by electro-coagulation has been increasingly practiced in 20th century, but with limited success and popularity. However, in the last decades, this technology has been optimized to minimize electrical power consumption and minimize effluent throughput rate [2-6], so that it is more and more used for treatment of different types of industrial wastewater containing; suspended particles chemical and mechanical polishing waste in wastewater [7], organic compounds [8], fats oil and grasses, heavy metals bacteria, algae and larvae [9]. The principle of electro-coagulation is the same as in chemical coagulation. The difference is only how the coagulant is added. In the electro-coagulation process the coagulant is generated in situ by electrolytic oxidation and reduction on appropriate choice of electrodes in electrochemical reactor. The system is connected to an external power source and as the process of oxidation occurs sacrificial anodes are corrodes and release coagulant cations in the reactor where wastewater is electrolyte. In reality electro-coagulation is the electrochemical production of destabilization agents such as Al and Fe ions that neutralize electric charge of the colloidal particles. At the same time the evolution of gases bubbles, i.e. oxygen at anode and hydrogen on cathode can produce, as a result of water decomposition. Aluminium cations dissolve from the anode according to the reaction

$$Al_{(s)} \rightarrow Al^{3+}_{aq} + 3e^-$$

In acidic electrolytes

$$Al^{3+}_{(aq)} + 3H_2O \rightarrow Al(OH)_{3(s)} + 3H^+_{(aq)}$$

In alkaline electrolytes

$$Al^{3+}_{(aq)} + 3(OH)^- \rightarrow Al(OH)_{3(s)}$$

For iron anode

$$Fe_{(s)} \rightarrow Fe^{2+}_{(aq)} + 2e^-$$

In acidic electrolytes

$$Fe^{2+}_{(aq)} + O_2 + 2H_2O \rightarrow 4Fe^{3+}_{(s)} + 4OH^-$$

In alkaline electrolytes

$$Fe^{2+}_{(aq)} + 3OH^{-} \rightarrow Fe(OH)_{2(s)}$$

In addition, the oxygen evolution reaction occurs which is more accentuated for Al than for Fe anode [10].

$$2H_2O \rightarrow O_2 + 4H^{+} + 4e^{-}$$

And the reaction of the cathode is

$$2H_2O \rightarrow H_2 + 2OH^{-} - 2e^{-}$$

The nascent ions of Al^{3+} and Fe^{2+} are very active coagulants for colloidal suspensions.

Electro-coagulation reactors design an operation

The operation system for electro-coagulation consists: electrochemical reactor, electrodes, a power supply, pipes and pumps. The key components in electro-coagulation reactors are: coagulants and contaminants. There is not any uniform instruction, empirical or systematic approach which will give more scientific recommendation for electro-coagulation reactor design and operation. Generally, so far the reactors are designed for a specific process, including the mode of operation (butch or continuous) [11, 12]. In the designed phase, as is proposed in ref. [13], always must consider the following physical and mechanic factors as: reactor geometry, scale-up issues and current density. The reactor scale-up define the relationship between laboratory and full scale equipment. For specific type of pollutants it is recommended firstly to perform investigation in laboratory scale for determining the operational parameters and then, start engineering phase of design.

During the electro-coagulation in the same time there are multiple electrochemical process occurring simultaneously at the anode and cathode, fig.2

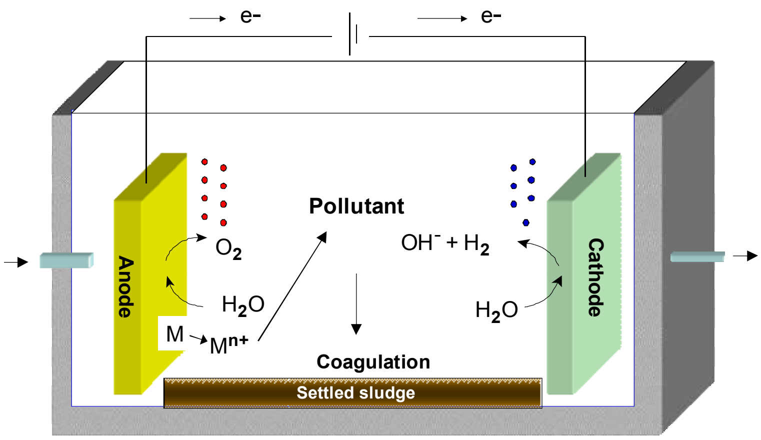
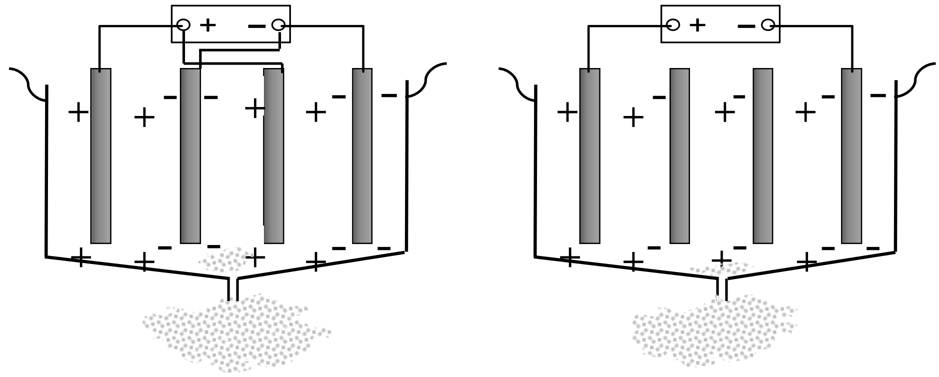


Figure 2. Schematic representation of electro-coagulation process

In electrochemical reactor there exist several methods how electrodes can be arranged. Water flow between the electrodes and can follows vertical or horizontal direction, so that in practice are used two types of reactor units for electro-coagulation: monopolar and bipolar connection of electrodes



(a) (b)

Figure 3. (a) Monopolar connection, (b) Bipolar connection

The question is; which kind of connection is better? The answer is; depends from specific pollutant contain in treated wastewater. Generally is accepted that monopolar arrangement has lower operating costs but bipolar arrangement has higher removal efficiency.

CONCLUSIONS

From the presented theoretical and practical knowledge of electro-coagulation in waste water treatment, the following conclusions can be drawn:

The application of advanced electro-coagulation technology of wastewater treatment in many countries is still in embryonic phases, but in the last 20 years the significant progress is evident. This technology in many cases become alternative, more efficacy, faster and chipper than classical ones. The advantages of electro-coagulation technologies are: simple equipment, smaller processing area, convenient operation and clean energy conversion and non-requirements of chemicals for the coagulation.

The main advantages are: Simple equipment, low initial investment, low operational costs and easy to operate. The main disadvantages are: Formation of anodic oxide film on the cathode, which diminishes the active electrode surface and conductivity reducing process efficiency, high conductivity of wastewater is required, to minimize the IR drop for enhancing current efficiency, maintenance and regularly replace of sacrificial anodes. Evolution of oxygen at the anodes sometimes represents unwonted leakage of current and in some countries the use of electricity may be expensive.

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AN "IN VITRO" INVESTIGATION OF THE GOLD COMPLEX BASED ON MERCAPTOTRIAZOLE TOXICITY

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ABSTRACT

The aim of this work was to investigate and compare toxicity of theelectrolyte based on the mercaptotriazole gold complex (pH=2, 4, 7, 9 and 12) and the classic alkaline cyanide electrolyte- AUROCIN DPB (pH=9) using *"in vitro"* method. For cytotoxicity testing, MTT assay on humaneritroleukemia,K562 cell line was used. Results showed that the toxicity of organic gold complex at pH=4, 7 and 12 was lower than the toxicity ofalkaline cyanide electrolyte, but higher at pH=2, while at pH=9 the relative cell viability was almost equal.

Key words: gold complex, mercaptotriazole, toxicity, *"in vitro"*,K562 cells.

INTRODUCTION

The electrodeposition of gold can be traced to the early work of Brugnatelli 1805 [1-2]. The first patent on the golddeposition wasrealized in 1840. [3]. Since then,the cyanide and ferrous cyanide solutions are used in practice for gold plating.

The electrodeposition of gold has been widely used in decorating, automotive and electronics industries, as well as inbiomedical processes, due to its excellent corrosion resistance, solderability, ductility, and high electricaland thermal conductivity [3-9].The traditional baths for soft and hard gold plating contain the cyanide complex, $[Au(CN)_2]^-$, as the source of gold.

The cyanide bath has a long and successful history of being highly stable and capable of yielding gold coatings with excellent physical properties. Cyanide baths also have a long life and due to the strength of the cyanide complex, $Au(CN)_2^-$ they are resistant to disproportionation, hydrolysis, oxidation and ligand substitution reactions that may cause instability or decomposition. Also, cyanide, and its gold salts can be easily manufactured [4].

The electrodeposition of gold is generally performed in a bath containing cyanide because it possesses a high current efficiency, good stability and good adhesion. However, the electrodeposition of gold from a cyanide bath has some disadvantages:

(1) the presence of cyanide, which is extremely toxic, in theelectroplating bath represents ahigh risk to human health and theenvironmentas a whole, especially when it is operated at high temperature(50–70℃);

(2) free cyanide ions are known to be incompatible with positive photoresists[10, 11].

The demands to meet standards of occupational safety and the protectionof the environment are usually very high,with the purpose to avoid accidents which mayendanger human life and ecosystems as well. A well known example is an ecological disaster of Baia Mare, Romania [12].

Gold potassium cyanide is extremely toxicsubstance.Liquid or gaseous hydrogen cyanide and alkaline salts of cyanide can enter the body through inhalation, ingestion or absorption through the skin. The rate of skin absorption is enhanced when the skin is cut, abraded or moist; inhaled salts of cyanide are readily dissolved and absorbed upon contact with moist mucous membranes[13].

The toxicity of hydrogen cyanide to humans is dependent on the nature of the exposure. Due to the variability of dose-response effects between individuals, the toxicity of a substance is typically expressed as the concentration or dose that is lethal to 50% of the exposed population (LC_{50} or LD_{50}). The LC_{50} for gaseous hydrogen cyanide amounts 100-300 ppm. Inhalation of cyanide in this range results in death of individuals within 10-60 minutes, with death coming more quickly as the concentration increases. Inhalation of 2000 ppmof hydrogen cyanide causes death within one minute. The LD_{50} for ingestion of hydrogen cyanide is 50-200 mg, or 1-3 mg/kg of body weight. For contact with healthy skin, the LD_{50} is 100 milligrams (as hydrogen cyanide) per kilogram of body weight [13, 14].

Animal tests indicate that it is corrosive to the eyes, and is a severe skin irritant with death resulting 7 hours after exposure. Itcan reactwith acids, acid fumes and slowly with carbon dioxide from moist air producing toxic hydrogen cyanide gas. Any level of exposure must be considered as hazardous.Severe over-exposure can produce lung damage, choking, unconsciousness or death[13].

The potassium form of the salt is preferred over the sodium analogue because the solubility is higher. In cases where solubility is not a matter ofconcern, sodium salts are sometimes used.

The pH range between 8 and 10 is a critical region becausethe pK_a of hydrogen cyanide is 9.46. The equilibrium constantfor $HCN_{(aq)}$ going to $HCN_{(g)}$ is $10^{1.4}$, making the $pK_a$for

$$HCN_{(g)} \rightarrow H^+ + CN^-, \qquad pK_a = 8.06 \tag{1}$$

Thus, at pH>10, the equilibrium in Eq. (1) is shifted to theright, and free cyanide is stable in the bath. At pH<8, thepredominate form of cyanide is $HCN_{(g)}$, which evolves as agaseous product. HCN gas is highly toxic, and its evolutionfrom plating baths is of health concern. Appropriate ventilationis are required for all cyanide baths. The presence ofsignificant concentrations of free cyanide in the bath, like in the case of alkaline baths, is also a risk becauseaccidental cyanide ingestion can occur[1].

At pH of 9.3 - 9.5, CN^- and HCN are in equilibrium, with equal amounts of each. At pH of 11, over 99% of the cyanide remains in solution as CN^-, while at pH 7, over 99% of the cyanide will exist as HCN. Although HCN is highly soluble in water, its solubility decreases with increased temperature and under highly saline conditions. Both HCN gas and liquid are colorless and have the odor of bitter almonds, although not all individuals can detect the odor[13-14].

The formulation and maintenance of cyanide bath is risky for the technical staff. Costsof wastewater treatment are up to 30% from total investment, and the technology is rated as a high-risk technology [15].

Due to this reason, and especially in modern time, there is a trend of using the electrolytesfree of cyanides. Content of those electrolytes is mainly based on some organic compounds. However, their usage has not found the satisfied industrial use due to the low stability constants, which is demonstrated by complex destruction and precipitationof the elementary gold from electrolyte [14]. Contrary to the other organic complexes, the organic gold complex based on mercaptotriazole, investigated in this work, has proved as a sufficiently stable within a year.

EXPERIMENTAL DESIGN

For a comparative toxicity study of the gold complex withmercaptotriazole (pH=2, 4, 7, 9 and 12) electrolyte and the classic alkaline cyanide electrolyte (pH=9), the *"in vitro"* method was applied. For cytotoxicity testing, the culture of K562 cells of human eritroleukemia was used. K562 cells were maintained in complete minimal essential growth medium (MEM) supplemented with 10% bovine serum at 37°C in 10% CO_2 atmosphere. Cells were treated with previously prepared solutions in the exponential fazeof their growth. The pH values of investigated solutions were adjusted using 1M KOH. Watertreated cells were used as a control.

Two kind of the organic electrolytes were subjected to the analysis: freshly prepared solutions at pH values: 2, 4, 7, 9 and 12, as well as solutions with the same pH values which were prepared a year ago. The conventional cyanide electrolyte (AUROCIN DPB) from the manufacturing was used for the toxicity comparison. It should be noted that the pH of the cyanide solution is set to 9, which is a common procedure with the aim to reduce the toxicity of cyanides (which is the lowest in alkaline medium). Namely, the toxicity of cyanide at pH<6 is extremely high (emission of gaseous hydrogen cyanide).

Viability of K562 cells was measured using MTT assay. MTT is a colorimetric assay that detects activity of a mitochondrial enzyme, NAD(P)H-dependent cellular oxidoreductase, which is able to convert yellow diphenyltetrazolium bromide into purple, insoluble farmazan. The rate of conversion is a measure of cells' viability.

We used 96 well plates for MTT assay. Each wellcontained 20,000 K562 cells in MEM medium, 2% (v/v)electrolyte solutions and 0.5mg/ml MTT in 100μl final volume. Each electrolyte solution treatment was tested in triplicate andevery electrolyte solution had corresponding blank wells in triplicate. Blank wells contained all components except for cells. After 4h incubation at 37°C in 10% CO_2 atmosphere, 100µl acidified isopropanol was added in each well in order to dissolve formazan. Absorbance was measured at 620nm wave length using Microplate reader Multiskan RC(Labsystems).

Viability of the cells were calculated according to the following formula: (Ai-Abi)/(Ac-Abc), where Ai was mean absorbance for wells containing cells treated with electrolyte i, Abi was mean absorbance for corresponding blank wells. Ac was mean absorbance for wells containing water treated cells, and Abc was mean absorbance for its blank wells. For each electrolyte solution, at least three independent experiments were done.

RESULTS AND DISCUSSION

The viability of electrolyte treated cells was calculated as a percentage ofviability of water treated K562 cells, which was set as 100%. The results of the toxicological testing, the percentage of cells'viability treated with fresh electrolyte, aged electrolyte (a year after preparation), conventional cyanide electrolyte and a control sample are shown in Table 1.

The results of toxicological testing of freshlysynthesized solutions of electrolyte, showed that the percentage of cells' viability (mean value) varied from 8.31% for a solution at pH=2 to 73.05% for the solution atpH=4. The mean value of viability at pH=7 was 60.88%, at pH=9was 35.68% and at pH=12was 48.00%.

The percentage of viability (mean value) of cells treated with aged electrolyte (a year after preparation) was in range of 7.16% for solution atpH=2 to 85.03% for solution at pH=4. At pH=7, the percentage of cell viability was 62.22%, at pH=9 was 40.38% and atpH=12was 57.53%.

The percentage of cells'viability (mean value) in the cyanide electrolyte was 36.32%.

Results showed that there was a certain difference in the percentage of cell viability treated with fresh solutions in comparison to aged solutions (Table 1). In general, the studied electrolytes showed the lowest toxicity at pH=4, and the highest at pH=2.

Table 1. The results of toxicological tests

	Cellviability(%)			Mean value
	I day	II day	III day	
pH=2 (fresh electrolyte)	11.55	4.66	8.72	8.31
pH=2 (agedelectrolyte)	9.86	4.10	7.51	7.16
pH=4 (fresh electrolyte)	61.62	75.59	81.94	73.05
pH=4 (aged electrolyte)	71.58	91.68	91.83	85.03
pH=7 (fresh electrolyte)	47.78	75.32	59.56	60.88
pH=7 (agedelectrolyte)	58.73	64.22	63.70	62.22
pH=9 (fresh electrolyte)	32.17	43.67	31.20	35.68
pH=9 (agedelectrolyte)	36.06	48.09	38.33	40.83
pH=12 (fresh electrolyte)	62.03	47.93	34.04	48.00
pH=12 (aged electrolyte)	64.35	72.98	35.25	57.53
Conventional cyanide electrolyte (pH=9)	45.60	37.05	26.32	36.32
Control sample	100.00	100.00	100.00	100.00

CONCLUSION

"In-vitro" toxicity study has shown that the tested organic gold electrolyte based on mercaptotriazole, exhibits the lowest toxicity at pH=4 and the highest at pH=2. The comparative toxicological study of the gold complex based on mercaptotriazole and conventional alkaline cyanide gold electrolyte showed that the toxicity of the organic gold complex at pH values of 4, 7 and 12 is lower than the toxicity of alkaline cyanide electrolyte, but higher at pH=2; at pH=9, the relative cell viability is almost equal for both kind of electrolytes.

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AIR QUALITY IN URBAN CENTER OF NIS

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ABSTRACT

The aim of the study was to analyze the air quality in the urban area of Nis in relation to the air quality index values for the period 1994-2010. For the investigation two measure places were selected:Trg Knjeginje Ljubice and the Public Health Institute Niš. Concentrations of sulfur dioxide were analyzed by spectrophotometry, while concentrations of black smoke were analyzed by reflectometry. Air quality index was calculated and commented as recommended by the European Union. Based on the air quality index value can be concluded that the air quality was unhealthy or lightly polluted in the recent years.

Key words: outdoor air pollution, air quality index, black smoke, sulfur dioxide.

INTRODUCTION

Air pollution in recent times takes on proportions that require special attention in terms of taking protective measures. Air quality in cities significantly deteriorated rapid industrial development, large volume of urbanization and the development of transport, so that a large number of different sources of pollution are concentrated in a relatively small area (1).

Air pollution in Nis monitored for many years along with the numerous studies carried out by the assessment of health risks. The main sources of air pollution in Nis are traffic and individual heating, since the industry in recent years has greatly reduced the volume of production. The main causes of a large release of polluting substances are from these sources are the use of low quality fuel and the increased number of vehicles .

The data obtained from the monitoring of air pollution are often not practical to determine the human exposure. Highly developed countries of Europe in order to better inform the public and the assessment of exposure to pollutants in the air, as well as better air quality assessment using a model based on the calculation of the air quality index. Calculating air quality index is intended to be faster and more accurate information about daily and annual levels of air pollution, the impact of air quality on human health and taking the necessary measures to protect air. In many countries the air quality index is an integral part of the daily weather reports and such reports, which have become part of modern life, based on the data provided allow people to plan their daily activities (2,3).

The aim of the study was to analyze the air quality in the residential area of the city of Nis in relation to the air quality index values for the period 1994- 2010.

METHOD

For the investigation two measure places were selected: Trg Knjeginje Ljubice (urban center) and the Public Health Institute Niš (wider city center). Pollutants were shown such as the average annual concentration of sulfur dioxide and black smoke. Sampling of these pollutants and laboratory testing was carried out in accredited methods. Sulfur dioxide and black smoke were determined every day in the 24-hour sample of the air, that is 2 - 3m^3 of air at a flow rate of 1.5 to 2 l/min. Air samples are collected at a height of 1.5 to 2 m from the ground level. The content of sulfur dioxide was determined by spectrophotometry, while the content of black smoke is determined by reflectometric method.

Test results are presented according to the Regulations on limit values, emission measuring methods, criteria for establishing measurement points and records data (Sl. No.54/92) and the Regulation on the conditions and requirements for monitoring air quality (Official Gazette of RS No.11/2010 and 75/2010) (4,5).

Air Quality Index (AQI2) was calculated and commented as recommended by the European Union. Index values were obtained equation that includes limit values (GVI) sulfur dioxide and black smoke and their average annual concentration (SGK):

$$AQI_2 = SO_2\,(SGK)/GVI_{S02} + \text{BLACK SMOKE}\,(SGK)/GVI_{\text{BLACK SMOKE}}$$

Classification of air quality index is given in Table 1.

Table 1. Air quality according to the air quality index

Values AQI_2	<0.4	0.4-0.6	0.6-0.8	0.8-1.0	>1.0
Air quality	good	lightly polluted	moderately polluted	unhealthy	very unhealthy

RESULTS

The table 2 shows the average annual concentration of sulfur dioxide and black smoke in the air at the measuring points Trg Knjeginje Ljubice and Public Health Institute in Nis in the period since 1994. till 2010.

Table 2. Average annual concentrations of sulfur dioxide and black smoke in the air at the measuring points Trg Knjeginje Ljubice and Public Health Institute in Nis in the period since 1994-2010. ($\mu g/m^3$)

Year	Trg Knjeginje Ljubice		Public Health Institute	
	SO_2	black smoke	SO_2	black smoke
1994	35	34	32	14
1995	35	35	31	11
1996	33	16	30	4
1997	52	21	33	4
1998	19	24	11	2
1999	12	37	8	10
2000	10	41	6	8
2001	15	39	8	7
2002	23	33	9	9
2003	29	39	7	9
2004	20	34	6	9
2005	25	38	5	9
2006	29	57	5	15
2007	31	47	5	10
2008	16	35	10	15
2009	14	51	10	15
2010	10	44	10	12

The average annual concentration of sulfur dioxide at the measuring point Trg Knjeginje Ljubice in air ranged from 10µg/m3 as measured in 2000. and 2010. to $52 \mu g/m^3$ as measured in 1997., when also the only time the value of the concentration of sulfur dioxide was over the limit values ($50 \mu g/m^3$). At the measuring point Public Health Institute Niš value of the concentration of sulfur dioxide were not over the limit values.

Limit values for the annual average concentration of black smoke in the air amounts $50 \mu g/m^3$ for residental areas. The data table shows that the concentration of black smoke does not show in any observed year higher concentrations than the maximum permitted except in the 2006 and 2009. at the measuring point on Trg Knjeginje Ljubice.

The results of the air quality index values are shown in Table 3 and Table 4.

Table 3. Air quality index in Trgu Knjeginje Ljubice in the period since 1994-2010.

Year	AQI_2	Air quality
1994	1.38	very unhealthy
1995	1.40	very unhealthy
1996	0.98	unhealthy
1997	1.46	very unhealthy
1998	0.86	unhealthy
1999	0.98	unhealthy
2000	1.02	unhealthy
2001	1.08	unhealthy
2002	1.12	very unhealthy
2003	1.08	very unhealthy
2004	1.12	very unhealthy
2005	1.26	very unhealthy
2006	1.36	very unhealthy
2007	1.56	very unhealthy
2008	1.02	unhealthy
2009	1.30	very unhealthy
2010	1.08	unhealthy

Table 4. Air quality index in Public Health Institute Niš in the period since 1994-2010.

Year	AQI_2	Air quality
1994	0.92	unhealthy
1995	0.84	unhealthy
1996	0.68	moderately polluted
1997	0.74	moderately polluted
1998	0.26	good
1999	0.36	good
2000	0.28	good
2001	0.30	good
2002	0.36	good
2003	0.32	good
2004	0.30	good
2005	0.28	good
2006	0.40	good
2007	0.30	good
2008	0.50	lightly polluted
2009	0.50	lightly polluted
2010	0.44	lightly polluted

Based on the air quality index value at the measuring point Trg Knjeginje Ljubice can be concluded that the air was all the time unhealthy or very unhealthy, and that the air quality in the study period is very unfortunate and that it can act harmful to human health. State of air quality measuring station, Public Health Institute Niš shows in the early years of testing negative quality which was later improved and moving towards good, but in the last three years had the status of lightly polluted.

DISCUSSION

As stated above, the analysis of air quality in the study period, taking into account the value of air quality index, it can be concluded that the air quality in measuring Trg Knjeginje Ljubice in not significantly compromised and as such can act harmful to the health of the population.

Measuring point Trg Knjeginje Ljubice is located in the urban part of the city, where there is no industry and sources of air pollution are boiler and individual heating in buildings, and road transport vehicles with high frequency. In the vicinity of the measuring point there are cross road and city bus station. On both sides of the street are residential buildings that are in a row so there is no possibility of horizontal air flow between the buildings and a cumulative pollution enabled.

On the other hand, the air quality in the metropolitan center is a little better quality. In fact, close to the measuring of the Public Health Institute also no industry, a major source of air pollution, the boiler room of the Clinical Center Niš, individual heating and transportation times less frequency than in the Trg Knjeginje Ljubice. Unlike the first measuring point, there is already countryside between sources of pollution and measuring point.

Different ways of displaying the results of monitoring can lead to completely erroneous information to the public. Existing rules and regulations do not take into account the effects on human health, but each pollutant monitored separately, so that does not realize the full possibility of harmful effects on health due to the simultaneous presence of a number of pollutants, which are the values below the limit values. This method of presentation is not only informative enough, but it can be misleading financiers and those involved in the assessment of environmental quality are not doctors, that at this station there is no problem when the air pollution from the period in question (6,7).

Due to the bad economic situation and less financial resources allocated for environmental monitoring and epidemiological studies, it is expected that based on the results shown by the regulations, many measuring points show a little polluted and out of the monitoring. Also in the publication of public information through the media, there is a danger that citizens consider that a measuring point is not contaminated because the value does not exceed the limit values, and therefore does not provide public support for action to solve the problem of air pollution (8,9).

Air quality was examined by calculating indices of air quality index compared with previous investigations in the center of town the last few years did not show improvement (8,9).

Today, throughout the world conducting numerous health education programs aimed at the population at large, or at-risk groups, in order to influence the attitudes and knowledge about a problem. Health education work within their communication methods (lectures, mass media) and organizational methods (social action campaigns) must provide information to residents about the harmful effects of air pollution on health. Newspapers and media are the main source of information, so that our people about the harmful parts of air pollution on health usually informed through magazines and ecological character of the program (10).

CONCLUSION

The tendency is to make the public daily report about the daily value of certain pollutants into the air, and the value of air quality index, which gives us a better understanding of the air quality of our environment.

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THE BEHAVIOR OF Cu37Zn IN A HYDROCHLORIC ACID SOLUTION IN THE PRESENCE OF CYSTEINE AS A NON-TOXIC CORROSION INHIBITOR

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ABSTRACT

The efficiency of cysteine as a non-toxic corrosion inhibitor for brass (Cu37Zn) in 0.05 M HCl solution was investigated. Potentiodynamic measurements and open circuit potential measurements were used to study the inhibition effect of cysteine on the corrosion of brass. The obtained results show that cysteine acts as cathodic inhibitor. Adsorption of cysteine on the surface of brass is the most important step in the inhibition mechanism, and the adsorption follows the Langmuir adsorption isotherm.

Key words: cysteine, corrosion, brass, hydrochloric acid.

INTRODUCTION

Brass has wide applications in different industries due to its high stability in various aggressive media., Hydrochloric acid is one of the most widely used acid solutions for the removal of rust and scale in several industrial processes [1, 2]. The corrosion processes of copper alloys under the influence of chloride ions are a major problem [3]. The application of inhibitors is one of the most practical methods to protect metals against acid attack. Unfortunately many common corrosion inhibitors are health hazards. To solve this problem, some researchers investigated the inhibition effect of environmentally friendly inhibitors such as amino acids on metal corrosion [4]. Amino acids are attractive as corrosion inhibitors because they are nontoxic, relatively cheap and soluble in aqueous media [5]. Organic compounds reduce corrosion through adsorption on the metal surface and complex formation with metal ions [6]. The adsorption process is affected by the chemical structures of the inhibitors, the nature and surface charge of the metal. The corrosion rate decreases when the inhibitor molecules become adsorbed and block the active sites on the metal surface [7]. Cysteine (cys) is a very interesting amino acid that contains, in addition to the amino group the –SH group, which has a strong affinity for copper [1, 6].

MATERIALS AND METHODS

The working electrode was made of Cu37Zn, reference electrode was a saturated calomel electrode (SCE) and auxiliary electrode was made of platinum. The experiments were conducted in hydrochloric acid solution (0.05 M) with and without the addition of cysteine ($1\cdot10^{-4}$ M, $1\cdot10^{-3}$ M, $1\cdot10^{-2}$ M). The open-circuit potential measurements (OCP), and potentiodynamic measurements were the methods used for electrochemical investigation of brass in a 0.05 M HCl solution without and with the addition of cysteine as a corrosion inhibitor. The OCP was determined for 1h upon which polarization curves were recorded. Linear voltammograms were recorded from the OCP to 0.25 V (vs. SCE) in the anode direction and to -0.6 V (vs. SCE) in the cathode direction. Scan rate was 1 mVs^{-1}. Cyclic voltammograms were recorded from -1.0 V (vs. SCE) to 1.2 V (vs. SCE), at a scan rate of 50 mVs^{-1}.

RESULTS AND DISCUSSION

Open circuit potential measurement

The open circuit potential change with time for brass, in 0.05M HCl solution without and with the addition of various concentrations of cysteine ($1\cdot10^{-4}$ - $1\cdot10^{-2}$ M), is shown in Figure 1. In the presence of cysteine, the open circuit potential was shifted towards negative values. This can be attributed to the adsorption of cysteine molecules or to deposition of reaction products on the metal surface [8, 9]. The negative shift of OCP values also indicates that cysteine acts as a cathodic corrosion inhibitor in acidic chloride solutions [1, 10]

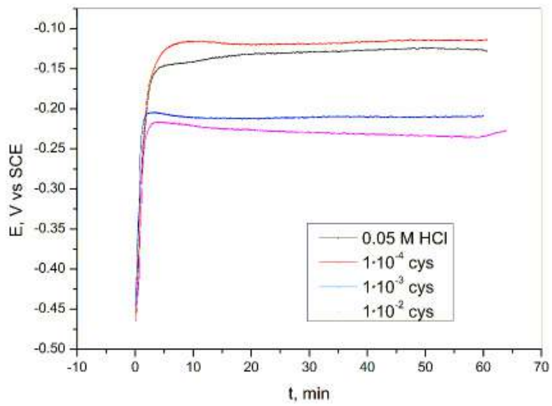

Figure 1. Open circuit potential of Cu37Zn in 0.05 M HCl solution, with and without the addition of various cysteine concentrations

Potentiodynamic measurements

It is well known that ionization of amino acids, in aqueous solution, depends on pH. Amino acids are predominantly present in protonated form in the acidic solutions.

Therefore, cysteine in protonated form can be attracted to the cathodic sites on the metal surface [1] through SH group in its structure, which has a positive effect on the inhibition efficiency [11]. Corrosion of brass in naturally aerated acidic chloride solution generally includes anodic dissolution of substrate. Since zinc is a more electronegative metal than copper, the dissolution of zinc is expected to occur at lower potentials according to the reactions [12, 13]:

$$Zn + H_2O = ZnO + 2H^+ + 2e^-$$
$$Zn^+ + 4Cl^- = ZnCl_4^{2-} + 2e^-$$

Subsequently, dissolution of copper in acidic solutions occurs according to the equations [14, 15]:

$$Cu = Cu^+ + e^-$$
$$Cu^+ = Cu^{2+} + e^-$$

Cyclic voltammetry curve (Figure 2) recorded upon brass polarization in bare 0.05M HCl solution contains anodic peak indicating the dissolution of Cu to Cu^+. Further, Cu^+ ions react with Cl^- and form CuCl by the reaction [14, 15]:

$$Cu^+ + Cl^- = CuCl$$

Upon further polarization CuCl reacts with Cl^- [14, 15]:

$$CuCl + Cl^- = CuCl^-_2$$

According to the literature data $CuCl^-_2$ may be adsorbed on the electrode surface, then it will dissolve into the bulk solution or further oxidize to cupric ions by equations [14, 15]:

$$CuCl^-_{2\ ads} = CuCl^-_{2\ sol}$$
$$CuCl^-_{2\ ads} = Cu^{2+} + 2Cl^- + 2e^-$$

In the reverse scan, a clear cathodic peak appears at −0.07 V (Figure 2) due to the reduction of copper ions. Ismail et al. [16] noticed similar behavior of copper in acidic chloride solution. Also, it can be seen from Figure 2 that CV curves obtained in HCl solution with addition of cysteine still contain anodic peak. The existence of the anodic peak in these solutions suggests that copper oxidation takes place regardless of the presence of cysteine. However, the absence of cathodic peak in the reverse scan in solutions with higher cysteine concentration ($1\cdot10^{-3}$ and $1\cdot10^{-2}$M) indicates the absence of copper ions reduction. During the anodic dissolution of brass, generated Cu (I) ions are able to react with cysteine when it is present in higher concentrations in the solution [18, 19]:

$$Cu^+ + cysteine \rightarrow Cu(I) - cysteine + H^+$$

The cathodic corrosion reaction in naturally aerated acidic chloride solution is [17]:

$$4H^+ + O_2 + 4e^- = 2H_2O$$

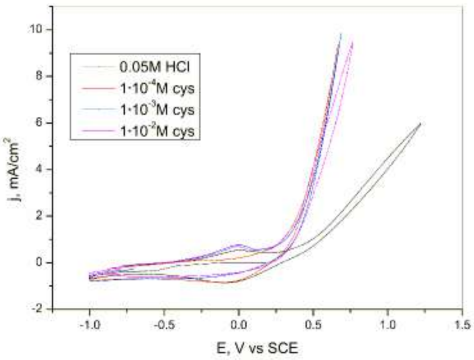

Figure 2. Cyclic voltammograms for Cu37Zn in 0.05 M HCl solution, with and without the addition of various cysteine concentrations

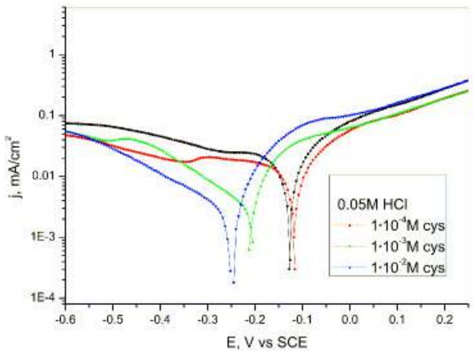

Figure 3. Polarization curves for Cu37Zn in 0.05 M HCl solution, with and without the addition of various cysteine concentrations

As can be seen from Figure 3, various concentrations of cysteine lead to a decrease in the cathodic current densities. It is clear that the presence of cysteine in electrolyte shifts the corrosion potential of Cu37Zn to the negative direction, which can be attributed to a decrease in the rate of the cathodic reaction.

Kinetic parameters of brass 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.

Table 1. Kinetic parameters of brass corrosion in hydrochloric acid solution in the presence of various cysteine concentrations

$C_{cys.}$, mol/dm^3	E_{corr}, V (vs. SCE)	j_{corr}, mA/cm^2	b_a	b_c	IE, %
/	-0.124	0.012	0.15	-0.256	/
$1\cdot10^{-4}$	-0.119	0.0086	0.14	-0.216	28.3
$1\cdot10^{-3}$	-0.210	0.0027	0.088	-0.169	77.5
$1\cdot10^{-2}$	-0.251	0.002	0.143	-0.165	83.3

The inhibition efficiency is calculated according to the following equation:

$$IE = \frac{j_{corr} - j_{corr(inh)}}{j_{corr}} \times 100[\%]$$

Where j_{corr} and $j_{corr\ (inh)}$ present corrosion current density, without and with the addition of cysteine, respectively. It is clear from the results in Table 1 that the current density decreased with cysteine concentration increase, indicating its inhibitory effect.

Adsorption isotherm

The adsorption of inhibitor molecules on the metal surface is an important step in the inhibition mechanism.

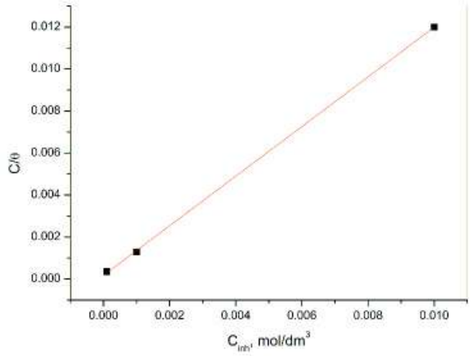

Figure 4. Langmuir isotherm of the adsorption of cysteine molecules on the Cu37Zn in 0.05 M HCl solution

Figure 4presents C/θ as a function of C, which shows a linear relationship with a slope of unity, and indicates that cysteine adsorption follows the Langmuir adsorption isotherm. Similar results were obtained by other authors [1, 4]. The Langmuir adsorption isotherm can be represented as the following equation:

$$\frac{C}{\theta} = C + \frac{1}{K}$$

Where K represents adsorption constant, C is cysteine concentration, whereas θ represents the degree of surface coverage. The Gibbs energy of adsorption is calculated according to the equation:

$$K = \frac{1}{55.55}\exp\left(-\frac{\Delta G}{RT}\right)$$

Where ΔG is free energy of adsorption, R is a universal gas constant and T represents thermodynamic temperature (298 K).

The free energy of adsorption was calculated and found to be equal to -32.27 kJ/mol, indicating a spontaneous adsorption of cysteine on the brass surface.

CONCLUSION

Cysteine can be considered as effective corrosion inhibitor for copper alloy (Cu37Zn) in 0.05 M HCl solution. The presence of cysteine shifts the open circuit potential of brass toward negative values compared to the blank solution. A decrease of the cathodic current density in the solution with cysteine in comparison with blank solution indicates that cysteine acts as a cathodic inhibitor. The mechanism of the corrosion inhibition process is based on the adsorption of cysteine on the active corrosion sites. The adsorption of cysteine follows Langmuir adsorption isotherm and Gibbs energy of adsorption indicate spontaneous adsorption (-32.27 kJ/mol) of cysteine on the electrode surface in hydrochloric acid solution.

Acknowledgement

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STAND FOR EXPERIMENTAL STUDY OF DYNAMIC PROCESSES IN ELECTRO-PNEUMATIC TRACKING SYSTEM

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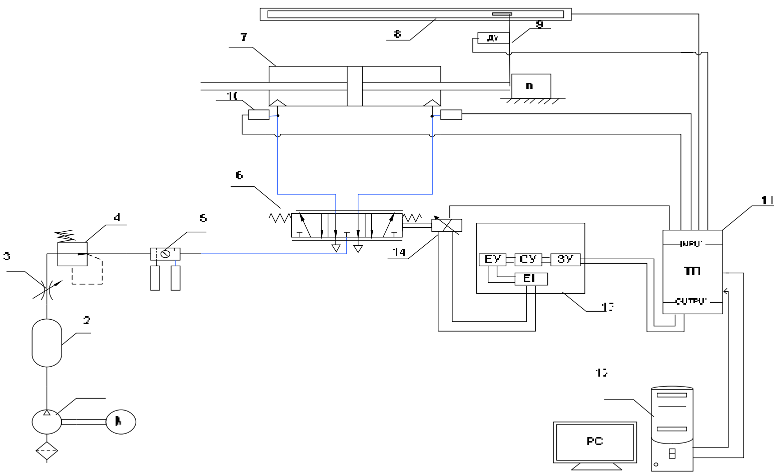
ABSTRACT

Paper deals with methodology and stand for experimental study of dynamic processes in electro-pneumatic tracking system in order to determine the parameters that cannot be calculated theoretically. Results obtained from the experimental studies can be used to verify the mathematical model of electro-pneumatic system. Virtual instruments have been developed for computerized control and recording of research results.

Key words: electro-pneumatic system, dynamic processes, experimental stand, virtual instrument.

INTRODUCTION

When designing closed-loop electro-pneumatic drive systems methods of computer modeling and simulation of the processes in the different modes are widely used [1, 3]. In many cases it is not possible to determine theoretically some important parameters and coefficients entering in the mathematical model equations [4, 5].



1 – compressor,
2 – air receiver,
3 – adjustable throttle valve,
4 – pressure control valve,
5 – air preparator,
6 – electro-pneumatic servo-valve,
7 – pneumatic double-acting cylinder with double piston rod,
8 – potentiometric transducer,
9 – acceleration transducer,
10 – pressure transducer,
11 - terminal board, 12 – computer with interface card mounted,
13 – electronic analog PID controller,
14 - servo-valve control coil

Figure 1. General view of the experimental stand

To specify the mathematical model and to reflect the most accurate real processes it is necessary are to compare results of the computer simulation to those of a real experiment. To this end, experimental stand at the Department of Energy Engineering at the Technical University of Gabrovo has been implemented.

DESCRIPTION OF THE EXPERIMENTAL STAND

For the study of electro-pneumatic tracking system a laboratory stand has been designed and constructed, the schematic diagram is shown in Figure 1. Stand allows experimentally study the dynamic processes of electro-pneumatic system, in case of different types of input signals and different types of loading forces.

The system includes electro-hydraulic servo-valve PVM 65 made by company Schneider Kreuznach, Germany, controlled by an electronic analog PID controller.

Control of the experimental process, the collection and processing of data, archiving is done automatically by the PC and the corresponding interface board of the National Instruments – NI PCIe-6321. For the purpose of the experiment specialized software for control of processes LabVIEW has been used, which has the ability to create virtual instruments for real-time measuring and data processing.

METHODOLOGY OF EXPERIMENTAL STUDY

1. Objective Measurement

To capture real-time transient modification of the basic parameters of electro-pneumatic system at different modes of operation and different loading forces.

2. General

Developed experimental stand is based on the methodology of experimental research. Measurement and recording the results is controlled by a personal computer. Data are stored in the form of text files that contain data in columns. Because of their great length more convenient data appears in graphical form. Graphs combine the results of the measurement of all variables as a function of time.

3. Criteria for assessment of the object state

For evaluation of the object its input and output parameters have to be measured:

Input parameters:

Voltage U_v supplied from set device – basic control signal of the system. It may be varied in amplitude from 0 to 5 VDC, and may be carried out staged change or other type of randomly varying in time alteration.

Output data:

Voltage U_{fb} of potentiometric sensor feedback 0 - 5VDC.

Voltage U_{p1} of pressure transducer in the left chamber of the pneumatic cylinder.

Voltage U_{p2} of pressure transducer in the right chamber of the pneumatic cylinder.

Voltage U_a of acceleration sensor 0 -5V DC.

Sequence of the experiment

1. Initially check if the mains is switched on, the compressor is run to create the necessary amount of compressed air to power the stand. Check the pressure in the receiver. air preparator for setting operational pressure for experiment - 4 bar (it is possible to have an experiment with other pressures).
2. Switch on power supply of the measuring equipment and the PC, the software is started measuring, processing and archiving of data from the experiment. Start of virtual tools designed for the needs of the experiment. A check and test for the operation of the primary measuring devices – pressure transducer, potentiometric displacement transducer, acceleration transducer is carried out. The virtual instrument for a stepped entrance effects starts. Checking out the signals from the inputs and outputs of the terminal board. After the testing of the measuring circuit, irregularities have to be removed.
3. Dispense required loading forces – mass load or springs.
4. Setting the initial position of the electro-pneumatic system.
5. Adjustment of parameters of the controller or excluded, if necessary.

After completion of the static positions proceed to the start of the experiment. There is a screen test results converted from digital graphically from the input signals as well as setting output signals. If all of the signals are there record the data.

6. After recording system is reset. The experiment was repeated as many times as necessary to avoid the error. The results obtained are recorded in the appropriate directories, indicating the conditions of the experiment. Filename and experimental conditions are recorded in diary.

Number of observations

For specific conditions making several measurements shall be continued until two experiments with matching results have been obtained.

Form of presentation

Data from each experiment can be presented in tables as arrays of numbers. They are very long as the data recorded from 20 to 200 times per second. More convenient is presentation in graphical form. In the graphs may be displayed as the data of a measurement device as a function of time, and family of data from all the meters, which is more convenient for analysis of the process.

Accuracy of measurements

For experimental study of dynamic processes in the electro-pneumatic system it is assumed that the measurements made in the manner described above have a much smaller time constants than those of the test system. In practice, their transient responses are much faster and are assumed to be proportionate common units.

Virtual instrument

For the purpose of the experiment virtual instrument has been designed in the programming environment of the software LabVIEW performing several key features. The block diagram of the virtual instrument is shown in Figure 2.

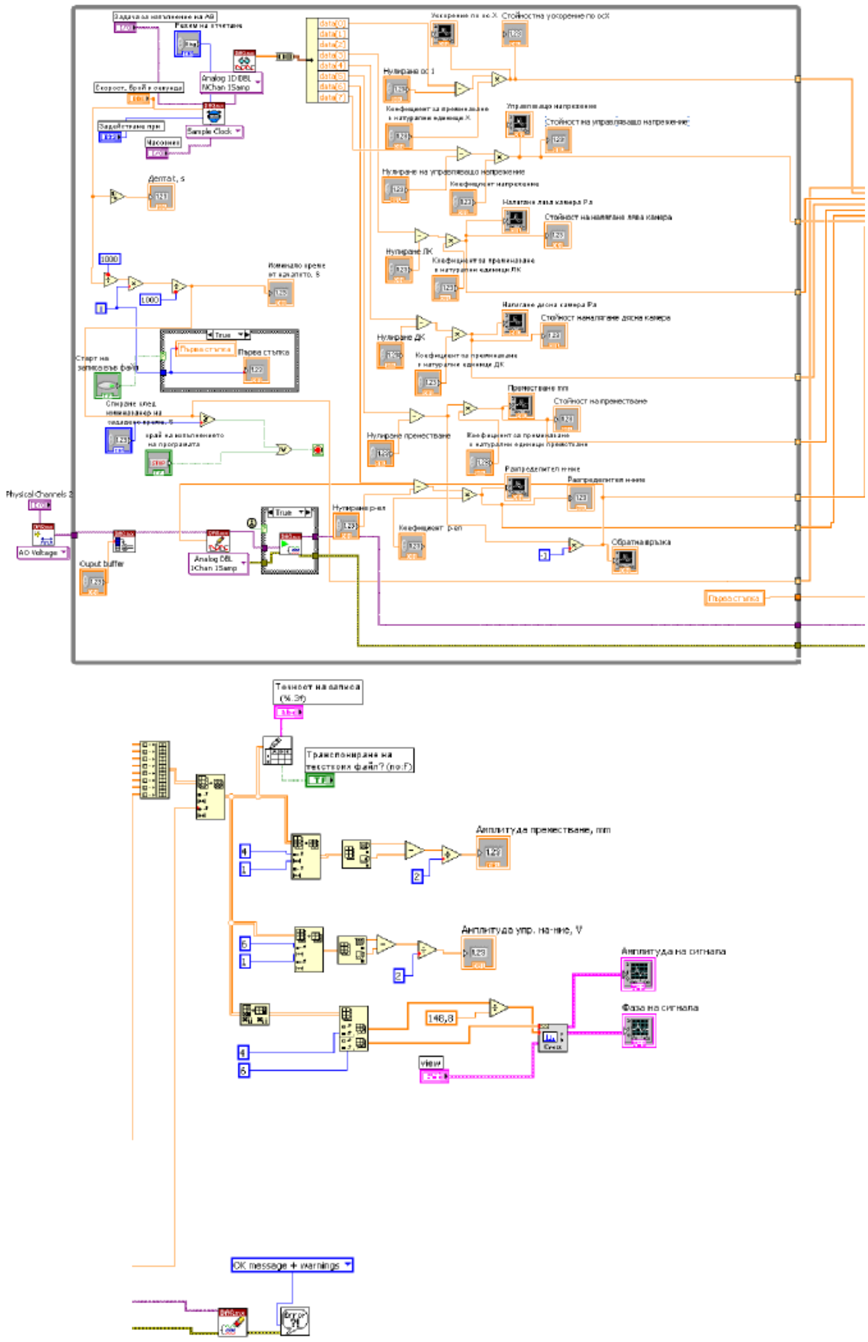


Figure 2. A block diagram of a virtual instrument developed.

Inputs are read from the interface card in the following order:

a) a sensor signal to an acceleration along the axis of movement coincident with the axis of the piston.
b) sensor input control voltage of the input signal specifies.
c) a signal from a pressure transducer of the pressure in the left chamber of the cylinder.
d) a signal from a pressure transducer of the pressure in the right chamber of the cylinder.
e) voltage of electro-pneumatic servo-valves.
f) signal from a potentiometric transducer for measuring the displacement.

Additional functionality of the virtual instrument is transformation in natural units of each of the measured channels.

Development of signal serving as a controller feedback that is fed to the analog output of the board, is also created by the virtual instrument.

There is a possibility to write to a text file of all input signals from a given point in time (Figure 2).

Figure 3 represents the part of the user-developed virtual instrument, wherein it can be monitored in real time values of the input quantities - after completion of the measurement the signal data are displayed.

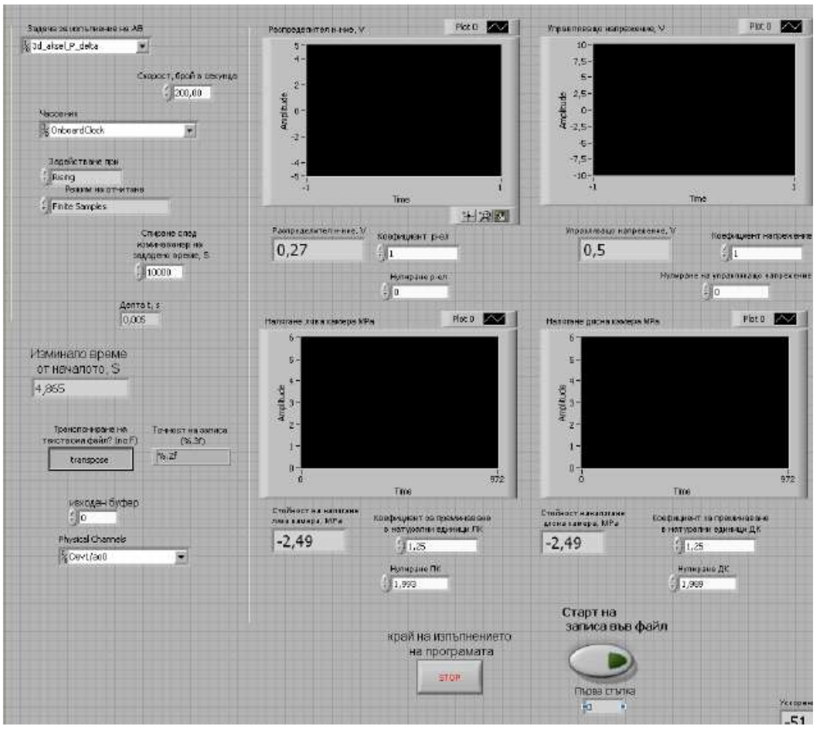


Figure 3. User interface of the virtual instrument developed

In user interface the value of the write speed, accuracy of records in the source text file can be assigned also and define the input tasks to be performed by the virtual instrument.

EXPERIMENTAL RESULTS

A number of experimental transient responses at different types of control law and parameter settings of the controller have been obtained.

Some experimental results are presented in Figure 4, and variation of different variables can be traced in a step input signal.

CONCLUSION

The experimental results obtained can be used for verification of the mathematical model of the dynamics of the closed electro-pneumatic drive system. The resulting transient responses will be compared with those obtained from the simulation of the mathematical model. By varying the parameters of the model and the model structure will be possible to achieve identity of the transient processes generated by the simulation and the experiment.

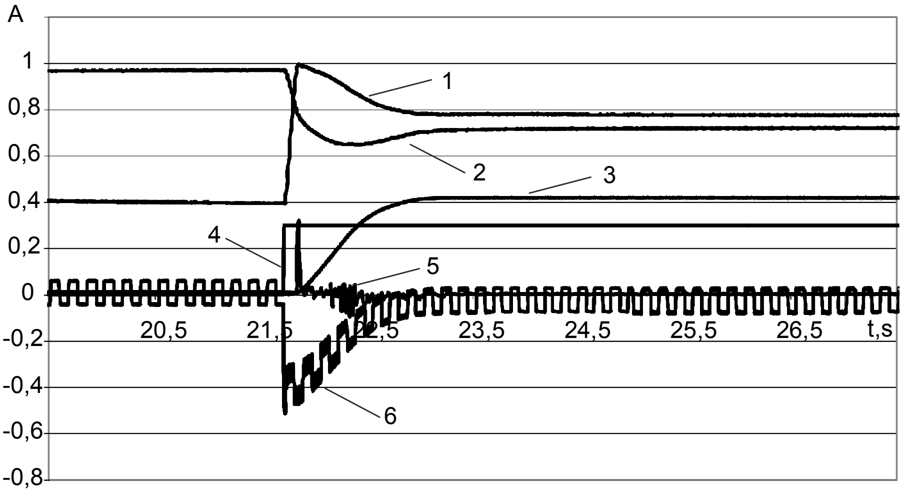


Figure 4. Change of variables in a single step input signal

1 – pressure variation in the right chamber of the pneumatic cylinder;2 - pressure variation in the left chamber of the pneumatic cylinder; 3 - displacement of the rod of the cylinder; 4 - control voltage; 5 – acceleration of the rod of the cylinder; 6 - voltage of pneumatic servo-valve control coil

Besides transient responses on the experimental stand can be tested and the frequency responses of the system and electro-hydraulic servo-valve. These characteristics can be used both to analyze the dynamic characteristics and the synthesis of control algorithms in the system.

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RESEARCH ON ENERGY LOSSES IN ELECTRIC INDUCTION MOTOR FOR FORGING FLY-PRESS DRIVE

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ABSTRACT

The dynamic behavior during operation of the forging fly-press as application of induction motors has been studied in the paper. The purpose is to draw out more clearly picture of operation of induction motors. The frequency control of induction motor has been applied. The system of differential equations has been transformed and solved using suitable software. As a result the values of the energy losses components in the induction motor have been obtained. Some of the study results have been presented graphically. An analysis has been made and conclusions from the results obtained have been done.

Key words: induction motor, electric drive, transient processes, forging fly-press, energy losses.

INTRODUCTION

Europe accounts for 14% of the final uses of energy in the world. Almost the same level as China and the United States (17%). Electricity represents 20% of the final uses of energy in the EU, basically the same as in the United States, according to Eurostat.

Approximately 60% of electric energy is consumed by electric motors: in the industry and in our houses induction motors are the workhorses. About 90% of the electric motors are induction motors. They are relatively inexpensive to make, easy to maintain, and reliable and robust in their operation. Seen from the power system, the induction motor can cause some dynamic problems. These dynamic problems may occur when the machine starts and stops and also when the mechanical load on the motor shaft changes. The initial starting current is high, easily as high as three to eight times the nominal rated current of the motor. The power system experiences the starting current of large induction motors as an inrush current, similar to the inrush current of large power transformers [12].

In order to have more clearly picture on operation of induction motors it is necessary to study the mechanical and electrical phenomena of dynamic behavior arisen.

Paper deals with performance of forging fly-press electric drive as application of induction motors in manufacturing processes of technological cycles from energy efficiency point of view.

MATHEMATICAL MODEL

A mathematical model has been proposed in [10] for research on transient processes in the forging fly-press electric drive. The special features of crank forging fly-press – kinematics scheme, relationships between parameters, and resisting moment curve are given in [10] also.

The equations for the voltages of the stator and rotor windings of the induction motor are presented in a coordinate system which rotates at a synchronous speed and they are expressed in relative units. The parameters of the equivalent circuit of the electric motor have been determined using calculation method for a value of the slip $s = 1$.

The driven mechanism is presented by means of a single-mass dynamic model. The initial data for forging fly-press modeled are given in [10]. For the duration of cycle it is determined $t_{CYCLE} = 1.5s$. The operation time is $0.125s$ while idle running time - $1.375s$.

The system of equations is presented in *Cauchy*-form. The analysis of the transient processes in the induction motor is carried out with the generally accepted assumptions [9]. For example, the induction motor is assumed to be connected to a symmetrical, three-phase power supply source. The limiting factor is normally the allowable temperature rise of the windings [2].

The impact pattern of the resisting moment leads to impact cycling loading of electric motor – main feature of forging fly-press operation. In order to smooth the electric motor loading for cycle duration a flywheel with large moment of inertia is provided for in the kinematics scheme. During the working operation the flywheel gives a part of its kinetic energy helping in this way the electric motor for loading overcome. During the idle running the electric motor returns kinetic energy back to the flywheel (charges it again). In this way the electric motor loading during the impact decreases while during the idle running increases, i.e. smooth of *M= f(t)* is completed (smooth of loading). By applying of flywheel it is possible to decrease rated power of electric motor required on the average $6 \div 10$ times in comparison with case of drive without flywheel [10].

It should be understood that different design groups and different authors have different ways of handling losses in induction machines which have proved satisfactory in their own work [7]. In this paper we analyze the behaviour of the machine both from the stator and rotor position.

Induction motor transforms electrical energy loaded from power supply mains to the stator into mechanical energy received at the rotor shaft. Moreover this energy conversion is accompanied by a losses. При това преобразуването на енергията се съпровожда със загуби. The equation of the active power balance can be written as [13, 8, 7]:

$$P_1 = \Delta P_{e1} + \Delta P_{M1} + \Delta P_{e2} + \Delta P_{MECH} + \Delta P_{ADD} + P_2 , \qquad (1)$$

where:

$P_1 = m_1 U_1 I_1 \cos\varphi_1$ – electrical power received from power supply mains to the stator; (2)

$\Delta P_{e1} = m_1 I_1^2 R_1$ – electrical losses of power related to the heating of the windings of the stator, wherein the current flows in them; (3)

$\Delta P_{M1} = U_1^2 f^{1,3}$ – magnetic losses of power related to steel core of the stator remagnetization and its heating by eddy currents; (4)

$\Delta P_{e2} = m_2 I_2^2 R_2$ – electrical losses of power in rotor windings; (5)

ΔP_{MECH} – mechanical losses of power due to friction in the bearings and rotating parts of air (ventilation losses); (6)

ΔP_{ADD} – additional difficult accounted power losses from eddy currents, determined by the magnetic stray field, by the magnetic flux pulses, by the presence of harmonics (additional losses are $\Delta P_{ADD} \approx 0{,}005 P_{1NOM}$); (7)

P_2 – mechanical power on the motor shaft.

The electrical losses in the rotor are directly proportional to the slip [4]:

$$\Delta P_{e2} = s P_{EM}\,, \tag{8}$$

where

P_{EM} – electromagnetic power of the motor:

$$P_{EM} = P_1 - (\Delta P_{M1} + \Delta P_{e1})\,. \tag{9}$$

According to magnetic ΔP_{M1} and mechanical ΔP_{MECH} losses of power, they are essentially not dependable on the load [4]. The sum of these losses is roughly constant [7].

Mechanical losses of power for motors with outer blowing (with outer diameter of the stator 0,1≤D_a≤0,5 m) are [5]:

$$\Delta P_{MECH} = K_T \left(\frac{n}{10}\right)^2 D_a^4\,; \tag{10}$$

$n = n_S(1-s)$ – rotational frequency of the motor; (11)

$K_T = 1$ for motors with 2p=2 and $K_T = 1{,}3(1 - D_a)$ at 2p≥4;

D_a – outer diameter of the stator.

Bearing-friction and windage losses are small as a rule, and may be neglected for rough calculation [8].

The choice of the point of maximum efficiency depends on the designer, efficiency has a maximum in the area where fixed losses (ΔP_{M1} and ΔP_{MECH}) are equal to the variable losses – electrical (ΔP_{e1} и ΔP_{e2}). The electrical losses in rotor are proportional to the slip and thus induction motors are economical in small slips – 1÷4% [6].

Adopted energy from the grid in starting mode is:

$$W_{ST} = \sum_{k=0}^{a_{n-1}} \left[\left(P_{a_k} \right) t_n \right] + \sum_{k=0}^{a_{n-1}} \left[\left(P_{b_k} \right) t_n \right] + \sum_{k=0}^{a_{n-1}} \left[\left(P_{c_k} \right) t_n \right] \tag{12}$$

a_{n-1} – number of point of the time axis, which lasts until the transient process.

P_{a_k}, P_{a_k}, P_{a_k} – power consumed respectively by phase A, phase B and phase C.

Adopted energy from the grid at steady state mode is:

$$W_{SS} = \sum_{k=a_{n-1}}^{n-1} \left[\left(P_{a_k} + P_{b_k} + P_{c_k} \right) \right] \left[(n-1)\delta t - t_n \right] \tag{13}$$

δt – a discrete of time axis in seconds;

t_n – duration of the transient process in seconds.

The energy losses in butts (frontal connections) in starting mode are:

$$W_{1ST} = 0.5 r_1 \sum_{k=0}^{a_{n-1}} \left[\left(I_{a_k} \right)^2 + \left(I_{b_k} \right)^2 + \left(I_{c_k} \right)^2 \right] \delta t \tag{14}$$

r_1 – resistance of one phase of the stator winding;

I_a, I_b, I_c – phase stator currents.

The energy losses in butts (frontal connections) in steady state mode are:

$$W_{1SS} = 0.5 r_1 \sum_{k=a_{n-1}}^{n-1} \left[\left(I_{a_k} \right)^2 + \left(I_{b_k} \right)^2 + \left(I_{c_k} \right)^2 \right] \delta t \tag{15}$$

The energy of moving parts and effective work in starting mode is:

$$W_{MMST} = 0.5 J \omega_b^2 + M_L \omega_b t_{a_{n-1}} \tag{16}$$

J – total inertia moment of the electric drive;

ω_b – rated circular frequency; M_L – resisting moment, Nm

The energy of moving parts and effective work in steady state mode is:

$$W_{MMSS} = \sum_{k=a_{n-1}}^{n-1} \left[M_k \omega_k \delta t \right] \tag{17}$$

Heat released in motor in starting mode:

$$W_{HST} = W_{ST} - W_{MMST} \tag{18}$$

Heat released in motor in steady state mode:

$$W_{HSS} = W_{SS} - W_{MMSS} \tag{19}$$

It has been pointed out in [10] that the most advisable, effective and economical way for increasing of the energy given by the flywheel is increasing of electric motor speed at the beginning of every cycle. It is necessary to ensure speed control of the electric motor. The most expediently is applying of electric motor frequency control since when the frequency of power supply increases, the synchronous speed increases also, from there the initial speed at the beginning of working operation also. In case of such kind of control even at short idle running time the fast speed increasing have been achieved. Using of adjustable electric drive raise the cost of forging fly-wheel presses up to 5-15% but the additional expenditures will be recovered quickly because of productivity increasing.

Solving of differential equations system which describes the dynamic behavior of forging fly-press electric drives is a complicated task. Because of this reason there is a need of applying of numerical methods for integrating in combination with micro-processor devices.

RESULTS

Technical data of the electric motor:

$P_N = 22kW$; $U_N = 380V$; $f_N = 50Hz$; $p = 2$; $n_N = 1464\min^{-1}$;

$Iph_N = 24.1A$; $J = 0.07646kgm^2$; $M_N = 143.5Nm$; $\frac{I_{ST}}{I_N} = 7.0$; $\frac{M_{ST}}{M_N} = 1.7$; $\frac{M_{MAX}}{M_N} = 2.2$

$r_1 = 0.4843\Omega$; $x_1 = 1.154\Omega$; $r_2' = 0.619\Omega$; $x_2' = 1.195\Omega$; $x_m = 51.719\Omega$; $D_a = 0.327m$

The software product *MathCAD* [1] has been used for solving the system of differential equations. Using the proposed mathematical model, the components of energy losses have been calculated in case of different values of power supply frequency. Some of the results obtained are presented in the paper - Figure 1 and Table 1. Important characteristics of induction motors are the starting torque, the maximum torque, and the torque-speed curve [11].

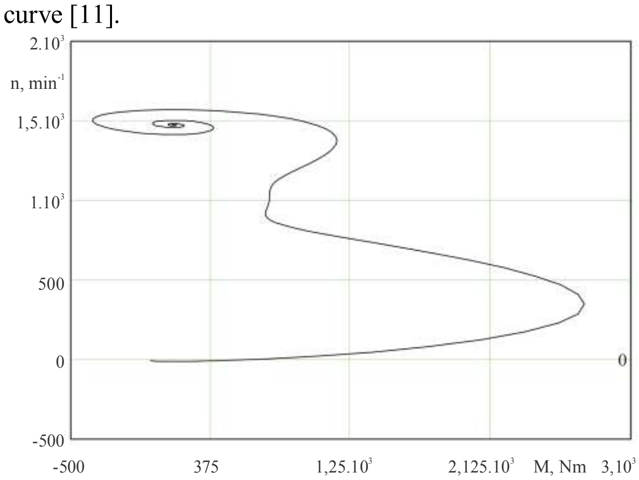

Figure 1. Torque-speed characteristic M=f(n), frequency 50Hz

Table 1. Components of energy losses

Frequency, Hz	t_{st}, s	W_{ST}, x10^6 Joule	W_{SS}, x10^6 Joule	W_{1ST}, x10^3 Joule	W_{1SS}, Joule	W_{MMST}, x10^4 Joule	W_{MMSS}, x10^4 Joule	W_{HST}, x10^6 Joule	W_{HSS}, x10^6 Joule
50	0.492	4.971	7.062	2.539	144.49	5.356	4.466	4.917	7.017
60	0.248	3.167	10.990	4.012	225.25	5.640	6.628	3.110	10.930
70	0.346	6.734	9.476	6.136	253.05	7.710	7.118	6.657	9.405
80	0.594	17.460	5.918	9.019	241.73	10.710	6.357	17.350	5.854

CONCLUSION

The mathematical model developed in the paper helps to examine the transient processes when starting a forging fly-press mechanism with frequency control. The mathematical model developed makes it possible to determine the proper adjustment of frequency control parameters in order to achieve customized requirements.

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RESEARCH ON OPERATION OF HYDRO-GENERATOR WITH THYRISTOR EXCITATION SYSTEM

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ABSTRACT

Hydroelectric power station are a future leader in environmentally friendly production of electricity. Hydropower will be the foundation of power on the continent in the coming years. Thus, the examination and improvement of hydro-generators becomes even more relevant. This work examines operational modes of hydro-generator with replaced excitation system, leading to a safer and more sustainable operation.

Key words: hydro-generator, excitation system, excitation winding, automatic regulation system.

INTRODUCTION

Development of the power sector bears the scars of the overall economic and social development. Largest pollutant in the energy sector are thermal power stations. Production of electricity from hydropower power stations is not related to the separation of technological waste. Hydropower development in Europe with the longest tradition and is characterized by greater maturity of the technology.

Systems for excitation control of synchronous generators operating in large power systems must provide:

- Maintaining clamp load on the network;
- Economical distribution of reactive load between parallel running generators;
- Increasing the security of the grid.

Implementation of the first two functions having essentially of economical mode of power stations and energy system and quality of energy produced. The third function is associated with the continuous supply of consumers with electricity.

Excitation system of hydro-generators could be divided into three main groups:

- Powered by an auxiliary DC generator to direct current (exciter), driven by the shaft of the main generator;
- Powered by an auxiliary DC generator powered by an AC motor.
- Powered by AC and rectifying by controlled rectifiers.

In the last case, the main exciter can obtain excitation from sub-exciter and from self-excitation. The control of generators excitation with mechanical exciters is implemented by means of field rheostats in excitation circuit or by adding DC in them. Automatic excitation control (AEC) in normal mode as a rule take place by adding a DC in the excitation circuit of exciters. Control with change in resistance is done by adjusting the excitation scheme and by boost of excitation in emergency conditions.
In terms of sustainability of the grid quality of AEC with mechanical exciters is evaluated by the rate of rise of the voltage of the exciter and the multiplicity of its maximum voltage (maximum excitation) at the boost ($U_{e\,max} / U_{e\,nom}$).

The rate of increase of exciter voltage is characterized by the average speed of 0,5 s after the start of the boosting relative to the rated voltage of the exciter, which is determined by the rate of change of current in the excitation coil I_e.

The process of changing of I_e in case of increasing of the excitation coil is given by the following formula:

$$L_e \frac{dI_e}{dt} + r_e \Delta I_e = \Delta U \qquad (1)$$

where ΔU – increasing of voltage of the excitation coil;
r_e, L_e – ohmic resistance and inductive reactance of the excitation coil;

Therefore, the rate of change of I_e and U_e depend on ΔU and the ratio $L_e / r_e = T_{ec}$, where T_{ec} is time constant of the excitation coil.

The initial rate of rise of the voltage of the exciter in case of boosting after shunting r_{sh} is determined by increasing the voltage of the winding of the exciter.

$$\Delta U_{ec} = r_{sh} I_e, \qquad (2)$$

where ΔU_{ec} for scheme with excitation by sub-exciter is

$$\Delta U_{ec} = U_{se} - U_{ec} \quad \text{at constant voltage of sub-exciter } U_{se}. \qquad (3)$$

For scheme without sub-exciter:

$$\Delta U_{ec} = U_{se} - U_{ec} \qquad (4)$$

Excitation systems of the generators are calculated so that U_{se} in operational mode of the generator is greater than U_e. Therefore, in the beginning of the boost rate of change of U_e for the scheme with excitation driver is larger than the scheme with self-excitation of the exciter one.

In terms of the quality of voltage regulation in normal modes for regulators without dead band two excitation systems are practically equal in value. Scheme without sub-exciter is simpler and more secure, it is used with success where there are no special requirements for the rate of rise of the voltage of the exciter in emergency conditions.
Schemes with self-excitation are applied to the generators with rated power of several tens of megawatts. For more powerful generators with mechanical excitation schemes with sub-exciter are applied.

Excitation systems with separate DC generators are mainly applied for slow running hydro-generators when there is a need to reduce the inertia of the excitation system. In many cases the exciters are not mounted on the shaft of the generator due to design reasons e.g. in capsular type hydro-generators.

Individual exciters are driven by synchronous generators with common shaft with the main generator or asynchronous motors powered by a generator voltage transformers. The second way is simpler, but more uncertain, because depends on the mode of operation of the generator. In case of short circuits close to the generator busbars the excitation system might fail.

Individual exciters work with self-excitation or with sub-exciters. Their control is usually done by adding DC in the excitation coil of the AEC. The third group of excitation systems currently implemented with mercury rectifiers. Recently for this purpose semiconductor diodes and thyristors are used.

Systems for automatic control (SAC) of generator excitation with individual action normally performed only by electric elements with continuous operation (electronic, electromagnetic and ion devices, resistors, capacitors, etc.). A simplified structural diagram of the SAC of this type is given in Figure 1.

This excitation system with shunt field is well proven and is designed to work with almost no maintenance, characterized by the use of thyristor type converters such as power components. The energy of the excitation system is taken from the busbars of the generator and fed to the field through a transformer and converter. Voltage control of the field is done by controlling the thyristors.

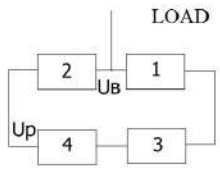

Figure 1. A structural diagram of a system for excitation control of the hydro-generator

Basic units of SAC are: subject to regulation – generator 1, measuring unit – sensor for voltage set variation of the generator 3, amplifier for signal from the measuring unit 4, a regulatory unit – exciter 2.

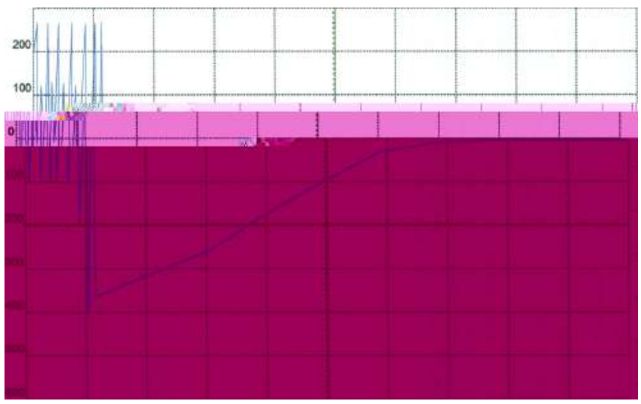

Figure 2. Operational mode of hydro-generator in case of emergency stop U=f(t)

Operational mode of hydro-generator in case of emergency stop is given in Figure 2.

CONCLUSION

The advantages of the new excitation system are:

- Lack of moments of inertia;
- Lack of sub-exciter and exciter requiring special maintenance.

The biggest benefit of this system is that it increases the operational range of the generator. In emergency situations the operation of the generator is much more sustainable.

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COMPARATIVE ANALYSIS OF MOTORS APPLICABLE FOR ELECTRIC VEHICLES

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ABSTRACT

In modernelectricvehicleschoice of driving (traction) motors is not only stick to the criterionprice/quality. Oftentimes specific mass-overall dimensions indicators are determinative because these motors mustfit intoa certain volume while they havesatisfactoryelectromagnetic andmechanical performance. Paper deals with comparative analysisbetweendifferent types of motors used as adriveinelectricvehicles.

Key words:electric motor, electric vehicle, BLDC,overall dimension, torque-speed characteristics.

INTRODUCTION

BLDC motors with permanent magnets are undisputed leader. They have high energy performancefor the entirecontrol rangeofspeed but still maintaina high price. A brushless DC machine is synchronous machine operated in such a way as to behave like a DC machine. On theother hand,althoughthe inconvenience of the commutatorDC motorsprovide an opportunity for smooth regulation atlowcost of the materialsembedded. Paper deals with comparative analysisbetweenthese two types of motors used as adriveinelectricvehicles.Leading criterionforthe optimal choice are specific mass-overall dimensions indicators: specific weight (motor weight per unitpower output), specific weight of active materials (electrotechnics steel, conductors, magnets), torque produced per unitof motorweight, costof activematerialsper unit ofpower output, torque produced against cost of materials embedded, etc.

RESULTS

The relationship between relative power developed and principal dimensions is given by the known expression [2]:

$$p = \frac{P^{`}}{D^2.l_\delta} = \frac{m.I_H.E}{D^2.l_\delta},$$

where: p – relative power, [W/m^3]; m–number of phases; I_H – rated current, [A]; E – induced electromotive force, [V]; D – outer diameter of the stator, [m]; l_δ - activelength ofthe air gap, [m].

More convenient forcomparisonis thecriterionutilization factorwhichgives the relationshipbetween the torque developedand the volume of the active partsof the motor:

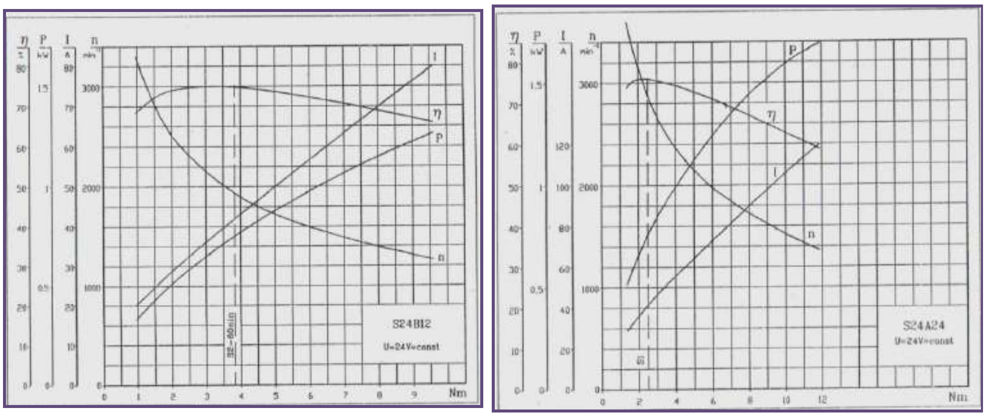
$$K_U = \frac{P}{D^2 . l_\delta . \Omega},$$

where:K_U –utilization factor; Ω – angular speed of the rotor, [rad/s].

Fourtypes of motorssuitablefor built in useand applicable to electric vehicles have been considered. Three of them are DC motors with series excitation:KA96 и KB68 are alreadyproduced, DCM 0,7/24 – prototype model and one model BLDC motor with permanent magnets – also in draft. Table 1 presents their main quantities and mass-overall dimensions indicators. On Figure 1 a) andb) operating characteristics are presented for KB68 and KA96 respectively.

Table 1. Main technical data and mass-overall dimensions indicatorsof motors investigated

Type of motor	**M,** N.m	**P,** W	η,%	**P*,** W/kg	**M*,** N.m/kg	**v,** x10^{-3} m^3	**m,** kg
KA96	2,5	750	76	111,6	0,372	2,22	6,72
KB68	3,8	750	75	74,3	0,376	3,39	10,1
DCM 0,7/24	3,5	700	73	71,4	0,375	3,56	9,8
BLDCPM	8,5	400	90	101,26	2,15	1,44	3,95



a) b)

Figure 1. Operational characteristics of DC motor:a) type KB68; b) type KA96.

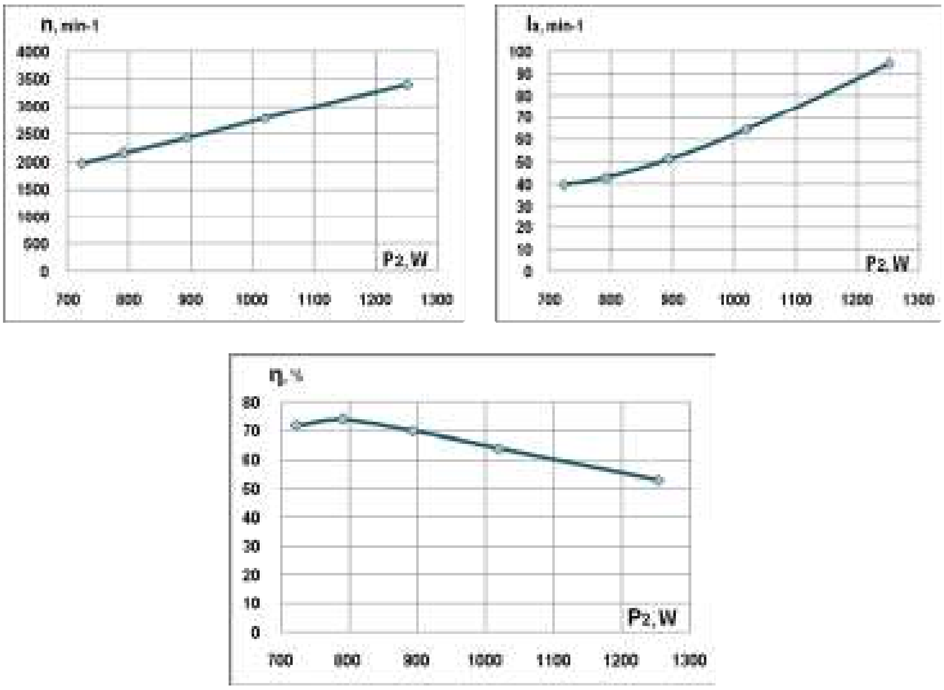


Figure 2. Operational characteristics of DC motor type DCM 0,7/24.

The three types DC motors have similar rated power and produce close in value torques [1]. BLDC motor has 1.875 times less power, produces 2,24 to 3,4 times larger driving torqueat 1,54 to 2,47 times smaller volume occupied. Analytically determined torque-speed characteristic of BLDC motor is presented on Figure 3.

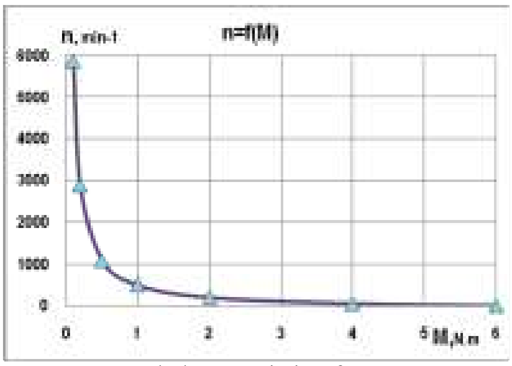


Figure 3. Torque-speed characteristic of BLDC prototype model.

Obviously BLDC motors compared to DC motors have a smaller diameter and a shorter length of the active part of the rotor and substantially larger torque developed per unit volume of the active parts Consequently appear and smaller mass and dimensions of contact less motors on the whole. The main 'reasons' justifying these advantages are the use of hard-magnetic materials with high magnetic energy (rear-earth magnets) while the losses in the rotor of such a non-contact motor are mostly smaller than the rotor of the DC motor ones. This leads to a reduction of the dimensions of the rotor and the stator, in which, in a relatively uniform current density in the copper conductors of the stator winding and the same number of wires a smaller amount of heat is released, which in turn allows to increase the current density and more again reducing the dimensions of the active parts.

BLDC motor is energy-superior to the other two types of motors. It also has a very good use of the active parts - 1kg of active materials embedded "develop" 101,26 W and "produce" 2,15 Nm driving torque. As the only draw back may be given the still high cost of these motors (they a renearly 6.15 times more expensive than DC motors) due to the high cost of rare-earth permanent magnets and electronic components in thesen sorposition of the rotor [1]. But given theemerging technologies for their manufacture and the irincreasing accessibility- this is a problem thath as a solution.

For application in electric vehicles BLDC motors are preferred due to the follow ing advantages:

- provides more driving torque at less power.
- Better energy performance (there isefficiency0.9).
- It occupies less volume and is very convenient for embed.
- There is an opportunity to vary the torque in wide range and smooth regulation of angular speed.

Environmental impact of the application of this type of motors, determined on an annual basis for100 electric vehicles, an average utilization factor of 0.5 is evidenced by the expression [4]:

$$R_{CO_2} = \sum \Theta_i . f_i . e_i . 10^{-3} = 0{,}35.4380.100.0{,}683.3.10^{-3} \approx 314\, tons,$$

where:R_{CO2}- reduced CO_2 emissions, [t]; Θ_i- electricity saved annually, [kWh]; f_i - coefficient of ecological equivalent of this energy source, f_i=*0,683t/kWh* for electric energy; e_i–coefficient accountinglossesforgeneration and transmission ofthisenergy source, $e_i=3$ for electric energy.

CONCLUSION

Issue of great importance for the correct choice of motor is to specify still in the beginning the conditions for operation and parameters to be responsible. Only the na choice price/quality can be done.

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METALLURGICAL SLAG UTILIZATION IN CEMENT AND CONCRETE PRODUCTION

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ABSTRACT

This review paper presents some aspects of metallurgical slag (especially copper slag) utilization in construction industry. Due to cementitious or pozzolanic properties, metallurgical slag can be used primary in cement and concrete production, but also for other purposes. Copper slag can be used in different applications, like in the manufacturing of cement, fill, ballast, abrasive, cutting tools, aggregate, roofing granules, tiles. Beside this, other utilizations are related for glass ceramics production and waste water treatment. For cement and concrete utilization, metallurgical slag must have appropriate chemical, physical and mechanical characteristics. Some data about cooper slag in Serbia are presented. Also, some Serbian and international standards, as well as results of some investigations which follow this utilization are presented.

Key words: metallurgical slag, utilization, cement, concrete, standards.

INTRODUCTION

The chemical, phase and granulometric composition of metallurgical slags has always attracted a great deal of interest in view of their reuse in the process of production or use for other purposes, such as the extraction of certain metals from them or for the production of construction materials [1].

Most important type of metallurgical slag are fast cooled iron blast furnace slag, steel slag, phosphorous slag, copper slag and lead slag. These slags, which have cementitious or pozzolanic properties, should be used as partial or full replacement for portland cement rather than as bulk aggregates or ballasts because of the high cost of portland cement. Because the use of these slags as cementing components needs only grinding, it will save substantial amounts of energy compared with the production of portland cement. For example, the energy required to grind granulated blast furnace slag is only approximately 10% of the total energy required for the production of portland cement [2].

Today, it has been estimated that for every tonne of copper production about 2.2 ton of slag is generated and in each year, approximately 24.6 million ton of slag is generated from world copper production. Copper slags which are produced during matte smelting and converting steps from pyrometallurgical production of copper from copper ores, have favourable physico-mechanical and chemical characteristics. These slags can be used in different applications, like in the manufacturing of cement, fill, ballast, abrasive, cutting tools, aggregate, roofing granules, tiles [3]. Beside this, other utilizations are related for glass ceramics production and waste water treatment. Also, applying mineral processing technologies, such as crushing, grinding, magnetic separation and flotation, followed by hydro- and/or pyrometallurgical processes, it is possible to recover metals such as Fe, Cr, Cu, Al, P, Zn, Co, Ni, Nb, Ta, Au Ag, etc from slags [4].

The main constituent of a copper slag are FeO and SiO_2, each present at about 20-55 %. The copper content of a smelter slag is normally around 1%, while converter slag contains in general much more (2-2.5 %), which is much higher than that of copper ore (0.5~1%). The mineralogical compositions of slags generated from different origin are quite diverse due to many factors, such as ore types, processing techniques and cooling rate. Normally, fayalite and magnetite are two dominant phases [4].

Metallurgical slag from pyrometallurgical process of smelting ore and copper concentrate in Bor Copper Mine smelting plant represents a significant economic potential, as well as big ecological problem. Approximately about 16.500.000 tons of slag and 700-1000 tons of daily produced slag in Bor Copper Mine smelting are deposited in smelter slag dumps for over 100 years of ore exploitation in Bor Copper Mine [5].

Copper slag is one of the materials that is considered as a waste which could have a promising future in construction industry [6]. The use of copper slag in cement and concrete provides potential environmental as well as economic benefits for all related industries, particularly in areas where a considerable amount of copper slag is produced [7].

This paper presents some aspects of metallurgical slag utilization, especially copper slag, in the construction industry (in cement and concrete production), with the retrospection of the standards followed this usage.

UTILIZATION OF METALLURGICAL SLAG IN CEMENT AND CONCRETE PRODUCTION

Blast furnace slag is a nonmetallic coproduct produced in the process of production of iron, when iron ore, iron scrap and fluxes (limestone and/or dolomite) are charged into blast furnace along with coke for fuel. It consists primarily of silicates, aluminosilicates, and calcium-alumina-silicates. Different forms of slag product are produced depending on the method used to cool the molten slag. These products include air-cooled blast furnace slag, expanded or foamed slag, pelletized slag, and granulated blast furnace slag. All these slags may be used in building material industry. Air-cooled blast furnace slag (ABS) has been used as an aggregate in Portland cement concrete, asphalt concrete, concrete, asphalt and road bases. Granulated blast furnace slag (GBS) has been used as a raw material for cement production and as an aggregate and insulating material. Granulated slag has also been used as sand blasting shot material. Ground granulated blast furnace slag (GGBS) is used commercially as a supplementary cementitious material in Portland cement concrete (as a mineral admixture or component of blended cement). Beside these, pelletized blast furnace slag has been used as lightweight aggregate and for cement manufacture. Foamed slag has been used as a lightweight aggregate for Portland cement concrete [8].

Steel making slag is produced during the conversion of hot metal to crude steel in a basic oxygen furnace of during of melting of scrap in an electric arc furnace. Basic oxygen furnace slag (BOS), electric arc furnace slag (EAF S and EAF C) and secondary metallurgical slag (SECS) are identified [9].

The use of ferrous slag – crystalline or vitrified – instead of natural rocks such as limestone or granite not only saves the energy that may be required to mine natural aggregates, but also eliminates the negative impacts associated with mining such as effects on biodiversity or disruption of the landscape. In the case of cement manufacture, the use of granulated blast furnace slag, instead of clinker reduces the overall process CO_2-emissions as a result of fuel savings and avoidance of sintering limestone or other calcareous materials. Calculations made by the German FEhS – Institute for Building Materials Research have shown that CO_2-emissions were reduced by about 22 million tones in the cement industry (hence in the industry as a whole) in Europe in 2008, because of the use of 24 million tones of granulated blast furnace slag. The reduction is equivalent to the Kyoto objective of countries like Belgium and Netherlands together. Thus, blast furnace slag contributes positively to the sustainability of the whole European industry and in the fight against climate change [10].

In Europe in 2010 about 25.6 million tones of blast furnace steel slag was used for cement production and concrete addition (66% from total purposes). From the total production of steel slag (about 22.3 million tones in 2010 in Europe) 6% was used for cement production and 48% for road construction [11].

According to Serbian standard for cement (SRPS B.C1.011:2001) [12] which is harmonized with European standard EN 197-1:2000, metallurgical slag can be a component of four types of cements, including:

- Portland cement with the addition of slag; the content of slag varies from 6% to 35%; marked as PC 20S and PC 35S according to Serbian standard or CEM II/A-S and CEM II/ B-S according to European standard;
- Portland composite cement; the content of slag and/or natural or artificial pozzolan and/or limestone varies from 6% to 35%; marked as PC 20M and PC 35M according to Serbian standard or CEM II/A-M and CEM II/B-M according to European standard;
- Metallurgical cement; the content of slag varies from 36% to 95%; marked as M 35K, M 20K and M 5K according to Serbian standard or CEM III/A, CEM III/B and CEM III/C according to European standard;
- Composite cement; content of slag and also, natural or artificial pozolan varies from 18% to 50% separately; marked MP 30 and MP 50 according to Serbian standard or CEM V/A and CEM V/B according to European standard.

According to Serbian standard for cement (SRPS B.C1.011:2001) [12] and metallurgical slag as nonmetallic raw material for cement production (SRPS B.C1.017:2001) [13], slag is firm mass that originates as byproduct during the pig irons melting. Type of slag depends from type and chemical composition of pig iron and process after the discharge from blast furnace. Standard specifies the classification of slags according to process after the discharge from blast furnace and the classification according to mechanical properties (bending and compressive strengths). Bending strength after 7 days must be minimum 0.5 MPa or 2 MPa, while the compressive strength must be minimum 2 MPa or 10 MPa, depending from class. Standard gives the requirements for quality (the impurities, free water, particle size distribution, chemical composition, mechanical properties, radioactivity, expansion). Slag must have minimum 66.67% $CaO+MgO+SiO_2$, while grain size distribution varies -4 mm to +80 mm.

In Europe today exists more standards for slag using in the construction sector, beside EN 197-1 for cement, they are: EN 206 (concrete), EN 15167-1 (ground granulated blast furnace slag for use in concrete, mortar and grout Part 1: Definitions, specifications and conformity criteria, EN 14227-12 (Hydraulically bound mixtures - Specifications - Part 2: Slag bound mixtures), EN 12620 (Aggregates for concrete), EN 13139 (Aggregates for mortar), etc. [14].

CHARACTERIZATION OF COPPER SLAG RELEVANT TO THEIR UTILIZATION IN CEMENT AND CONCRETE PRODUCTION

Cooper slag can be used as pozzolanic materials (i.e. pozzolan) in the production of cementing materials. A pozzolan is a siliceous or siliceous and aluminous material, which in itself possesses little or no cementitious property, but which will, in a finely divided form and in the presence of moisture, chemically react with calcium hydroxide at ordinary temperatures to form compounds possessing cementitious properties [15].

Cooper slag is iron silicate, $Fe_2(Si_2O_4)$, a by-product of flash smelting in copper manufacture. Flash smelting enables the iron to be removed from the copper ore by reacting with the silicates and floating on the molten copper mass as a slag. The resulting product is extremely hard and abrasive and is widely used in shot blast cleaning of products ranging from iron and steel to concrete and stone. The chemical nature of the copper slag also makes it a potential source of iron and silica in cement manufacture [16].

During the cooling of the slag, crystallization processes are known, and they depend on the cooling conditions of the metallurgical slag at the certain stages in the production process. The flash smelting furnace slag and converter slags in copper production contain mainly fayalite due to the nature of the process of production [1]. Fayalite is the iron reach member of the olivine group of minerals with a pure formula Fe_2SiO_4 and extremely high hardness 6.5-7 and specific gravity of approximately 4.3 [17].

The chemical composition of copper slag varies with the type of furnace. The typical composition of smelting slags are: 30-40% Fe (as FeO, Fe_3O_4), 35-40% SiO_2, up to 10% Al_2O_3 and CaO, respectively [2].

Concrete mixtures with different proportions of copper slag used as partial or full substitute for fine aggregates were prepared in order to investigate the effect of copper slag substitution (from 10% to 100% by weight) on the strength normal concrete. It is observed that maximum compresive strength of concrete increased by 55% at 40% replacement of fine aggregate by copper slag, and up to 75% replacement, concrete gain more strength than control mix strength [6].

Based on theoretical considerations proposed by the field researchers, some authors deals with the determination of the proportions of copper slag and portland cement in the blended cement, having the objective of adding just enough of copper slag to consume all the excess calcium hydroxide produced during the hydration of the portland cement. The pozzolanic tests of mixes with various content of copper slag determined according to ternary phase diagram, showed that the copper slag can be used successfully as portland cement substitute (up to 30% by weight) in the cement industry [18].

According to the available data, copper slag from Bor Copper Mine smelting have the next average chemical composition: 36.62-38.45% Fe, 34.04-34.76% SiO_2, 5.066-5.38% Al_2O_3, 0.892-2.03% S. Beside these elements and compounds, slag contains on the average 0.747-079% Cu, 3.725-7.57 g/t Ag and 0.4-0.525 g/t Au. Mineralogical investigations confirmed mainly the presence of fayalite and magnetite and also the presence of bornite, chalcopyrite, pure copper, chalcosine, coveline, pyrite [5, 19].

Many authors published papers about copper slag utilization in cement and concrete productions and also for other purposes. When copper slag is used as a raw material for clinker production, it can act as both iron adjusting and mineralizing component. Further, it also improves the grindability of the clinker. When it is used as a cement replacement or an aggregate replacement, the cement, mortar and concrete containing different forms of copper slag have good performance in comparison with ordinary Portland cement having normal and even higher strength [7].

The potential benefits of using of flotation wastes of copper slag (FWCS) as cement raw material was confirmed in investigation from some authors. The chemical and mineralogical analysis of the FWCS sample has shown that it can be considered as a ready source of iron due to its sufficiently high content of iron present mainly as fayalite and magnetite. Further physical and mechanical tests have confirmed that the cements obtained from the FWCS is a suitable material as iron source for the production of Portland cement clinker [20].

Investigation about effect of copper slag on the hydration of cement based materials is confirmed that up to 15% by weight of copper slag was successfully used in concrete as a portland cement replacement. Results indicate a significant increase in the compressive strength for up to 90 days of hydration [21].

The dynamic compressive strength of the copper slag reinforced concrete is generally improved, compared with the control concrete, with the increase of copper slag replacement up to 20%, due to the excellent physical and mechanical properties of copper slag [22].

Other authors established that copper slag in the range of 40-50% could potentially replace sand in concrete mixtures. The copper slag was ground in the laboratory into a fine powder to the required size in accordance with standard. For cement mortars, all mixtures with different copper slag proportions yielded comparable or higher compressive strength than the strength of the control mixture. There was more than 70% improvement in the compressive strenngth of mortars with 50% copper slag substitution in comparison with the control mixture. Copper slag, in the range of 40-50%, could potentially replace sand in the mixture [23].

Also, some other authors report about the potential use of granulated copper slag as a replacement for sand in concrete mixes. The experimental investigation showed that percentage replacement of sand by copper slag shall be up to 40% [24].

CONCLUSION

Utilization of metallurgical slag in construction industry has more positive aspects (technological, environmental and economical). These statements are confirmed from practice experience and, also from investigations from many countries. Many researchers from other countries confirmed that the copper slag can be used in construction industry, especially in cement and concrete production (mainly as a cement replacement or an aggregate replacement). Beneficial use of cooper slag as industrial waste must be in the scope of sustainable materials management - systematic approach to the using and reusing of materials in the most productive and sustainable way across their entire life cycle. Sustainable materials management conserves resources, reduces waste, slows climate change, and minimizes the environmental impacts of the materials we use. According to EPA's Sustainable Management Program this approach helps to identify waste materials as commodities that can be utilized to grow key industries and associated jobs [25]. Beside iron and steel slag as well known industrial materials, copper slag is considered as promising industrial material. It can be supposed that copper slag from Serbia can find the usage in cement and concrete production, but it demands investigations. Grinding as mineral processing technologies can be included in further treatment of copper slag.

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HEAVY METALS AND TOTAL SULPHUR CONTENT IN VEGETABLES COLLECTED IN THE BOR REGION (SERBIA)

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ABSTRACT

This study was aimed to assess the levels of Cu, Zn, Mn, Ni and total S in edible parts of vegetables. The vegetables were sampled from an agricultural area of Bor. The descriptive statistics of element concentrations in vegetables and hierarchical cluster analysis are given in the paper. The concentrations of elements were highest for S, followed by Cu and Zn. Cluster analysis showed that some elements formed a separate cluster due to higher concentrations. High concentrations of Cu, total S and Zn in the vegetables from Bor region, compared to the results obtained from the literature, may indicate contamination.

Key words: vegetable, heavy metal, sulphur, mining-metallurgical complex.

INTRODUCTION

Vegetables are important components of human food intake [1,2] and these foodstuffs are rich sources of vitamins, minerals, and fibers, and also have beneficial antioxidative effects [1]. Rapid urbanisation, industrialisation and emission of hazardous pollutants into the environment increases metal concentrations, thus contaminating the crops [1,3]. Mining and processing of metal ores are a significant source of heavy metal contamination of the environment [4,5]. The contamination of vegetables with heavy metals and other elements poses a risk to the human health if they are transferred through the food chain [1,4]. Crops can uptake toxic elements through their roots from contaminated soils, and even leaves can absorb toxic elements deposited on the plant surfaces [4,5]. High concentrations of the essential elements may also be toxic for the plants. Therefore, the safety of vegetables is very important. Scientists around the world are engaged in research of cultivated vegetables which are grown in areas with different level of pollution [1-7].

This study aims to assess the content of heavy metals (Cu, Zn, Mn, Ni) and total sulphur (S) in edible parts of vegetables sampled from the surroundings of Bor which is known for copper mining and metallurgy.

DESCRIPTION OF THE STUDY AREA

The territory of Bor and its surroundings is located in the central part of the Eastern Serbia and covers an area of 856 km^2. The town of Bor is well known for copper deposits, which are among the largest in Europe. Mining in Bor started in 1903, when rich copper ore deposits were discovered in this region. The first smelting plant started working in 1906, and the present smelting plant was built during the 1961-1968 period. The copper smelter is the biggest source of SO_2 and particulate matter (heavy metals, dust) emissions in the region [8,9]. As depicted in Fig. 1, the study area is situated in the vicinity of mining and metallurgy complex (from 1 to 13 km).

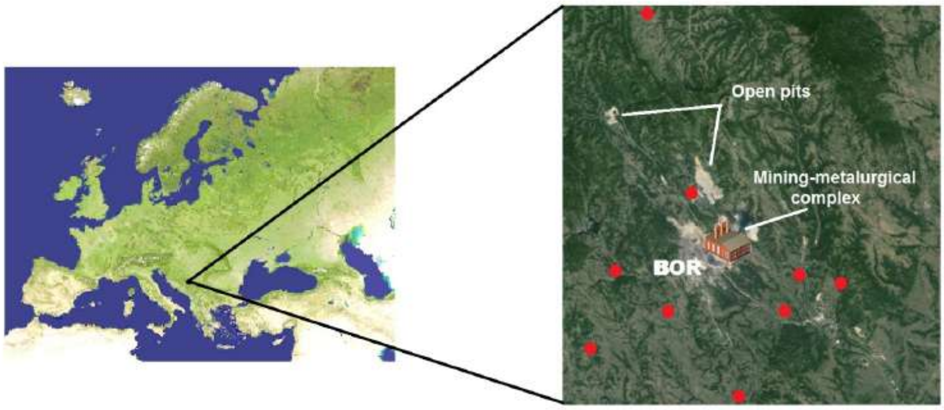

Figure 1. Map of Bor and its surroundings showing sampling sites

MATERIALS AND METHODS

The examined vegetable samples from the agricultural areas given in Fig. 1, were collected during June and September 2009. Samples were also taken from green market which is situated in the close vicinity of the industrial complex. Edible parts of potato, carrot, tomato, cucumber, and green bean were collected. Fresh samples were air-dried and grinded according to the procedure in the papers of Kalinovic *et al.* [10], and afterwards were digested according to the US EPA method 3050B [11]. Concentrations of heavy metals (Cu, Zn, Mn, Ni) and total S in vegetables were analyzed using ICP-AES in the Mining and Metallurgy Institute Bor.

RESULTS AND DISCUSSION

Mining and processing of copper ores are the major pollution sources in Bor. Air pollution is also caused by dust from ore waste and the flotation tailing ponds. Non continuous work of sulphuric acid plant (in which SO_2 from waste gases is converted to H_2SO_4) affects the air quality. Air pollution originating from the industrial complex is transported to the surrounding rural settlements [8]. The Mining and Metallurgy Institute Bor implemented air quality monitoring in the study area which is performed in accordance with the Law on Environmental Protection of the Republic of Serbia [12,13].

Copper smelters are one of the biggest pollution sources of SO_2, particulate matter and metals [9]. Figure 2 shows box plots of the monthly SO_2 concentrations in Bor during the period 2007-2009. The data are obtained at the measuring site Town park which is located 0.5 km southwest of the dominant source of pollution, i.e. copper smelter [14]. During the examined period the average monthly SO_2 concentrations were the lowest in 2009. The average annual SO_2 concentrations in 2007, 2008, 2009 were 175.0, 132.19, 54.89, respectively, which exceeds the annualy maximum allowable concentration (MAC) [13]. Although SO_2 concentrations are not measured continuously in the neighbouring villages, the residents distinguish it easily by sharp smell and by the damage that it causes to agricultural crops [8].

Particulate matter (PM) with a high content of metals can be expected from processing and storage of ores and concentrates, as well as from flotation tailing ponds and ore waste heaps [9]. In the Bor area, during the period 2007-2009, the content of Ni in PM was elevated only in 2009. The MAC for Mn and Cu from PM is not defined, and neither for Zn [12].

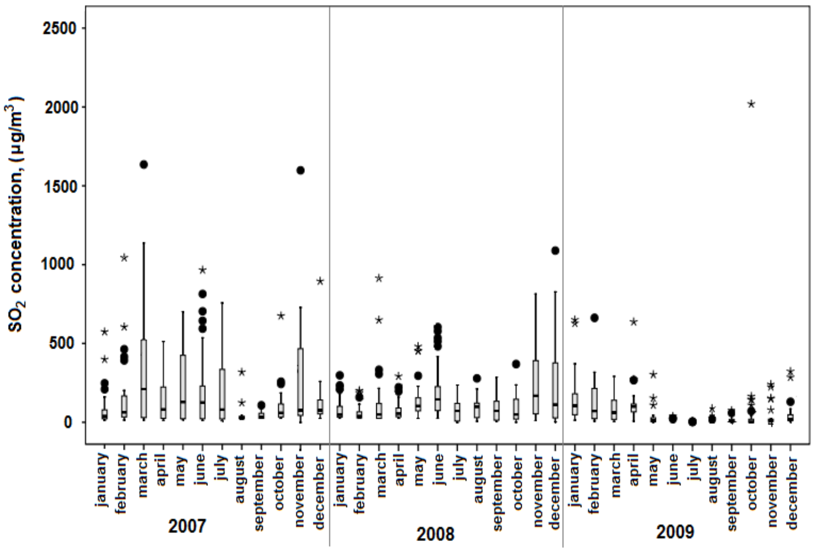

Figure 2. Average monthly concentrations of SO_2 during 2007-2009 in Bor

Most of the analysed fruit and vegetable samples were cultivated on private farms and, therefore, information on applied protection product, such as pesticides and fertilizers, was not available.

The mean, range and standard deviation of Cu, Mn, Zn, Ni and total S concentrations in the selected vegetables grown in the Bor surroundings are listed in Table 1. All the concentrations were expressed on a dry weight basis (mg/kg DW).

Table 1. Descriptive analysis of Cu, Mn, Zn, Ni, and total S concentrations (mg/kg) in edible parts of vegetables in the studied area

	Elements (mg/kg)				
Potato (n=16)	**Cu**	**Mn**	**Zn**	**Ni**	**S**
Range	1,82-110,47	3,08-7,70	0,99-31,05	0,05-7,93	359,00-1042,00
Mean	42,59	4,84	12,73	2,34	710,11
SD	36,96	1,44	10,95	2,95	174,99
Carrot (n=9)	**Cu**	**Mn**	**Zn**	**Ni**	**S**
Range	89,39-563,42	4,90-65,99	33,61-199,56	0,05-6,09	695,70-1162,10
Mean	283,07	13,60	87,96	2,31	967,57
SD	196,01	19,69	52,96	2,41	148,43
Tomato (n=10)	**Cu**	**Mn**	**Zn**	**Ni**	**S**
Range	1,00-297,25	3,62-13,64	1,74-141,36	0,05-9,78	647,40-1414,60
Mean	78,13	8,26	30,82	2,66	1063,43
SD	96,55	3,54	40,86	3,11	241,36
Cucumber (n=11)	**Cu**	**Mn**	**Zn**	**Ni**	**S**
Range	19,11 - 412,50	0,05 - 17,87	16,02 - 294,65	0,05 - 8,79	1154,70 - 2525,10
Mean	201,42	11,42	104,09	2,64	1865,07
SD	153,29	5,05	88,37	3,07	412,44
Green bean (n=10)	**Cu**	**Mn**	**Zn**	**Ni**	**S**
Range	24,86-99,57	1,08-18,57	7,51-192,02	0,31-6,21	517,10-1498,20
Mean	54,26	12,19	41,55	2,11	1185,35
SD	28,33	6,12	54,65	1,97	292,55

SD - Standard deviation

High values of standard deviations of element concentrations indicate their large variability in the studied area. The concentrations of elements were highest for total S, followed by Cu and Zn, with Mn and Ni being the lowest. The maximum concentration of total S (2525.10 mg/kg) was recorded in the samples of cucumber and the maximum concentration of Cu (563.42 mg/kg) was in a carrot tuber.

Table 2 shows Cu, Mn, Zn, Ni and total S concentrations obtained by scientists around the world. However, only a few data of total S concentration in vegetables was found in the literature. Comparing the results obtained in this study (Table 1) with the results of other scientists (Table 2), it can be concluded that the concentration of Cu, S, and Zn in edible parts of vegetables were several times higher in the samples from the surroundings of Bor. The Mn concentrations were approximate, and the Ni concentration in vegetable samples of the present research were lower than the concentrations in other studies. It is obvious that high concentrations of Cu and total S indicate contamination of the edible parts of vegetables in the studied area.

Table 2. Concentration of elements (mg/kg) in edible vegetable parts from the literature

Vegetable	Cu	Mn	Zn	Ni	S	References (pollution source)
Potato	6.08 ± 0.23^{a}	8.80 ± 0.32^{a}	14.97 ± 0.54^{a}	10.74^{g}	-	[a] Ali and Al-Qahtan [1]
	6.41 ± 0.22^{a}	7.61 ± 0.57^{a}	17.65 ± 1.10^{a}			(industrial and urban area)
	2.06 ± 0.08^{a}	5.33 ± 0.35^{a}	14.28 ± 0.82^{a}			[b] Zhuang *et al.* [4]
	2.30 ± 0.08^{a}	8.49 ± 0.31^{a}	16.41 ± 0.61^{a}			(mine of polymetallic
	$1.82\text{-}1.85^{c}$	5.67^{g}	$5.51\text{-}5.52^{c}$			sulfide meso-hypothermal
	0.534^{e}		5.11^{e}			ores)
	0.88^{g}		4.5^{g}			[c] Miller *et al.* [6]
Carrot	3.60 ± 0.22^{a}	7.11 ± 0.45^{a}	10.28 ± 0.67^{a}	17.54^{g}	$1.46\pm0{,}1^{f}$	(precious metal mine)
	4.49 ± 0.19^{a}	7.44 ± 0.23^{a}	26.64 ± 0.98^{a}		$1.91\pm0{,}31^{f}$	[d] Liu *et al.* [5]
	4.44 ± 0.26^{a}	12.04 ± 0.31^{a}	8.27 ± 0.42^{a}		$1.59\pm0{,}26^{f}$	(Pb/Zn mine)
	7.82 ± 0.43^{a}	30.33 ± 0.88^{a}	12.97 ± 0.55^{a}			[e] Marković *et al.* [3]
	$1.33\pm0.26^{b*}$	24.6 ± 11.6^{f}	$6.92\pm0.71^{b*}$			(agricultural area)
	$0.85\pm0.16^{b*}$	23.8 ± 22.2^{f}	$5.70\pm0.28^{b*}$			[f] Warman and Havard [7]
	$0.58\text{-}3.49^{c}$	14.8 ± 1.4^{f}	$2{,}07\text{-}29{,}6^{c}$			(conventional vegetable
	7.4 ± 1.2^{f}	6.18^{g}	25.0 ± 3.9^{f}			production)
	8.3 ± 4.1^{f}		26.0 ± 7.9^{f}			[g] Mohamed *et al.* [2]
	8.4 ± 2.3^{f}		24.0 ± 2.2^{f}			(farm)
	0.98^{g}		9.6^{g}			
Tomato	5.80 ± 0.06^{a}	10.51 ± 0.52^{a}	22.44 ± 0.88^{a}	14.64^{g}		
	7.46 ± 0.41^{a}	27.84 ± 0.33^{a}	22.91 ± 1.02^{a}			
	3.57 ± 0.25^{a}	18.05 ± 0.27^{a}	8.93 ± 0.53^{a}			
	7.30 ± 0.28^{a}	17.10 ± 1.10^{a}	27.91 ± 1.52^{a}			
	$0.76\pm0.08^{b*}$	7.39^{g}	$2.85\pm0.31^{b*}$			
	$0.79\pm0.05^{b*}$		$5.14\pm0.46^{b*}$			
	$9.11\text{-}12.4^{e}$		$15.3\text{-}21.\ 3^{e}$			
	4.47^{g}		14.4^{g}			
Cucumber	3.21 ± 0.06^{a}	9.55 ± 0.52^{a}	29.78 ± 1.28^{a}	10.88^{g}		
	7.18 ± 0.25^{a}	10.92 ± 0.29^{a}	22.30 ± 0.64^{a}			
	3.95 ± 0.07^{a}	7.43 ± 0.26^{a}	15.71 ± 0.37^{a}			
	5.65 ± 0.15^{a}	33.98 ± 1.51^{a}	22.88 ± 0.57^{a}			
	2.48^{g}	8.02^{g}	32.3^{g}			
String bean	22.98^{d}		97.08^{d}			
	12.92^{d}		74.00^{d}			
	22.02^{d}		86.84^{d}			

[*]fresh weigh

Fruits from the same sampling area around Bor were investigated by Kalinovic et al. [10]. Concentrations of Cu, Mn, Zn, Ni and S were also higher than in the fruits from other polluted areas in the world.

Cluster analysis of Mn, Ni, Zn, Cu and total S concentrations in the samples of potato (2a), carrot (2b), tomato (2c), cucumber (2d), and string beans (2e) are shown in Figure 3. Mn, Ni and Zn are generally at significant Euclidean distances, while Cu is closely related to those elements. Total S is at considerable Euclidean distance for all the vegetables due to its highest concentrations. The exception is the cluster of Mn, Ni, Cu and Zn in the sample of string bean. Considering the concentration of elements in Table 1, it can be concluded that the elements with lower concentrations are grouped in a separate cluster.

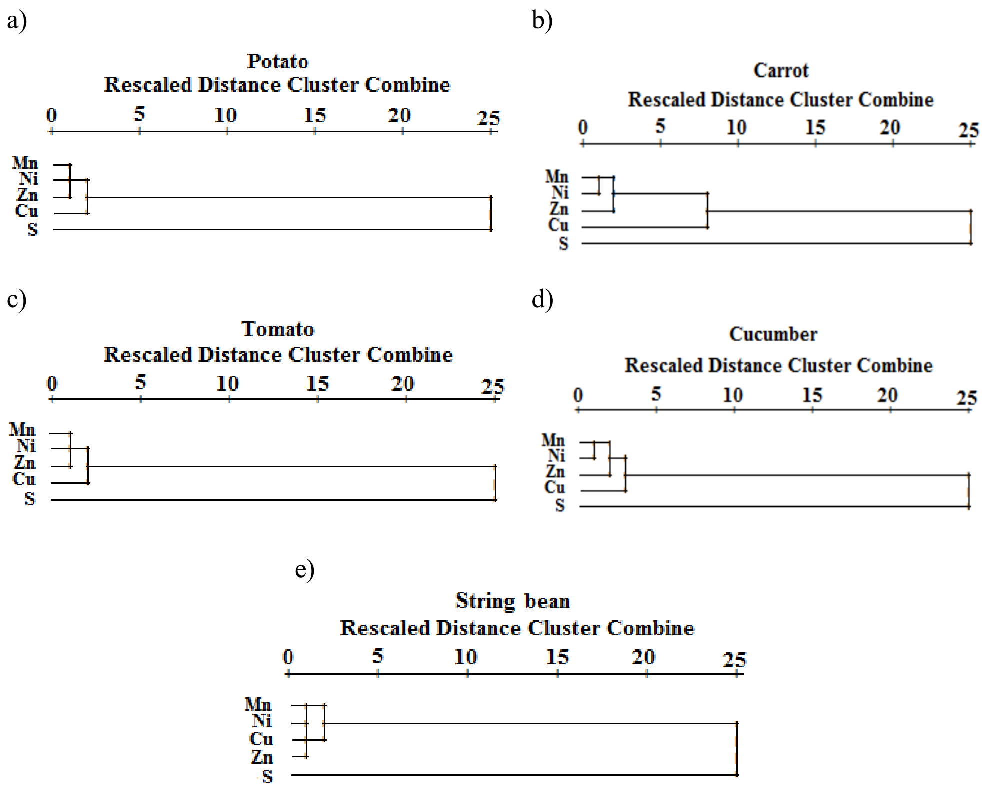

Figure 3. Cluster analysis of Mn, Ni, Zn, Cu and total S concentrations in edible parts of vegetables: (a) potato, (b) carrot, (c) tomato, (d) cucumber, (e) string bean

CONCLUSIONS

Vegetables are an important part of the human food intake, and can accumulate the toxic elements from the environment, so its safety is very important. Regarding the presented results, the origin of the analysed elements in vegetables can not be identified with certainty. The increased levels of elements (Zn, Cu, S) in vegetable samples may be associated with the use of mineral fertilizers and some pesticides commonly applied in crop production or it can be a consequence of emissions from the mining and metallurgical complex.

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DANDELION AS AN ENVIRONMENTAL BIOINDICATOR IN THE BOR REGION

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ABSTRACT

Wastewaters originating from the copper production pose a great threat for the environment, especially the rivers. Alkaline wastewaters from the Krivelj and Bor flotation plants, as well as acid wastewaters from underground exploitation, are discharged into the flow of the Krivelj river. Topsoil, as well as root and leaves of dandelion (*Taraxacum officinale*), were sampled along the Krivelj riverbed during 2012. Levels of arsenic, lead, copper, zinc and cadmium in the soil and plant samples were analysed. Based on the obtained results of the heavy metals content, it was found that dandelion acts as excluder for all the analysed elements.

Key words: wastewater, riverbed, heavy metals, biomonitoring, soil, dandelion.

INTRODUCTION

Heavy metals are the most dangerous pollutants of the environment. The industrial development leads to uncontrolled emissions of metals into the atmosphere and hydrosphere and to subsequent accumulation in soil and sediments. Through bioaccumulation by plants from soil, heavy metals enter human food chain and can be deposited in human body [1].

Dandelion (*Taraxacum officinale*) is a self-fertile perennial plant which flourishes from April to May, and its seeds ripen from May to June. It can survive on acid, neutral, alkaline and very alkaline soils. In spite of being suitable for sandy, loamy and clay soils, it still prefers moist soil. Edible parts are flowers, leaves and roots. Leaves are very nutritious food, 100 g of the raw leaves contain about: 2.7 g protein, 9.2 g carbohydrate, 187 mg Ca, 66 mg P, 3.1 mg Fe, 76 mg Na, 397 mg K, 36 mg Mg, 0.19 mg vitamin B1, 0.26 mg vitamin B2, and 35 mg vitamin C. Dandelion is a commonly used herbal remedy. It is especially effective and valuable as a diuretic because it contains high levels of potassium salts. Root can be used fresh or dried and should be harvested in autumn, while leaves are harvested in spring when the plant is in flower and can be dried for later use. The plant has also an antibacterial effect [2]. Dandelion has also been used in many biomonitoring surveys [3,4,5,6,7,8,9].

The aim of the paper is to assess biomonitoring ability of dandelion sampled at the Krivelj riverbed (Bor, Eastern Serbia), which is polluted with wastewaters from the copper production processes and communal wastewaters originating from the town of Bor.

MATERIALS AND METHODS

Pollution of the river basin of the Bela reka (which includes tributaries of the rivers Krivelj, Bor, Cerovo and Ravna reka) is an important environmental issue, since the wastewaters are discharged without treatment into the basin which is a part of the Timok and Danube basins.

The mine waters in the studied area occur: (1) in the process of mining copper ore at the surface mines Cerovo and Krivelj and at the underground pit Bor; (2) in the process of concentration of copper ore at the flotation plants Krivelj and Bor; and (3) in the abandoned open pit Bor. The wastewaters are similar in composition but differ in volume and content of heavy metals. The pollution usually consists of low pH value, increased content of heavy metal ions (Cu, Fe, Zn, Ni, Cd, Cr, Pb, etc.), suspended particles and fine particles from flotation, which are deposited in the river valleys on an area of over 2000 ha [10,11].

Sampling of dandelion parts and soil was carried out in mid-April, May and June of 2012, at six locations (Figure 1) along the Krivelj river: sampling point 1 (SP1) is situated about 500 m above wastewaters of the mine Cerovo; sampling point 2 (SP2) is between wastewaters of the Cerovo mine and the Cerovo river; sampling point 3 (SP3) is before the rural settlement Krivelj; sampling point 4 (SP4) is at the estuary of the Bor river deviation into the Krivelj river, about 50 m before the collector; sampling point 5 (SP5) is below the collector of wastewaters of the flotation tailings from the Bor mine; sampling point 6 (SP6) is about 250 m of the estuary of the Bor and Krivelj rivers. The SPs were selected because the river valleys have been used to deposit sludge and other waste materials originating from the copper production, causing many environmental problems in the study area. Only SP1 is considered to be an area without industrial influence.

a) b)

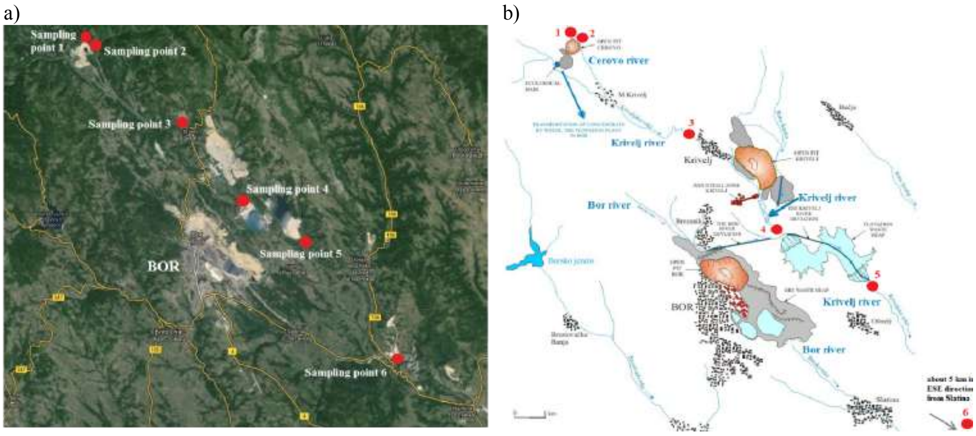

Figure 1. Maps of sampling points of dandelion along the Krivelj riverbed

Samples of leaves, root and topsoil of dandelion were collected by stainless still blade. All the samples were placed in labelled plastic bags before being sent to the laboratory where they have been air-dried, homogenized, milled and prepared for acid digestion.

Samples of plant material in the quantity of 0.5000 g (METTLER, type B5) were digested in microwave (CEM MARS 5) at the temperature of 180°C with 10-15 cm^3 of concentrated HNO_3 and H_2O_2 which was added portionwise. The soil samples (0.2500 g) were digested with reverse *aqua regia* ($HCl:HNO_3$=1:3) and 5 cm^3 HF in microwave at 200°C. After the completion of the first digestion, 30 cm^3 of 4% H_3BO_3 was added in the solution, in order to remove HF at 170°C. The concentrations of As, Pb, Cu, Zn, Cd were determined by ICP-AES (Spectro Ciros Vision Model) in the Mining and Metallurgy Institute Bor. The lower limits of detection for As, Pb, Cu, Zn, Cd were: 3.0 mg kg^{-1}, 2.0 mg kg^{-1}, 1.0 mg kg^{-1}, 1.0 mg kg^{-1}, and 0.5 mg kg^{-1}, respectively. Determination of soil pH (potential acidity) was performed according to the ISO standard 10390:2007 [12].

RESULTS AND DISCUSSION

In Table 1, concentrations of As, Pb, Cu, Zn and Cd in soil and plant parts of dandelion are given for three monthly sampling periods. In all the soil samples Cd was below the limit of detection (<0.5 mg kg^{-1}). As can be seen, heavy metal concentrations in soil at the SP1, SP3 and SP5 are generally lower in comparison to the rest of the sites. No conclusion can be drawn about the concentrations of heavy metals in the root. Dandelion leaves sampled at the SP1 contained the lowest content of metals compared to the other SPs.

Soil pH value was in the range 6.0-6.5 for all the analysed samples (N=18, data not presented in Table 1).

Table 1. Concentration of heavy metals (mg kg^{-1} dry weight) in soil and parts of dandelion

Sampling point	Sampling period	Soil				Plant material									
						R	L	R	L	R	L	R	L	R	L
		As	Pb	Cu	Zn	As		Pb		Cu		Zn		Cd	
1	April	2.1	3.8	263.5	11.0	<LD	<LD	5.1	3.9	124.4	69.5	48.0	34.2	<LD	<LD
	May	18.5	12.1	258.7	103.0	<LD	<LD	7.9	2.2	78.6	31.3	43.3	26.6	<LD	<LD
	June	14.6	11.1	233.4	101.8	<LD	<LD	5.1	1.8	66.7	37.9	42.3	25.7	<LD	<LD
2	April	**131.2**	85.5	378.6	152.5	<LD	4.5	3.8	11.2	82.4	190.7	71.8	**111.8**	0.9	**0.9**
	May	105.5	**86.6**	395.4	157.9	4.9	<LD	12.3	6.9	238.8	108.9	81.8	83.0	0.9	0.8
	June	22.6	58.0	303.6	**194.3**	<LD	<LD	2.2	7.2	68.4	101.1	61.6	76.0	0.7	0.7
3	April	12.3	18.8	150.9	105.1	**15.6**	5.6	**198.6**	**33.3**	**733.1**	182.8	**86.7**	60.2	**1.4**	<LD
	May	12.6	23.3	179.5	112.1	6.9	<LD	51.0	15.5	265.2	110.2	77.9	52.2	0.8	<LD
	June	10.9	20.3	208.0	124.6	4.3	<LD	6.5	4.4	126.9	86.5	68.0	49.8	<LD	<LD
4	April	23.9	21.6	750.3	91.7	<LD	**9.5**	<LD	7.1	192.8	175.9	49.6	104.4	<LD	0.5
	May	20.1	23.2	1187.4	99.3	5.2	5.7	12.1	12.0	216.9	158.0	51.5	75.7	0.5	0.5
	June	15.5	23.8	**2147.0**	110.4	5.3	4.8	20.4	19.4	163.1	159.7	48.2	69.9	0.5	<LD
5	April	9.6	16.6	329.8	77.3	4.1	<LD	2.8	2.3	225.2	**257.2**	31.0	48.2	<LD	0.7
	May	9.4	12.8	404.7	73.7	<LD	<LD	<LD	3.8	152.2	214.5	39.3	46.0	<LD	<LD
	June	9.2	9.8	536.8	69.4	<LD	<LD	<LD	3.8	156.5	105.9	38.9	42.8	<LD	<LD
6	April	85.1	54.6	604.7	134.9	<LD	7.2	<LD	8.3	291.4	138.7	29.9	67.2	<LD	0.6
	May	48.7	35.0	456.3	110.0	9.1	7.8	7.7	10.3	169.6	144.9	65.9	65.8	0.7	0.6
	June	35.7	33.4	418.2	107.4	9.2	5.6	10.1	4.8	187.7	161.1	78.9	54.3	0.7	<LD

R – root; L – leaves; <LD – below the limit of detection; the highest metal concentrations showed in bold

According to Keane *et al.* [9] concentrations of Cu, Pb and Zn were significantly higher in dandelion leaves collected in fall compared to those in spring, while Malizia *et al.* [7] detected an increase of Cu, Pb and Zn concentrations in summer compared to spring, but a decrease of concentrations in fall compared to summer. Also, it was noted that concentrations of Cu and Zn in root and Zn in soil increased from spring to fall [7]. Keane *et al.* [9] found that Zn concentrations in dandelion leaves collected in spring, and Pb and Zn collected in fall increase significantly as soil level of these metals increases. Malizia *et al.* [7] noted that dandelion linearly accumulated Cu in leaves in respect to Cu soil content.

Heavy metal concentrations obtained from the literature are given in Table 2. Detected monthly concentrations of Pb, Cu and Zn in soil are significantly lower compared to mining areas [3,4], except at the SP4 where the detected concentration of Cu is similar (June, 2147 mg kg^{-1}). Regarding the plant material sampled along the Krivelj river, the average concentrations in root and leaves compared to mining areas [3,4], are lower for Pb, higher for Cu, and similar for Zn.

Table 2. Concentration of heavy metals (mg kg^{-1}) in dandelion from the literature

Sample	Pb	Cu	Zn	Cd	References (pollution source)
Soil	11280[a] 14635[b] 796[e] 662.5[g] 3.12[h]	2822[a] 3367[b] 136[e] 91.89[g] 8.77[h]	1096[a] 1188[b] 374[e] 239[g] 24.73[h]	0.85[a] 9.56[g] 3.76[h]	[a] Bini *et al.* [3] (Cu mine) [b] Wahsha *et al.* [4] (Cu mine) [c] Normandin *et al.* [5]
Root	99.8[a] 109[e] 17.2[f]	58[a] 95[e] 19.7[f]	67[a] 52;53[c] 211[e]	1.05[a] 7.67[d] 0.51[f]	(10 m and 100 m from road) [d] Gjorgieva *et al.* [6] (Pb smelter)
Leaves	120[a] 78.8[b] 22[e] 14.2[f] 11[h] 45[g]	64[a] 42.73[b] 51[e] 16.5[f] 12.81[h] 58.41[g]	101[a] 79[b] 79;70[c] 148[e] 56.23[h] 179.7[g]	1[a] 7.24[d] 0.36[f] 1.08[h] 3.11[g]	[e] Malizia *et al.* [7] (traffic) [f] Mahmood *et al.* [8] (traffic) [g] Keane *et al.* [9] (urban)
Steam	-	-	45;46[c]	-	[h] Keane *et al.* [9]
Flower	-	-	62;51[c]	-	(rural)

"-" No data

In Figure 2, the average three-month concentrations of Pb, Cu and Zn in soil, root and leaves of dandelion at six sampling points are shown, according to which the average biological factors were calculated (Table 3.): bioconcentration factor (BCF), translocation factor (TF) and bioaccumulation factor (BAC). From the further analysis As and Cd were excluded due to the missing values that have not been detected in plant material (root and leaves) or soil,which are necessary for the biological factor calculation.

At none of the sites, both BCFs and TFs were >1, indicating that dandelion cannot be used for phytoextraction purposes [13], i.e. it does not effectively translocate metals from soil to root (BCF) and from root to leaves (TF). Phytostabilization potential

(BCF>1, TF<1) is noted only at the SP3 for Pb and Cu, which means that dandelion retains these metals in root which was uptaken from soil, and do not translocate them into leaves [13]. Regarding the BACs, which was <1 for all the analysed samples, it can be concluded that dandelion is rather an excluder and not an indicator or accumulator of Pb, Cu and Zn. The obtained results are not in an agreement with the literature. Bini *et al.* [3] concluded that dandelion can be used as an indicator of heavy metal pollution of soil contaminated by copper mining processes. Gjorgieva *et al.* [6] found that dandelion is a bioaccumulator of Pb, Cu, Zn and Cd. Wahsha *et al.* [4] showed that dandelion can grow in the presence of moderate to high level of heavy metal content in soil and that it accumulates metals particularly in leaves, so it can be used in phytoremediation.

However, by analysing the monthly metal concentrations, there is a possibility for:

- phytostabilization of Pb (SP1 – April; SP3 – April and May), Cu (SP3 – April and May) and Zn (SP1 – April);
- bioindication of Pb (SP1 – April), Cu (SP3 – April) and Zn (SP4 – April);
- accumulation of Pb (SP3 – April) and Zn (SP1 – April).

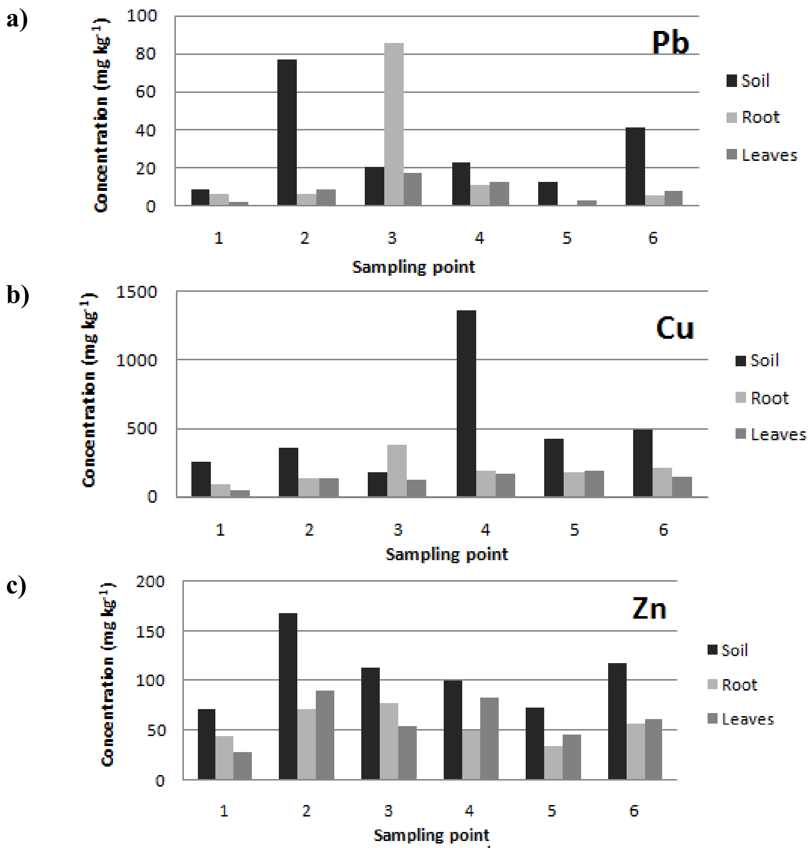

Figure 2. Average 3-month concentrations (mg kg^{-1}) of Pb **(a)**, Cu **(b)** and Zn **(c)** in soil, root and leaves of dandelion along the Krivelj riverbed

Table 3. Average biological factors calculated for 3-month period of sampling

Sampling point	Pb			Cu			Zn		
	BCF	TF	BAC	BCF	TF	BAC	BCF	TF	BAC
1	0.67	0.44	0.29	0.36	0.51	0.18	0.62	0.65	0.40
2	0.08	**1.38**	0.11	0.52	**1.03**	0.37	0.43	**1.26**	0.54
3	**4.10**	0.21	0.85	**2.09**	0.34	0.70	0.68	0.70	0.47
4	0.47	**1.18**	0.56	0.14	0.86	0.12	0.50	**1.67**	0.83
5	0.07	**3.55**	0.25	0.42	**1.08**	0.45	0.47	**1.32**	0.62
6	0.14	**1.32**	0.19	0.44	0.69	0.30	0.50	**1.07**	0.53

BCF – the ratio of metal concentration in the root to the concentration in soil; TF – the ratio of metal concentration in leaves to the concentration in root; BAC – the ratio of metal concentration in leaves to the concentration in soil; factors >1 showed in bold

CONCLUSIONS

Wastewaters from the copper production of the Bor, Krivelj and Cerovo mines and communal wastewaters of the town of Bor (Eastern Serbia) pose a great threat for the environment because they are discharged untreated into the Krivelj river which is a part of the Timok and Danube basin. Sampling of dandelion was carried out during 2012 in three monthly periods (April, May, June) along the Krivelj riverbed. Regarding the average three-month biological factors, dandelion did not prove to be a good bioindicator of soil pollution. However, based on monthly concentrations of Pb, Cu and Zn in soil, root and leaves, dandelion in some cases showed phytostabilization, bioindication and accumulation potential, which requires additional research.

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DUST EMISSIONS THAT CAN BE EXPECTED DURING THE EXPLOITATION OF LEAD-ZINC ORE FROM THE OPEN PIT AND ITS SUBSEQUENT PROCESSING IN THE FLOTATION PLANT

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ABSTRACT

The extraction and processing of minerals from surface mines can produce significant dust emissions as a result of site activities such as blasting, unpaved road haulage, loading, crushing and stockpiling. Expected amount of dust emission during production operations can be calculated on the base of the capacities and equipment.

In this paper are presented results obtained by methods defined in USEPA (United States Environmental Protection Agency) manual AP-42 (Compilation of Air Pollutant Emission Factors), and Emission estimation technique manual for mining, National pollutant inventory (NPI), Australian Government-Department of Sustainability, Environment, Water, Population and Communities, Version 3.1.

Key words: environment, dust emissions, lead-zinc ore.

INTRODUCTION

The process of exploitation and processing of mineral raw materials is unavoidably accompanied by adverse effects on the environment. The negative effects that have a lasting character are reflected in the disruption of the environment (changes in the physical appearance of the terrain), land degradation, destruction of autochthonous vegetation cover, changes in animal habitats, changes of water bodies, permanent loss of mineral resources, etc. In the category of temporary impacts can be classified effects that manifest during service life of mine and these include air and water pollution, increased noise and vibration, traffic congestion, etc.

The main pollutants in the air that can occur during the extraction and processing of mineral raw materials are particulate matters (dust). Dust is potentially hazardous to human health, the environment, the working conditions as well as the productivity of a mine. Dust is a generic term used to describe fine particles that are suspended in the atmosphere. According to the International Standardization Organisation (ISO) and British Standard Institute (BSI), dust is defined as small solid particles, conventionally below 75 μm in diameter, which settle out under their own weight but which may remain suspended for some time.

Dust can be generally expressed as total suspended particulate matters (TSP) or particulate matter PM_{10} or $PM_{2.5}$ fractions. Airborne particulate matter varies widely in its physical and chemical composition, source and particle size. PM_{10} particles (the fraction of particulates in air of very small size (<10 μm)) and $PM_{2.5}$ particles (<2.5 μm) are of major current concern, as they are small enough to penetrate deep into the lungs and so potentially pose significant health risks. Larger particles however, are not readily inhaled, and are removed relatively efficiently from the air by sedimentation.

Emissions of particulate matters (dust) occurred as a result of site activities such as blasting, unpaved road haulage, loading, crushing and stockpiling. Fugitive dust is often found deposited outside the mine boundaries or far away from major dust generation sources. Mine dust is typically less complex in its composition, consisting mainly of particles from exposed soil and rock.

Modelling techniques are increasingly being employed to give advanced warning of potential problem emissions in addition to providing a basis for future planning applications such as developing emission control strategies, determining applicability control programs, ascertaining the effects of sources and appropriate mitigation strategies, and a number of other related applications. The most common approach to assessing and monitoring pollutant loads is through pollutant release databases, with such systems now operating throughout Europe, North America and Australia.

In this paper are presented results obtained from the case-study of future extraction of lead-zinc ore from the open pit mine "Kizevak" and subsequent processing of ore in the floatation plant in Rudnica, municipality of Raska. These results are obtained by methods defined in USEPA (United States Environmental Protection Agency) manual AP-42 (Compilation of Air Pollutant Emission Factors), and Emission estimation technique manual for mining, Australian Government-Department of Sustainability, Environment, Water, Population and Communities, Version 3.1.

TECHNICAL AND TECHNOLOGICAL DETAILS

The open pit mine "Kizevak" and the floatation plant in Rudnica are located in south-westerner Serbia, in Raska municipality, near to administrative border with Kosovo. Exploitation of lead-zinc ore from "Kizevak" was carried out, with short breaks, during the period from 1986 to 2002. After more than a decade of inactivity, it is planned to continue exploitation and processing the ore. Planned continuation of exploitation of lead-zinc ore from the open pit mine "Kizevak" and further processing in the flotation plant in Rudnica, prompted a need for technical documentation among which are the Preliminary mining project and the Environmental impact assessment study.

In the Preliminary mining project technological process of exploitation and processing of the ore were considered as well as proposed equipment to be used. In the Environmental impact assessment (EIA) Study environmental factors and possible negative impacts of planned exploitation were analyzed. Measures to prevent or reduce harmful effects on the environment and human health were analyzed, too.

Based on capacity and mobile equipment proposed in the Preliminary mining project, the EIA Study was conducted assessment of the expected amount of dust from the mobile equipment, which will be presented in this paper.

The planned exploitation capacity is 450,000 tons per year, with the prospect to work 300 days per year in two shifts. It is anticipated that the most of the equipment in the mine and the flotation plant will have approximately 5.000 working hours per year.
The main activities carried out in the open pits that can lead to the occurrence of dust emissions are: the removal of vegetation and the topsoil, overburden and ore drilling and blasting, overburden and ore loading, transport and storage of overburden, excavation, and transport of ore.

Mobile equipment that will be used in production process includes: Atlas Copko rotary hammer drills with compressors, ammonium-nitrate powder explosives (in parts of the mine where boreholes are dry), water plastic explosives (in boreholes with water), tracked excavator with the front bucket capacity of 7 m^3 for overburden loading, four dumpers with load capacity of 50 - 60 t (Caterpillar 773 class) for transport of overburden to the landfills and four 20 - 25 t tippers to transport the ore to the flotation plant. In addition, two bulldozers (one Caterpillar D8 class and one Caterpillar D7 class) will be used on the mine as well as grader, two 2-5 t trucks, one 7.5 m^3 tank truck, backhoe and other auxiliary equipment. There will be no crushing of ore on the open pit mine.

The main activities carried out in the floatation plant that can lead to the occurrence of dust emissions are: crushing of ore, floatation and thickening, ore beneficiation, workshop operation and rehabilitations.

According to the planned technology flotation plant consists of the following technological units: primary and secondary crushing, tertiary crushing with washing and grading of ore, grinding and classification, flotation concentration of Pb and Zn minerals, drying of Pb and Zn concentrate, system for the preparation, distribution and metering of reagents and systems for the regulation and control of the equipment and process.
Primary and secondary crushing will be conducted in a jaw crusher, and tertiary in cone crusher. Washing of the ore will be carried out in drum washing machine and grading in sieve, classifier, and lamellar thickener. Transport of materials will be carried out by belt conveyors and slurry pumps and grinding in a cylindrical ball mill operating in closed circuit with a hydrocyclone battery and Derrick sieve (used for additional grading of hydrocyclone's sand). Coarse flotation of lead and zinc minerals will be conducted in four floatation cells, and control flotation in six floatation cells. Afterwards, lead concentrate and zinc concentrate will be separated from the final tailing which will be hydraulically transported to the tailings dam.

Generalised facility process diagram for open-cut metallic ore mining is presented in Figure 1.

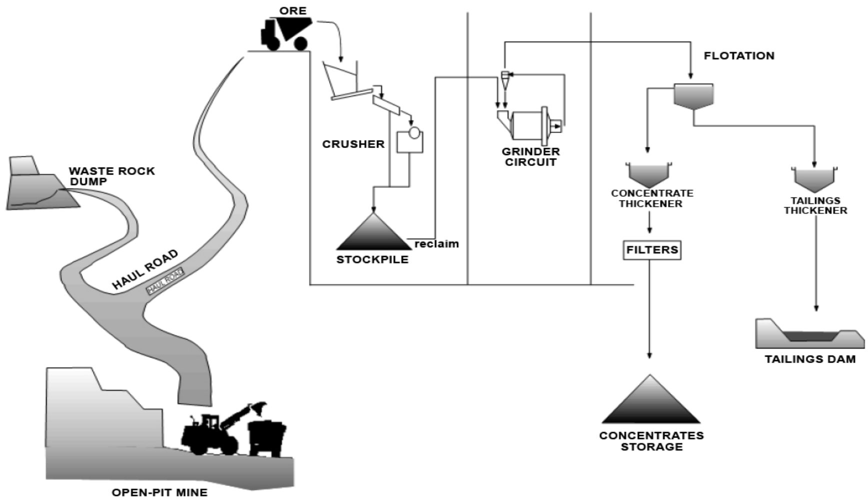

Figure 1. Open-cut metallic ore mining facility process diagram

METHODOLOGY

Estimation of amount of dust emitted by the mobile equipments from the open-pit "Kizevak" and by the equipments and processes from the floatation plant in Rudnica, have been carried out based on USEPA (United States Environmental Protection Agency) Manual AP-42 (Compilation of Air Pollutant Emission Factors) and Emission estimation technique manual for mining - Australian Government-Department of Sustainability, Environment, Water, Population and Communities, Version 3.1 in January 2012th year.

In most cases fugitive air emissions can be estimated using emission factors combined with site-specific information such as the silt and moisture content of material being handled. An emission factor is a tool used to estimate emissions to the environment. It is a representative value that attempts to relate the quantity of a pollutant released to the atmosphere with an activity associated with the release of that pollutant. These factors are usually expressed as the weight of pollutant divided by a unit weight, volume, distance, or duration of the activity emitting the pollutant.

The general equation for emissions estimation, if no emission controls are used, is:

$$E_{i\,(kg/yr)} = [A_{(t/h)} \text{ x } OP_{(h/yr)}] \text{ x } EF_{i\,(kg/t)} \qquad (1)$$

where: $E_{i\,(kg/yr)}$ - emission rate of pollutant i, (kg/yr); $A_{(t/h)}$ - activity rate, t/h; $OP_{(h/yr)}$ - operating hours, h/yr and $EF_{i\,(kg/t)}$ - uncontrolled emission factor of pollutant i, kg/t.

The most comprehensive compilation of emission factors is that in the USEPA document referred to as AP-42. Chapters from AP-42 are updated periodically and are available from the USEPA's website.

Emission factors can be used to estimate emissions of TSP and PM_{10} to the air from various sources. The main parameters that are the basis for the assessment are: exploitation capacity and equipment to be used, material to be excavated, type of roads, wind speed, etc.

Mining operations can be considered as a series of unit operations, and for each operation AP-42 provides emission factor equations and default emission factors for emissions of both TSP and PM_{10}. The emission equations should be used where site specific data such as silt and moisture content is available. Otherwise, the default emission factors can be used.

RESULTS AND DISCUSSIONS

Based on equations from EPA Manual AP-42 and Australian NPI Emission estimation technique manual for mining, in the Environmental Impact Assessment Study (EIA) were calculated emission factors for TSP and PM_{10} for every specific operation and equipment that will be used on the open-pit mine "Kizevak" and the floatation plant in Rudnica.

Values of the emission factors, mine capacity, site characteristic and other factors were used to calculate amounts of TSP and PM_{10} emissions which should be expected during future exploitation and lead-zinc ore processing for each specific operation. The estimated emission values for the most important sources from open-pit mine are presented in Table 1.

Table 1. The estimated emissions for TSP and PM_{10} in the open pit mine "Kizevak"

Work activity	Equipment	TSP emission	PM_{10} emission
Drilling and blasting	Mining drilling set and explosives	6.537 kg/yr	3.422 kg/yr
Dumping of overburden	Trucks	27.101 kg/yr	9.711 kg/yr
Using a bulldozer	Bulldozers	61.750 kg/yr	18.750 kg/yr
Loading of trucks and dumpers	Excavators and loaders	79.411 kg/yr	38.351 kg/yr
Landfills	Wind erosion	105.120 kg/yr	52.560 kg/yr
Unpaved roads	Dumpers (full and empty trucks)	193.410 kg/yr	59.010 kg/yr

As can be seen from the presented results the most prominent sources of fugitive dust emissions for selected equipment and site specific conditions are truck transport on unpaved roads and wind erosion from stockpiles and landfills.

Particulate matter emissions result from metallic mineral plant operations such as crushing and dry grinding ore, drying concentrates, storing and reclaiming ores and concentrates from storage bins, transferring materials, and loading final products for shipment. At most metallic mineral processing plants, each process operation requires several types of equipment. Emissions from these various pieces of equipment are often ducted to a single control device.

Applying emission factors on planed capacity, technology and equipment in floatation plant in Rudnica gave the values for estimated dust emission for partially wet ore which are presented in Table 2.

Table 2. The estimated emissions for TSP and PM_{10} in floatation plant in Rudnica

Work activity	Equipment	TSP emission	PM_{10} emission
Primary crushing	Jaw crusher	47.250 kg/yr	5.400 kg/yr
Secondary crushing	Jaw crusher	141.750 kg/yr	16.200 kg/yr
Tertiary crushing	Cone crusher	321.750 kg/yr	20.250 kg/yr
Handling, transferring, conveying	Belt conveyors	14. 625 kg/yr	7.200 kg/yr

The values of emissions from primary, secondary and tertiary crushing are obtained based on weight of material entering primary crusher. The value of emissions from handling, transferring and conveying are obtained based on weight of material transferred which includes every loading or unloading operation and each conveyor belt transfer point.

The most prominent sources of fugitive dust emissions for observed plant is tertiary crushing. Test data collected in the mineral processing industries indicate that the moisture content of ore can have a significant effect on emissions from several process operations. High moisture generally reduces the uncontrolled emission rates, and separate emission rates are provided for primary crushers, secondary crushers, tertiary crushers, and material handling and transfer operations that process high-moisture ore. For this study partially wet ore with moisture content of 3-6% was used.

The contributions to overall emission for all working activity on the open-cut min "Kizevak" and from floatation plant in Rudnica are presented in Figure 2.

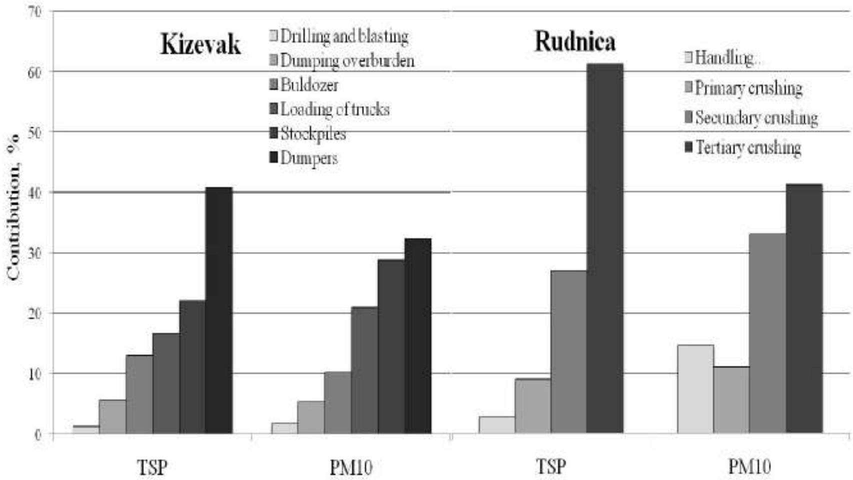

Figure 2. Contribution of the most important TSP and PM_{10} emission sources on the open pit mine "Kizevak" and floatation plant i Rudnica

Out of all it can be concluded that for the planed project, crushing activities and dust from unpaved roads represent the greatest burden on the environment.

However, it should be noted that presented emission levels could occur only in the case when no dust control equipment is used. There are a number of ways in which dust emissions from mining operations can be controlled (for example spraying, dust extraction, creating barriers, using wet scrubbers or baghouses, etc.). Application of some of these conventional dust control techniques should significantly reduce dust emissions.

CONCLUSION

Dust generated from mining activities is a major issue with impacts upon the environment, human health, safety and productivity of a mine. Dust related issues are difficult to approach, they are influenced by many parameters (i.e. climatic conditions, mechanical processes, materials properties, control techniques) and it is difficult to establish an efficient prevention and control methodology.

Nevertheless, emission factors can provide an insight into the magnitude of emissions from different types of dust emission sources and highlight the most problematic areas within production process where the highest emission levels can be expected. They are given in order to assess the expected conditions on the basis of experiences from a number of open pit mines of metallic raw materials. It should be noted that emission factors give just an empirical estimation based on site specific data and should be regarded as approximate values, but they can provide a basis for the planning of measures for environmental protection. The actual values can only be obtained by measurements during exploitation.

Analysis of the results obtained for the open pit lead-zinc mine "Kizevak" and floatation plant in Rudnica show that the highest levels of dust emissions can originate from overburden and ore transport by heavy trucks, wind erosion from the stockpiles and other exposed areas in the mine and from crushing activities in floatation plant. Application of some conventional dust control measures like water spraying and filtering should greatly reduce these emissions.

Acknowledgements

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GROUND VIBRATION DUE BLASTING AT OPEN PIT MINES BANOVICI

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ABSTRACT

Ground vibrations are seismic movements in the ground caused by blasting in open pit mines. The energy released from a blast propagates in all directions from the hole as seismic waves with different frequencies. The energy from these seismic waves is damped by distance. The waves with the highest frequency are damped fastest at short distances, while the waves with lower frequencies are damped slower and reach longer distance. The size of the ground vibrations depends on many factors. By selecting the right blasting method and correct drilling and firing patterns the size of the ground vibrations can be controlled.

Key words: blasting, pit mine, seismic waves, ground vibrations.

INTRODUCTION

At "Banovici" open pits "Grivice" and "Turija", the exploitation is done by following works: drilling, blasting, digging and loading, hauling of overburden and coal, as well as the disposal of overburden. Coal exploitation in the open pits is done with classic discontinuous complex, which includes drilling machines, shovels (electric and hydraulic), draglines and rigid trucks with auxiliary equipment (bulldozers, graders, wheel loaders etc.). Over the main coal layer, there are deposits of layered roof of marl. There are several predominated marls: filled marl, layered marl, dark marl, bright spotted marl, clayey marl and calcareous marl. Overlying sediments, in their different variations, can be observed in the benches of the open pit and their thickness is around 150 m over the coal layer. The conditions in which the mining operations are performed, especially works on the preparation of the rock for digging and loading are very complex. Particularly evident problems are at higher benches in humus material and clayey marl where the seismic restrictions caused by the vicinity of residential buildings additionally complicate mass blasting works. The restrictions caused by seismic impact during blasting on the upper benches cause the appearance of oversized pieces, which complicates the process of digging, loading and hauling of materials.

DESCRIPTION OF DRILLING AND BLASTING OPERATIONS

Holes drilling for mass blasting of overburden and coal is done by Griphon 5C and Hausher HBM-120 with a diameter Φ110-115 mm. Overburden drilling for loading by shovels is done at the height of a bench H = 12 m, and the length of clean mine holes is about 13 m. The width of a digging overburden block is determined on the basis of the technical characteristics of shovels. The inclination of blastholes (vertical) is 70º. The geometry of drilling also depends on the technical characteristics of shovels, the type of explosives to be used for mining and geotechnical properties of rocks intended for blasting [1]. Holes drilling are done with chess and square layout of holes, depending on the "quality" of rock material. Overburden and coal blasting is done by using ANFO and emulsion explosives. The maximum quantity of explosives at the mine hole is up to 77 kg for ANFO and 99 kg for emulsion explosives. As an initial explosive high brizant explosive and TNT boosters are used. Explosive charge in the holes is continuous and in conditions where it is necessary and doable it is discontinuous. Non-electric initiation system is applied for activating the explosive charge. The filling of blast holes is mechanized. Rock blasting is done by shaking, while the turning down method is applied only in exceptional cases when the height of benches exceeds the height of a shovel's range or if the blasted material is handled by loaders. Overburden blasting is done in conditions of open blocks with 3-4 rows of blast holes. There are many factors which effect vibration transmission. These factors are: burden, spacing, subdrilling, stemming depth, type of stemming, bench height, number of decks, charge geometry, powder column length, rock type, rock physical properties, explosive energy, actual delivered energy, number of primers, primer composition, boosters, geologic factors, number of holes in a row, number of rows, type of initiator, row to row delays, inhole delays, initiator accuracy, distance to structure and face angle to structure [2, 3, 4] . The above listing indicates the importance of the execution of the blast design in the field. Changes in burden, spacing, stemming, powder column length, number of rows, number of holes, and types of delays can change the vibration generated. Precise execution of the blast design with limitations of the tolerances and deviations from the design hole to hole will drastically reduce vibration. Vibration records will begin to resemble one another if the variability in the design parameter is controlled.

THE DEVELOPMENT OF MINING OPERATIONS

The satellite images of the open pit mine "Grivice" and the disposition of the surrounding residential buildings are shown on Figure 1. The direction of the future mining activities is shown by arrows on the figure. Also, the position of the objects on which seismic measurements are carried out is presented with circle (MO).

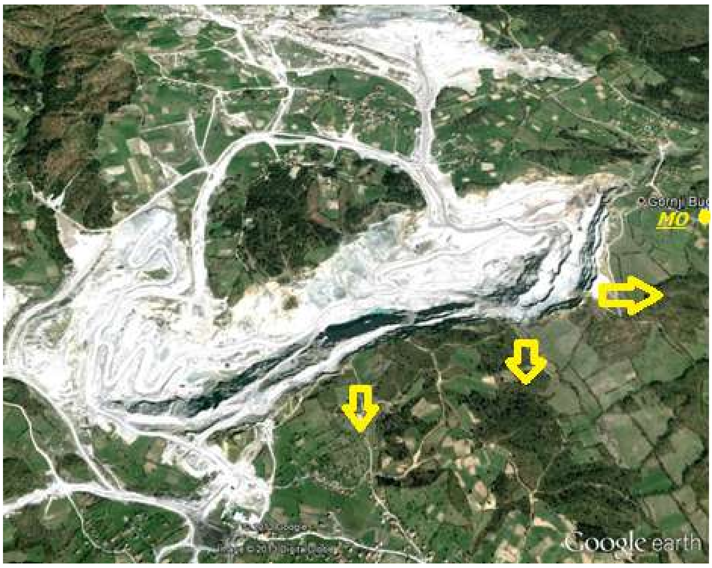

Figure 1. Satellite image of the Open Pit Mine "Grivice"

It can be seen from the image that in the immediate area of the open pits there are buildings. These buildings were built in different constructive systems. The following chart shows the share of residential buildings according to their constructive systems.

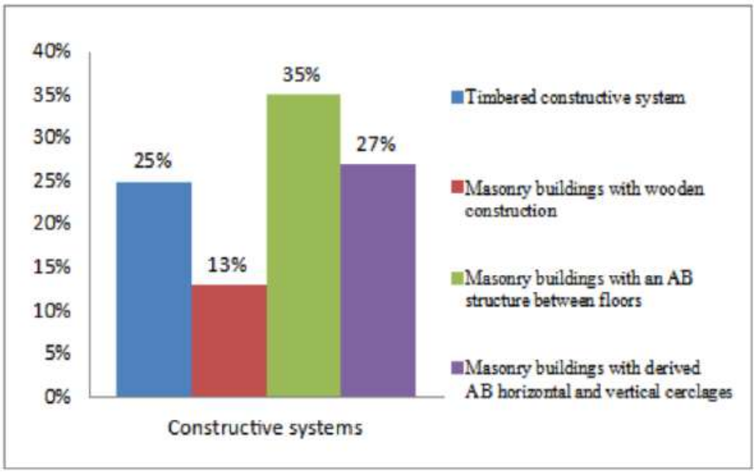

Figure 2. The share of residential buildings by their constructive systems

Masonry Buildings with Wooden Construction between Floors (figure 3a) **-** Interior and exterior bearing walls of this construction system are made on concrete strip foundation or stone foundations so called singles, which are placed in the depth of 40-60 cm. The walls are built of full bricks which are 25-38 cm thick, brick blocks or slag-concrete blocks (20-25 cm thick) and cement mortar. The walls are fixed by concrete horizontal beams in the width of the walls and their average height is 20 cm. The walls inside the house are usually built of full bricks (12 X 6.5 cm). They are bounded by cerclage or subsequently built and attached to bearing walls by iron rods. The construction between floors is made of wood.

Timbered Constructive System is the traditional method of the construction of residential buildings in this area (figure 3b). Most of these houses were built before 1970. These buildings generally do not have the foundation; they were built on four basic wooden beams that rely on several large pieces of stone called "tower". The structural skeleton of the houses was made of wood and it was filled with the mixture of wood, straw and mud or with bricks, slag and concrete.

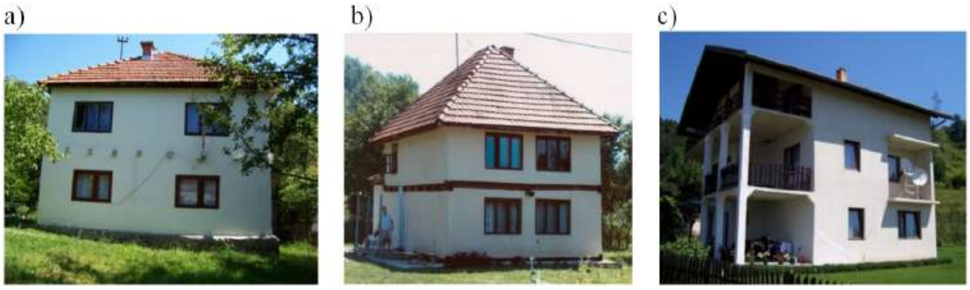

Figure 3. Residential buildings: a) with wooden construction between floors; b) built in timbered system; c) with derived AB horizontal and vertical cerclages

Masonry Buildings with Derived AB Horizontal and Vertical Cerclages (figure 3c) **-** This kind of buildings is built on iron-concrete strip foundation or on "single" foundations which are 60 to 80 cm deep. The basic system of these masonry structures are load-bearing walls in both orthogonal directions of the building made of bricks, blocks or "siporex" bounded in the height of solid structure between floors by horizontal beams made of iron rods and concrete which when crossing open spaces act as lintels.

Masonry Buildings with an AB Structure Between Floors - This kind of buildings is built on concrete strip foundation or on "single" foundations which are 40 to 80 cm deep. Bearing and inside walls are made of full bricks, brick blocks and slag-concrete blocks, and they are bounded by horizontal beams and lintels above windows and doors made of iron rods and concrete. Each of these different structural systems reacts differently on seismic waves created after mass blasting. To determine the reaction of buildings on negative impact of mass blasting seismic surveys were carried out.

MEASUREMENT EQUIPMENT

The seismic measurements have been done by using BlastMate III and MiniMate Plus instruments with required equipment. These instruments measure displacements, velocities, acceleration, oscillation frequencies and air shock waves. They consist of 3-axial geophone, a microphone and a recorder. Each transducer measured velocities on three mutually perpendicular axes (v_x, v_y, v_z) corresponding to a radial, transverse, and vertical component [1, 2, 3]. The results are presented in a report form, for the transversal, longitudinal and vertical waves. Also, the instruments measure the time of origin and the value of the summary waves. The particle velocity at a point is the vector sum (1) of the three components at the same instant of time. The peak value, known as Peak Particle Velocity (PPV), is the highest value of the vector sums [2, 3].

$$v = \sqrt{v_x^2 + v_y^2 + v_z^2} \tag{1}$$

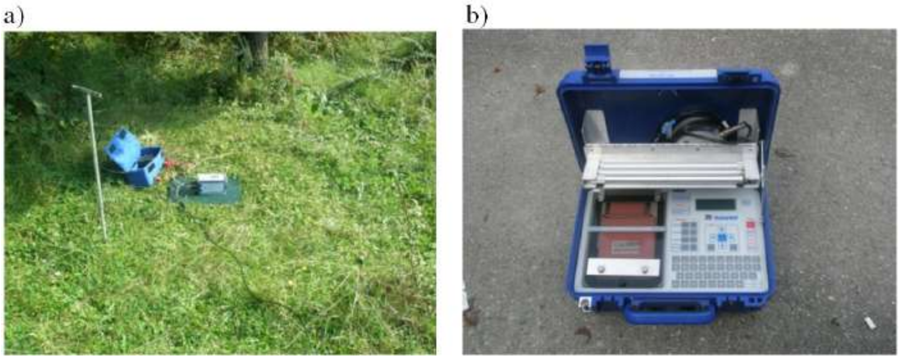

Figure 4. Seizmographs a) MiniMate Plus; b) BlastMate III

The measurements of ground vibration were carried out on the buildings constructed in different structural systems, by placing geophones (sensors) at the foundation, on the ground floor and upper floors of the buildings. The different conditions in which mass blasting was done were analyzed - on the lower and upper benches, at overburden and coal mining as well as the different distances of the observed building in relation to the minefield. The placing of geophones was carried out by sticking pins into solid ground at the building foundation. The geophones placed on the floors of the upper floors of buildings were covered by heavy objects in order to make better contact with the ground and to achieve accurate measurement. In this study two eight-channel seismographs are used which during the arrival of seismic waves registered the speed, acceleration, displacement and frequency of the waves. The data are reproduced in a software package that provides the ability of interpretation criteria according to different standards. On figure 5 and 6 presented data (the bar graph report dialog) of the seismic measured at foundation of a residential buildings for minefield number 109/12 and seismic data measured on the 3rd floor of a residential building same minefield respectively.

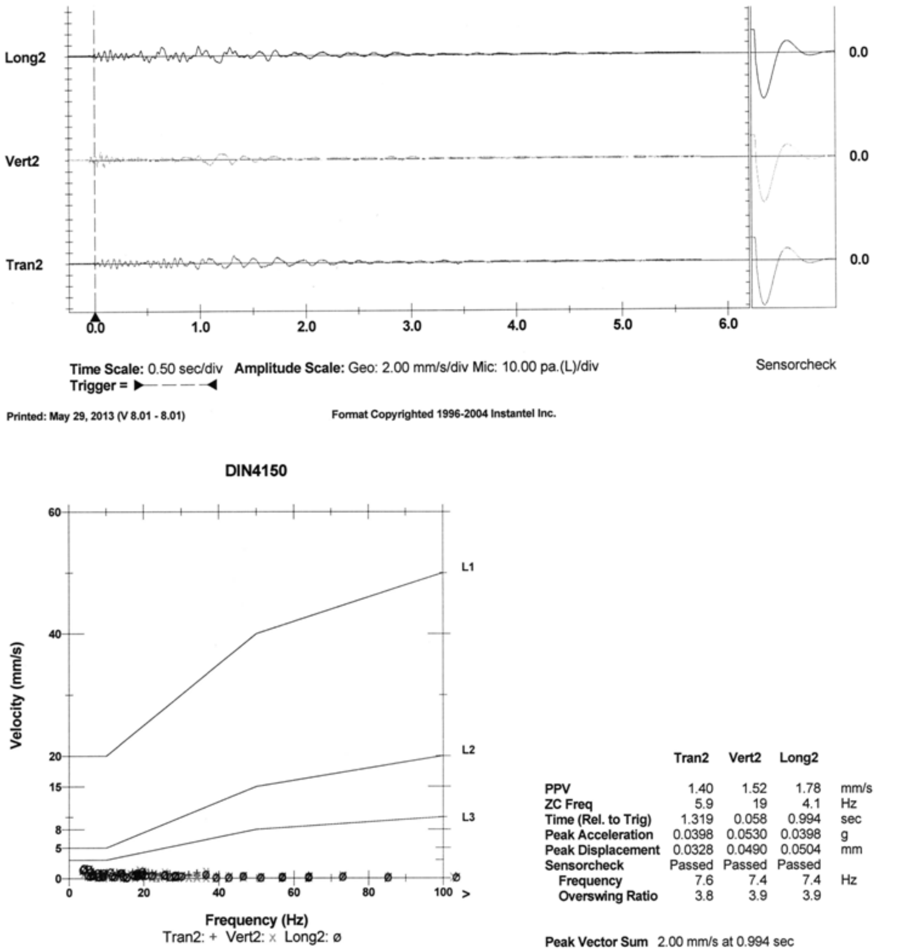

Figure 5. Seismic data measured at foundation of residential buildings

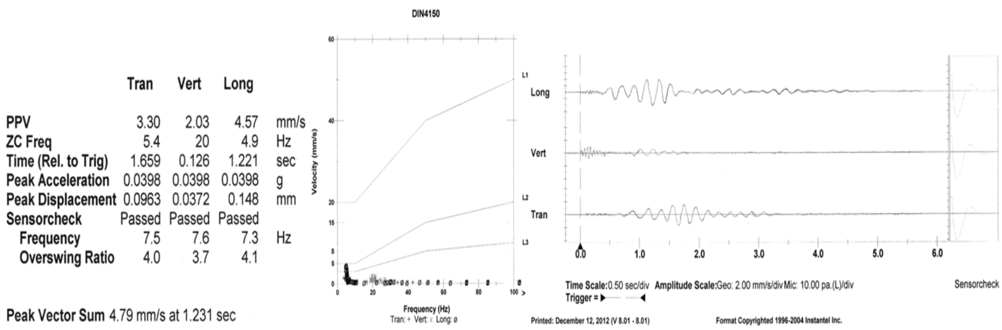

Figure 6. Seismic data measured on the 3rd floor of residential buildings

DISCUSSION AND CONCLUSION

Blasting operations at the "Banovici" open pit mines are performed in complex conditions. This complexity is reflected in the heterogeneity of overburden, the appearance of groundwater, the deposit discontinuity etc. The nearness of residential buildings and marl characteristics additionally complicate the conditions in which the mining operations are performed, especially works on the preparation of the rock for digging and loading. Particularly evident problems are at higher benches in the humus material and clayey marl. In order to overcome the problems and improve the production process the experimental mining and the analysis of seismic impacts of blasting are performed. This research examines the reaction of surrounding buildings on seismic impact.

These considerations are made on the basis of the seismic measurements and the following observations are determined:

- The different structural systems of buildings differently react on seismic impact. The toughest to seismic effects are masonry buildings with derived AB horizontal and vertical cerclages. The most unstable reaction showed buildings built in timber structure.
- With the increasing number of floors of the building, regardless of the structural system, seismic impact increases. This increase essentially reflects on the peak particle velocity and duration of the seismic waves that meets building. The differences in other seismic parameters (frequencies, acceleration, and displacement) are evident in the components of a resultant wave. These differences need to be further explored.
- The reducing of the negative impact is directly dependent on the amount of explosives currently activated, and especially of explosives milliseconds activated. The reducing of these amounts is provided by reducing the height of benches and by discontinuously filling of the mine holes.
- The introduction of new scheme of minefield initiation can contribute to the reduction of seismic impacts. The experimental blasting in order to study the scheme of blasting with discontinuously filling of the mine holes is still performed. The first preliminary results are favorable.
- The vibration frequency component is key in developing blast design [5]. The analysis of the seismic measurements report indicate that the seismic waves caused by blasting in the concrete "Banovici" mine conditions have mostly predominantly low frequencies. The dynamic response of structures to ground vibrations is its natural frequency and damping characteristics of the structure. The natural frequency is the frequency at which any structure vibrates freely after stopping ground motion, and varies between 4:20 Hz (Siskind and others 1980; Moderis 1978., Adhikari et al 1989., Pal Roy 1998.) [6].
- The amplification factor is maximized and prevails when the frequency of ground motion reaches the natural frequency of a structure. The structure at these frequencies absorbs most of the energy and oscillates for a longer period, which may result in structural damage. As stated, seismic waves frequencies measured on the ground are dominantly low. Taking into account the above, one

can make a general conclusion that the response of structures based solely on the speed of fluctuations has shortcomings. More reliable estimates of seismic impacts can be gained by a combination of the speed and the frequency of oscillation of the seismic waves. Damage can be caused by long duration vibration waves with high peak particle velocities and low frequencies [4, 5]. The most practical way to reduce the negative seismic impact is to, at the upper benches where the clay marl and humus material predominate, perform digging and loading masses by shovels with greater force and without blasting.

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THE REVIEW ON PET RECYCLING IN THE LAST DECADES

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ABSTRACT

As plastics recycling grows around the world, it would be interesting to observe and analyze its development in the last decades. As USA is one of the leading countries in the specified field, the data from this country were taken for analysis and compared to chosen countries on other continents. The polyethylene terephthalate (PET) was taken as the observed recycling material, because it is widely spread and of significant common use. As a solution to the problem of the trade of the recycled PET, the global market situation was also taken into consideration.

Key words: PET, recycling, recycling rate.

INTRODUCTION

Plastics recycling continues to grow around the world, although it has declined to some extent in the United States in the last several years. Interest in and availability of biodegradable plastics has increased substantially in the last decade. As concern about high oil prices and global climate change increases, sustainability of products and processes is becoming a concern, fueling increased interest in biobased products of various kinds, including plastics. These biobased plastics may or may not be biodegradable, just as biodegradable plastics may or may not be biobased. The main focus of this study is on the United States, but some comparisons between the United States, Canada, and selected countries in Europe and Asia are included, along with discussion of important developments affecting recycling and use of (PET) as one of the most common recycling material.

RESULTS AND DISCUSSION

The largest source of PET in the municipal solid waste (MSW) stream in the United States is packaging, as shown in Fig. 1. For many years, PET was the most recycled plastic in terms of both total amount and recycling rate, largely due to recycling of soft-drink bottles. However, as the use of PET in other types of bottles grew, the recycling rate fell. Also, recycling rates for high-density polyethylene (HDPE) increased significantly with the addition of HDPE bottles to many curbside and drop-off recycling programs. Consequently, HDPE recycling began to exceed PET recycling. For 2003, American Plastics Council statistics show the total amount of PET bottles recycled again exceeding PET bottles. [1] The US Environment Protection Agency (EPA) values, which report on containers rather than bottles only, still show HDPE with a larger amount of recycling in 2003.

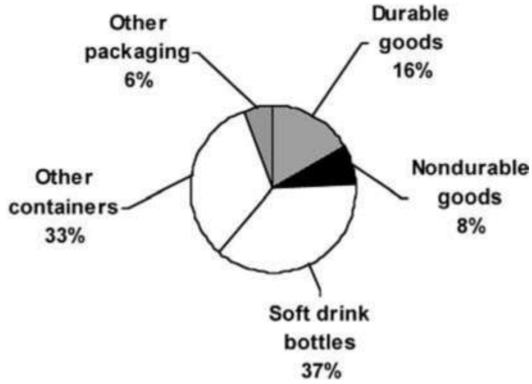

Figure 1. PET in U.S. municipal solid waste

In the United States, in 2003, 14 companies produced 517 million pounds of recycled PET flake from postconsumer bottles. The four largest companies accounted for nearly three quarters of the recycled PET. Capacity utilization was low, approximately 59 %, illustrating the supply difficulties that continue to plague this industry. Nearly 40 % of the total amount of bottles recovered for recycling, 321 million pounds of the 837.9 million pounds total, were exported, mostly to Asia. [1] The National Association for PET Container Resources (NAPCOR), reports very similar values: a total of 841 million pounds of postconsumer bottles recycled, 321 million of this sold to exporters, and 62 million pounds of postconsumer bottles imported. Of the exports, NAPCOR reports that 22.5 million pounds went to Canada and the remainder to China. [2] Soft drink bottles remain the largest single use of PET in packaging, but nonbeverage bottle use continues to grow at a faster rate, so the aggregate use of PET in "custom" (nonsoft- drink) bottles exceeds use in soft drink bottles, accounting for 57 % of available PET bottles. [1] Use of small size soft drink bottles has grown, while use of liter and larger size bottles has declined. Fruit juice and water represent a sizeable segment of custom bottle use. Use of PET in beer bottles has grown less than had been anticipated. NAPCOR estimated that a total of 4.3 billion pounds of PET bottles and jars were available for recycling in the United States in 2003. [2] The American Plastics Council (APC) reports similar numbers, with a total of 4.0 million pounds of PET bottles. [1] The EPA reports somewhat different numbers for the soft drink/custom bottle split, estimating that 53 %

of the 4.0 billion pounds of PET bottles and containers in the MSW stream in 2003 were soft drink bottles. The reason for this discrepancy in reported bottle types is not clear.

EPA reported an overall recycling rate for PET containers and packaging of 18.8 % in 2003, a total of 820 million pounds; a PET container recycling rate of 18.4 %, for 740 million pounds; and a PET soft drink bottle recycling rate of 25.2 %, for 540 million pounds. APC reports a PET soft drink bottle recycling rate of 30.2 % in 2003, 531.8 million pounds, and a custom bottle recycling rate of 12.1 %, 306.1 million pounds, for a total PET bottle recycling rate of 19.5 %, 837.9 million pounds. [1] NAPCOR reported a PET bottle recycling rate of 19.6 % in 2003, for a total of 841 million pounds. [2] Recycling rates for PET have been falling in the United States since 1994 (Fig. 2).

EPA reports a recycling rate for plastics in durables of 3.9 % in 2003, a total of 330 thousand tons, but has not broken this figure down by resin type since 2000That year, a PET recycling rate of 7.7 % was reported for durable goods. [3] No significant recycling of plastics in nondurables is reported. In the noncontainer segment, EPA reported a recycling rate for PET packaging of 23.5 % in 2003. The overall PET packaging recycling rate was 18.8 %, and the overall recycling rate for PET in municipal solid waste was 14.3 %. [4]

In contrast to the declining rates for PET bottle recycling in the United States, PET recycling continues to increase in much of the world. For example, Ontario reported a PET bottle recycling rate of 50 % in 2003.[5] The Japanese Council for PET Bottle Recycling reports that the aggregate recycling rate for designated PET bottles (soft drinks, soy sauce, and liquors) reached 61.0 % in 2003 after starting at only 0.4 % in 1993. (Fig. 3). Designated bottles accounted for more than 93 % of all PET bottles produced in Japan in 2003. The recycling rate calculated on the basis of all PET bottles, rather than designated bottles, was 56.7 % in 2003. PET bottles are collected separately from other wastes in 2891 communities, 91.6 % of all municipalities in the country. [6,7]

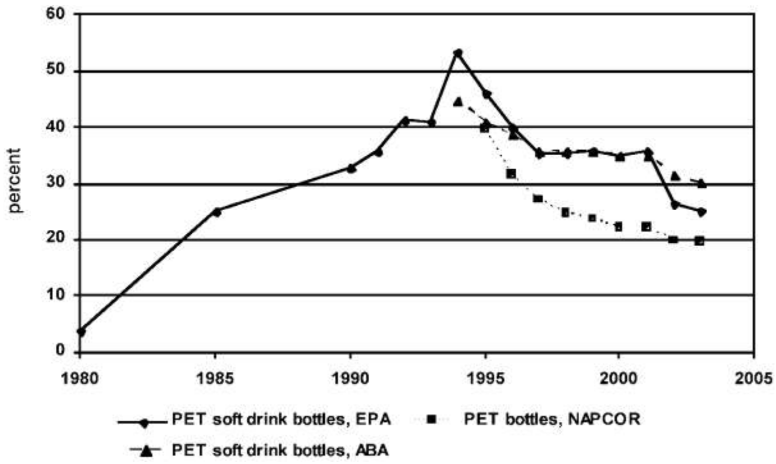

Figure 2. PET recycling rates in the United States up to 2005. [5]

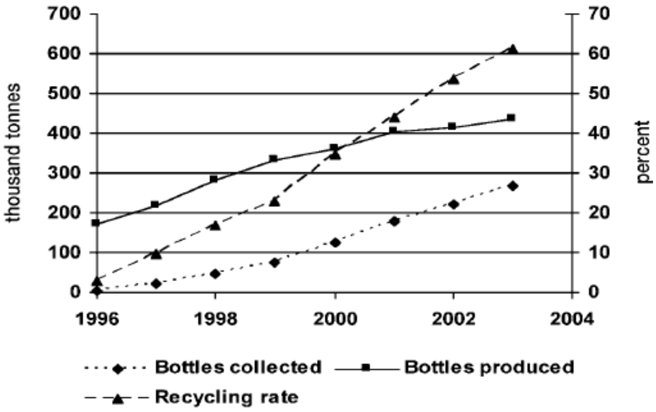

Figure 3. PET bottle recycling in Japan [6,7]

In Europe, Petcore reports that 665,000 tones of postconsumer PET were recycled in 2004, up 8.5 % from 2003 and continuing a well established pattern of growth (Fig. 4). The recycling rate was reportedly 30.0 %. Germany, France, and Italy accounted for 60 % of the total collected, but Ireland, Poland, and Spain had significant growth. By 2010, Petcore expects more than 1 million tons of European PET to be collected and recycled. [8]

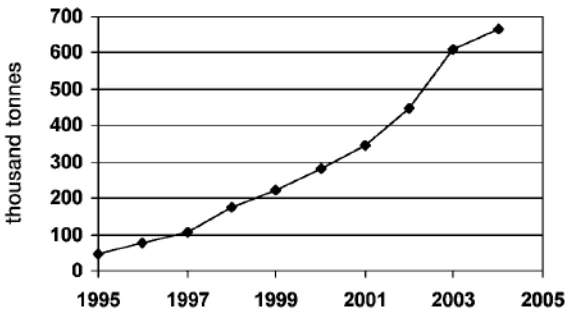

Figure 4. ET bottle recycling in Europe up to 2005 [8]

Nowadays, United States reclaimers reported average yield losses ranging from 25% for deposit bottles to 35% for curbside material and 29% for California CRV. After applying the yield losses to the various fractions purchased, it was determined that the clean flake equivalent of the 263991 tons of postconsumer PET bottles shipped export to all locations was 179623 tons. As calculated above, the resulting PET utilization rate was 21.1%, a slight rebound from 2011, but still far below the recycling rate, illustrating continuing low bale yields as previously mentioned. [9]

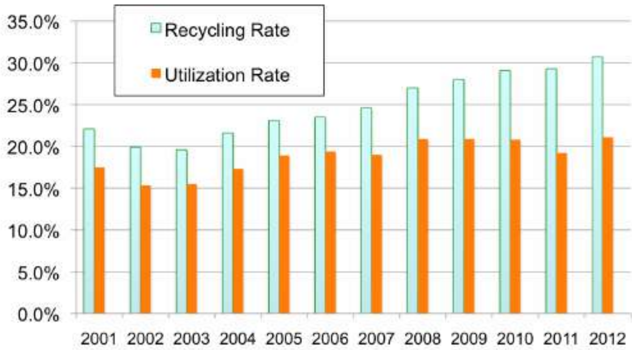

Figure 5. PET Recycling & PET Utilization Rates Compared [9]

Today in Europe, PET is also one of the largest plastic material recycled, with the equivalent of more than 60 billion bottles recycled in 2012. PETCORE EUROPE Chairman Roberto Bertaggia said: "Despite the poor economic situation in the European region, the consumption of PET bottles is still showing clear trends of penetration into new market segments through innovative packaging and the recognised capability of PET to be recycled. From a sustainability perspective, our industry is thrilled to have achieved an overall collection rate in 2012 of more than 52% of all post-consumer PET bottles available in the region." [10]

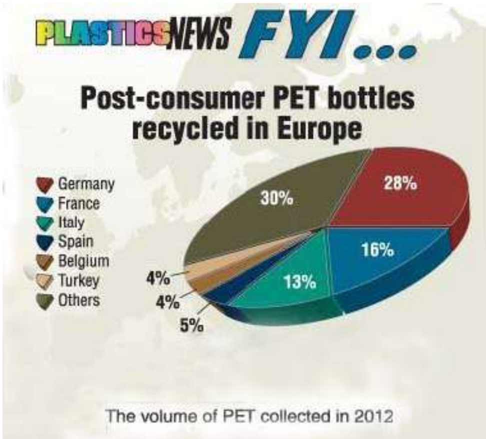

Figure 6. Post-Consumer PET bottles recycling in Europe in 2012.

CONCLUSIONS

With the general increase of recycling rate, the markets for recycled PET are necessary, in order to put it to a significant use. As is generally the case for recycled materials, the market situation is strongly affected by the supply and demand situation for virgin resin. The export market, as already discussed, is also a major factor. When virgin PET supply is low and prices are up, demand for recycled resin is strong. During the last half of the 1990s, there was a significant downturn in recycled PET demand caused by a large increase in production capacity for virgin resin that drove down prices. The situation was exacerbated by a temporarily plentiful supply of off-spec virgin resin from new facilities entering production. Some PET recyclers did not survive these lean years. Prices in 1995 for baled PET bottles were 54 to 70 cents per kg, [11] while prices in 2000 ranged from 14 to 40 cents per kg. [12] In the first half of 2005, prices were 40 to 52 cents per kg, largely due to strong demand from China and Vietnam. [13]

Use of RPET in the primary end-market conversion categories in the U.S. and Canada increased dramatically in 2012, up by 26% over 2011, with converter consumption totaling 595113 tons across all product categories United States and Canadian reclaimers also sold 33566 tons of PET byproducts to secondary markets. This is the highest converter consumption figure to date and represents a marked increase in this multi-year upward trend. U.S. and Canadian reclaimers supplied about 491240.5 tons of flake and pellet produced from all sources of feedstock. The remaining 103872.6 tons was either: PET byproducts; material provided by U.S. RPET "upgraders" (companies that purchase dirty PET flake, have it toll washed, then pelletize or solid-state it for resale); or PET imported from reclaimers in countries such as France, Italy, India, Israel, Taiwan, China, Mexico, Brazil, Peru and others in Central and South America.

Growth in fiber application end uses stands out in 2012, with an increase over 2011 of more than 28%, or 51709.5 tons. PET staple fiber applications rebounded in no small part due to the use of RPET; RPET use was also evident in bulk continuous filament (BCF) production.

Another notable trend is the strong and consistent year-over-year growth in the Sheet & Film and Food & Beverage Bottles categories as the preference for and manufacture of recycled content packaging continues. Sheet & Film uses alone increased by approximately 50 %.

Once again in 2012, the "Engineered Resins" category was folded into "Other," as there was insufficient survey response in this category to meet standard confidentiality guidelines. Although nylon-based compounds have dominated the market of late, Engineered Resins remains a potential growth market, particularly for green and colored recycled PET (RPET). Canadian RPET end-use markets continued to improve, as they have over the last two years, with particular growth in fiber and packaging applications. [9,14]

Taking all these data into consideration, the conclusion can be derived that the PET recycling pays itself off effectively, especially regarding the environment protection.

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STRUCTURE AND PROPERTIES OF BIODEGRADABLE STARCH-POLYURETHANE BLENDS

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ABSTRACT

Polymer blends are an important class of materials. Proper design of polymer blends produces material with improved mechanical and thermal properties. The very promising component, among others, for polymer blends is starch. Starch is not a thermoplastic in nature and prior blending must be plasticized in order to obtain the blend with improved properties. In order to improve properties of thermoplastic starch, it is blended with synthetic or bio-based polymers, such as poly(vinyl alcohol), poly(caprolactone), polyester, chitosan and polyurethanes (PUs). TPS-PU blends have a variety of structure and property features and they will be emphasized and analyzed by this review.

Key words: bio-based polymer blends, thermoplastic starch, polyurethanes, properties.

INTRODUCTION

Polymer blends are an important class of materials due to the relatively inexpensive route of mixing the two commercially available polymers. The focus in designing a polymer blend is on improved mechanical and thermal properties, i.e. strength and toughness, strength and solvent resistance, etc. According to the International Union of Pure and Applied Chemistry (IUPAC), a polymer blend is defined as a macroscopically homogeneous mixture of at least two different types of polymers [1]. Thus, the degree of homogeneity is the most important property of a polymer blend of two or more polymers. Blends are generally classified as heterogeneous or immiscible blends and homogeneous or miscible blends. The phase separation or miscibility in polymer blends can occur at different levels of mixing and in between tie lines (i.e. lowest critical solution temperature, LCST, and highest critical solution temperature, HCST). The processing conditions such as pressure, temperature, and polymer blend composition affect the miscibility as well. In order to produce miscible polymer blend the criteria of miscibility (Gibbs free energy of mixing, $\Delta G_m = \Delta H_m - T\Delta S_m < 0$) must be satisfied. There are many factors influencing miscibility of polymers such as morphology, crystallinity, intermolecular forces, and surface tension reduction [2]. The most common methods used for the study of polymer miscibility and polymer blend morphology are differential scanning calorimetry (DSC), dynamic mechanical analysis (DMA), rheology measurements, optical microscopy, small-angle light scattering (SALS) and small-angle X-ray scattering (SAXS), X-ray diffraction (XRD), and Fourier-transform infrared spectroscopy (FTIR). Commonly used parameters in polymer miscibility assessments are glass transition temperature (T_g), melting temperature depression and transparency in blends of amorphous polymers such as starch and polyurethane.

Starch is a polysaccharide produced through photosynthesis in many plants: wheat, corn, potato, rice, etc. Completely biodegradable, cheap and abundant material, starch represents a promising alternative to the common non-biodegradable polymers. Starch is considered to be a crystalline material because its chemical composition mostly consists of a linear molecule of amylose and a highly branched molecule of amylopectin [3]. Starch based materials are expected to be less transparent, resistant to water vapor and gas permeation, and processable. Starch is not a thermoplastic in nature. After being plasticized, exposed to high temperatures and shearing, it melts and flows [4]. The plasticizers currently in use for starch modifications are water, glycerol, urea, formamide, sorbitol, citric acid and amino acids [5]. Thermoplastic starch (TPS) can be processed with existing techniques used for synthetic polymers, such as extrusion, blowing, injection and compression molding [6]. Currently available commercial plastic products made from TPS are containers, vessels, forks, knifes and garbage bags [7]. However, low water resistance of TPS and poor mechanical properties dependent on moisture content in TPS limit the applications of TPS films [8]. In order to improve properties of TPS, it is blended with synthetic or bio-based polymers, such as poly(vinyl alcohol), poly(caprolactone), polyester or chitosan [9][10][11] and polyurethanes (PUs) to reduce the hydrophylicity [12]. The most interesting ones are TPS-PU blends.

Polyurethanes (PUs) are the most versatile class of polymers due to a variety of raw materials that can be used in their preparation and different macromolecular architectures that can be designed for specific applications. PUs are commercially available in a form of foams, elastomers, thermoplastics, adhesives, sealants, etc. PUs can be bio- and petrochemical based types. PUs are used for thermal insulation, cushioning in car seats and household furniture, the shoe industry, etc. [13]. PUs can be blended with many materials but the most promising ones are blends of PU with TPS. However, due to the environmental and health concerns PUs are being replaced with waterborne polyurethanes (WPU).

TPS-PU blends as well as WPU/TPS blends have a variety of structure and property features to be emphasized and analyzed. The aim of this paper is to give an overview and represent structure and properties of different types of starch-polyurethane blends and to emphasize their importance as biodegradable materials.

STARCH-POLYURETHANE BLENDS

In the work of Santayanon and Wootthikanokkhan [14] properties of starch/TPU blends were reported. The cassava starch was modified with propionic anhydride followed by blending polyester type thermoplastic polyurethane (TPU). Modification of starch with propionic anhydride was performed to improve compatibility with TPU. The prepared starch/TPU compositions were 20/80, 40/60 and 60/40 w/w%, respectively. The unmodified starch/TPU blends with the same compositions as modified counterparts were used as reference. The hydrophilicity of starch modified with different content of propionic anhydride decreased significantly compared with hydrophilicity of unmodified starch. Therefore, water stability of the blends was improved. Tensile strength, elongation and toughness of modified starch/TPU blends were improved compared with TPU blends containing unmodified starch. However, this improvement was not significantly taking into the standard deviations into account. This was confirmed by scanning electron microscopy (SEM) analysis. Although the interfacial adhesion between modified starch and TPU was evident due to the chemical modification of starch, it was found that compatibility between phases was dependent on starch content. The compatibility retained up to 20% of the modified starch in TPU while the 60% phase separation was almost complete. On the other hand, the biodegradation tests showed that TPU blends containing modified starch undergo biodegradation at a slower rate compared with TPU samples containing unmodified starch. This is in agreement with SEM analysis of starch/TPU blends. The work of the authors is very important in considering the methods of modification of starch and blending other polymers. In this case the overall improvements were achieved proving that biodegradability as important parameter can be design by varying the content of the modification agent.

The most reported research in the field of TPS and PU blends is for TPS/WPU blends. Nowadays, biocompatibility and biodegradability are big concerns in dealing with polymers. According to that, WPU was blended with TPS starch where biodegradable blends were obtained. Starch and PU together make these blends biodegradable. PUs can be made from mainly bio-based raw materials (i.e. polyols from vegetable oils) [15]. The isocyanate is the only component that is petrochemical. However, research in this field is conducted toward making the bio-based isocyanates [16] or synthesis of non-isocyanate PUs from organic carbonates [17]. There is potential for making totally bio-based PU/starch blends. The other reasons why TPS is blended with WPU are increased miscibility of components due to the presence of hydrophilic groups in starch and WPU, nontoxic and nonflammable properties of WPU, WPU biocompatibility, excellent mechanical properties of polyester type of WPU that can improve mechanical properties of starch, etc. One of the early reported WPU/TPS starch blends were in the work of Wu and Zhang [18]. The TPS was blended with a desirable amount of polyester type WPU (5-30% of WPU in starch). Reference samples were pure TPS and pure WPU. Mechanical tests revealed the increase of tensile strength and elongation at the break of WPU/TPS blends with WPU content. Reported values for the tensile strength of blends were higher than those of pure TPS and WPU samples. Elongation at the break was between pure TPS and pure WPU samples for all blends. This means that interaction and compatibility of two polymers were achieved and that was further evaluated by structural analysis of blends. This is in contrast with the work of Santayanon and Wootthikanokkhan [14], where significant improvements in mechanical properties were not achieved even though the modification of starch was performed prior to blending with PU. However, the water resistance of starch/PU blends was significantly improved in both cases of the starch/TPU and WPU/TPS blends. In addition, higher water resistance of the blends comes from the PU component due to a more non-polar nature of PU. The miscibility of the WPU/TPS blends was assessed based on an X-ray analysis (XRD). The obtained results suggested that TPS and WPU were miscible because of the disappearance of the peak at 2θ=24.3° due to interaction of the –COOH or –NH groups with the –OH groups from starch (Fig. 2 left). In addition, the DSC analysis revealed miscibility of the TPS and WPU which is in agreement with the XRD data. This was observed by the intensity and position of peaks for TPS, WPU and blended WPU, and by calculation of the melting enthalpies in DSC thermograms (Fig. 1 right). Also, good interaction of TPS and WPU was confirmed by FTIR and SEM analysis, respectively. Results from both methods revealed a good agreement with results and observations from the XRD and DSC analysis. What is not reported in this work is whether or not the phase separation occurred at higher WPU content.

The phase separation phenomenon at higher WPU content was reported in the work similar to the previous work by Cao et al [19]. The WPU was prepared from poly(ε-caprolactone) which is one more component that contributes toward the biodegradability of polymer blends. TPS was obtained by plasticizing the pea starch with glycerol and water. TPS/WPU blends were prepared with 10-50% of WPU content in plasticized starch. Compared with work of Wu and Zhang, in this blend the WPU content in starch is 20% higher, which allows the observation of the possible phase separation in the blends with higher than 20% WPU content in starch.

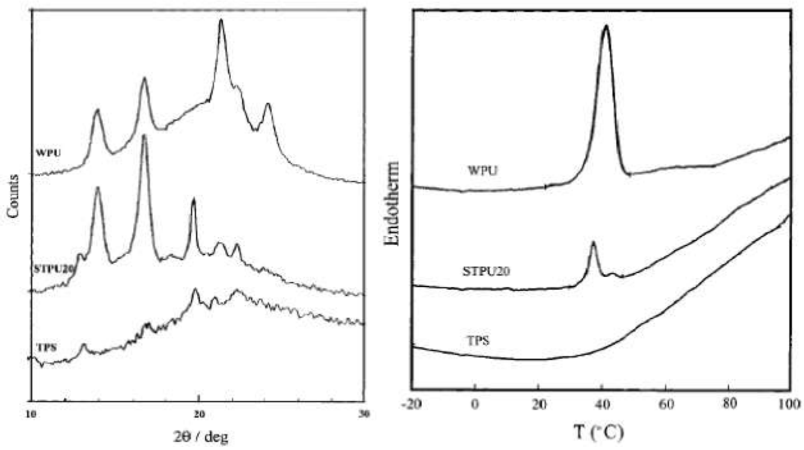

Figure 1. (Left) - XRD difractogram and (right) - DSC thermogram of TPS, WPU and WPU/TPS 20% blend [18].

Like in the work of the previous authors, results from mechanical testing reveled an improved tensile strength of up to 20% of WPU in starch, after what tensile strength decreased dramatically. Elongation at break was improved at all WPU loadings especially in the sample with 50% of WPU content when starting to increase dramatically. This proved that a wider range of WPU loadings can give a better picture of structure and property dependence of TPS on WPU content. Morphology analysis by SEM revealed the homogeneous morphology of blends with 10% and 20% WPU content, respectively, while with higher WPU content, the fracture surface appeared as rough (Fig. 2). Polymer miscibility was up to 30% of the WPU content. However, the good adhesion between polymers was retained due to the hydrophilicity of both polymers and hydrogen bonding interactions between them. Based on DSC data, miscibility of the polymers could not be assessed. Water absorption of TPS/WPU blends was decreased with WPU content.

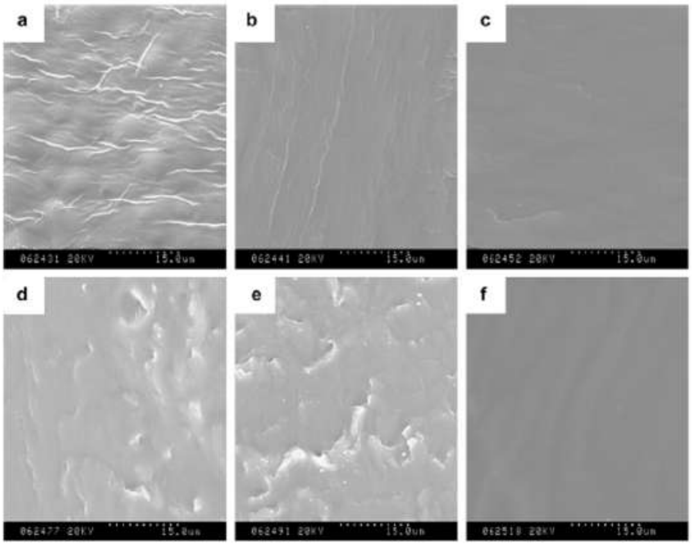

Figure 2. SEM images of the WPU/TPS blends with different WPU content: a) 0 wt%; b) 10 wt%; c) 20 wt%; d) 30 wt%; e) 50 wt%; and f) 100 wt% (scale bar: 15.0 μm) [19].

There are other ways of TPS and PU miscibility improvement reported in literature. Zhang et al [20] reported the improved miscibility between TPS and PU, and improved toughness and thermal stability of modified starch by changing the OH number of polyols used for PU synthesis. The PU content was fixed at 20 wt% in TPS. Through a series of blends prepared from polycaprolactone diol, triol, and terol, the miscibility, mechanical and thermal properties, and viscosity were evaluated. It was found that viscosities of the TPS/PU blend suspensions are not dependent on temperature, while viscosity of pure TPS strongly depends on temperature due to the gelatinization of starch. This means that hydrophobicity of the starch blended with PU was increased. In addition, the strong difference in viscosity values among the TPS/PU samples were not observed. This indicates that viscosities of blend suspensions were not dependent on an OH number. As expected, tensile strength and thermal stability of blends increased the OH number due to a higher cross-linking density of PUs prepared from triols and terol, respectively. However, the tensile strength of samples prepared from diol was lower than for TPS because the linear structure of PU is prepared with diol. Therefore, TPS and PU miscibility was low. On the other hand, the toughness of blends increased with the OH number and it was significantly improved. This research is a good example of how properties of TPU/PU blends and miscibility of starch and PU can be improved at a fixed PU content by simply changing the structural architecture of the PU. Other parameters that can be controlled in order to improve miscibility and properties of starch-PU blends are changing the hydrophobicity of polyurethane prepolymer [21] and content of prepolymer in the blend through reactive extrusion of blend [22]. Furthermore, controlling the molecular weight of soft segment in PU results in increased or decreased miscibility and different mechanical properties. These facts are very important in designing the specific properties for the specific applications of starch-PU blends. Rheology behavior of polymer blends, in this case TPS/WPU blends, is not only important for processing the blends but it's also important in predicting the mechanical properties of the TPS/WPU blends.

CONCLUSIONS

Blending of two or more polymeric materials is a useful technology when requirements for specific applications need to be satisfied. This technology is inexpensive and does not require installment of new equipment. By blending two or more polymers, the variety of different properties can be tailored for the specific applications. TPS/PU blends are one of the existing blends where properties can be designed through TPS modification, and through changes in the macromolecular structure of PU. In this manner and as discussed in this review, the different structures and properties of polymer blends can be obtained in order to fulfill requirements for their application.

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THE ARTIFICIAL NEURAL NETWORK BASED SYSTEM FOR AIR POLLUTION PREDICTION

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ABSTRACT

Air pollution has a big influence on the human health, including effects on the respiratory and cardiovascular systems, asthma and mortality. Measuring and predicting of the sulphur dioxide concentration in the air are very important tasks, as they allow taking the right-time actions to prevent the occurrence of air pollution. Measured data about SO_2 concentrations, obtained from the automatic measuring station, can be used for training of the system based on artificial neural networks. Forecasting is performed on the basis of the actual SO_2 emission, as well as some measured parameters, such as temperature, wind speed and direction, humidity and atmospheric pressure.

Key words: sulphur dioxide, air pollution, ANN model.

INTRODUCTION

Sulphur dioxide (SO_2) is one of the most common air pollutants. It is toxic, non-flammable, colourless, irritating gas, which have big, negative influence on the live nature. Sulphur dioxide is present in contaminated, as well as no contaminated areas. Nature sources of sulphur dioxide include release from volcanoes, oceans, and biological decay and forest fires. Actual amounts of natural sulphur dioxide are difficult to estimate. In 1983 the United Nations Environment Programme estimated a figure of between 80 million and 288 million tonnes of sulphur oxides per year. Sulphur dioxide emissions also result from combustion of fossil fuels due to varying amounts of sulphur being present in these fuels. World-wide emissions of SO_2 are thought to be around 69 million tonnes per year (2000) [1].

The fuels combustion in the heating plants in the cities, during winter period, causes increased air contamination, too. Negative effects of the presence of the SO_2 are especially noticed on the human's respiratory system. It causes cough, bronchitis and weakness, and high concentrations of this gas are very toxic.

In the atmosphere sulphur dioxide reacts with water steam, and makes sulphuric acid (H_2SO_4) which is one of the main causers of the acid rains. Acid rain comprehends the acidity of wet and dry deposition, Figure 1. Wet deposition includes acidity falling as rain, snow, sleet, hail, mist or fog, while the dry are deposition of gases and particles. Today, acid rains are a big problem.

The Municipality of Bor is placed in a mountainous and forest area in the south-eastern part of Serbia, east from mountain Crni Vrh, south-east from mountain Veliki Krš and south from mountains Stol and Deli Jovan. It has a total population of 50,000 citizens. The area has been the major centre for mining and processing of copper and other precious metals for more than a century. Air pollution is perceived as the main environmental problem in the Municipality Bor. The main source of air pollution with SO_2, heavy metals in particulate matter and aero sediments are the copper smelter. The smelter operates within the RTB Bor Company (Copper Mining and Smelting Complex) which producing copper for more than 100 years [2, 3].

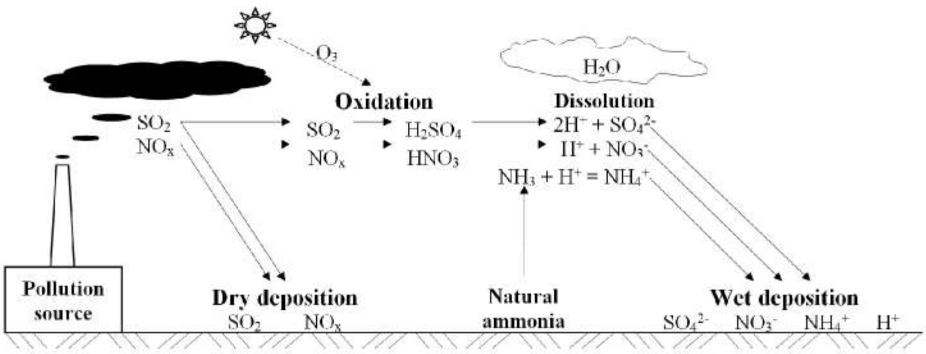

Figure 1. Dry and wet deposition of the SO_2 and NO_x pollutants

The technology of copper production in the copper smelter in Bor is outdated (classic pyrometallurgy with melting in furnaces and utilization of SO_2 gas in production of H_2SO_4 with a relatively small degree of utilization <60%) which leads to the environmental pollution of higher concentrations of SO_2 and particulate matter as well as aero sediments ($PM > PM_{10}$). The ore melted in the copper smelter plant in Bor is of chalcopyrite-pyrite type with the increased contents of arsenic, which is found in the form of $FeAsS$ and Cu_3AsS_4. The oxidation, roasting and melting of such a mineral forms results in increased heavy metal's oxides and SO_2 gas which in certain quantities contaminate the environment. Reportedly, 170000 to 250000 tons of SO_2 are emitted to the atmosphere each year [2, 3].

THE REAL-TIME MONITORING OF THE SO_2 CONCENTRATIONS

The monitoring of sulphur dioxide, particulate, and toxic metals has been carried out for many years in Bor. Since beginning of 2004, the new, suitable atmospheric monitoring equipment has been put into operation. The measured data about SO_2 concentrations was obtained from the automatic measuring station (AMS) Park. The AMS Park is fixed station, located 650 m west from the Copper Smelter Plant, downwind of the easterly prevailing wind as shown in Figure 2. A dense population (mainly high-rise) is directly downwind from the Copper Smelter Plant during east winds. A large effect on the local environment is often noted at this location – burning eyes, throat, taste of sulphur dioxide is experienced. This station is also equipped with meteorological instrumentation.

The AMS Park contained automatic analyzer for the real-time measurements of SO_2 concentration. This instrument provides continuous and reliable measurement of SO_2 in ambient air. The content of SO_2 in the air is determined by UV-fluorescence after excitation to higher energy level and light emission measurement. This method enables automatic determination of SO_2 contents in ambient air according to ISO 10498 Standard. The reference method for sulphur dioxide measurement is that described in EN 14212:2005 'Ambient air quality - Standard method for measurement the sulphur dioxide concentration by ultraviolet fluorescence' [4]. Using UV-fluorescence method, the analyzers perform automatic measuring of SO_2 in ambient air in a concentration range from 0 to 10000 $\mu g/m^3$ with linearity of ±1% and minimum detectable limit (2σ) of 0.001ppm (< 3$\mu g/m^3$) [5]. The analyzer was calibrated with standard gas mixtures (200 ppb) from certificated gas cylinders at least once in every three weeks. The AMS Park also contained automatic meteorological station.

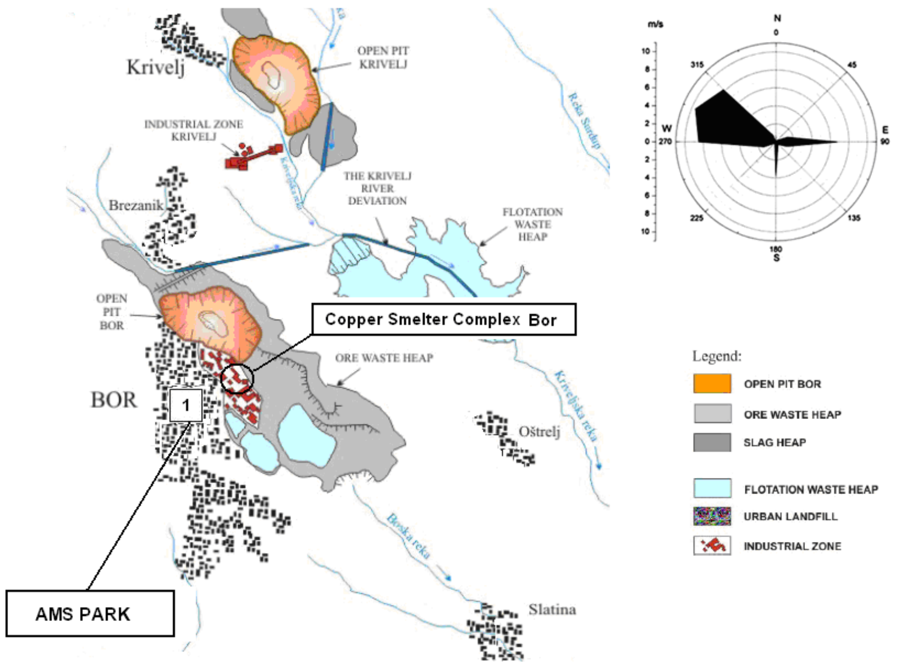

Figure 2. Map of the Bor town area with the position of the AMS Park and the wind rose diagram for the time interval from 2001 to 2010.

Estimated daily emissions of sulphur dioxide in tones per day, as well as average daily sulphur dioxide concentrations in the ambient air in $\mu g/m^3$ for January

2006 (measuring point Park) are shown in Figure 3. From Figure 3 it is obvious that concentration of the SO_2 in the ambient air doesn't strictly follows trends in SO_2 emission changes. The reason for this phenomenon is in the fact that there are a large number of factors which has the influence on the measured values of the sulphur dioxide concentration, such as: temperature, humidity, air pressure, wind speed and direction etc.

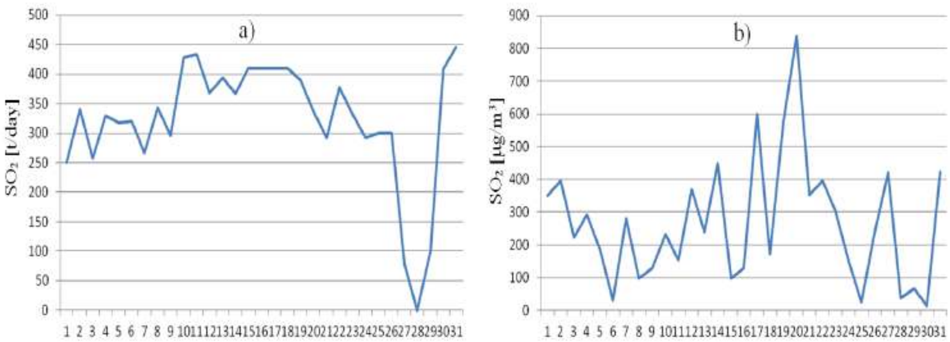

Figure 3. Sulphur dioxide emission and concentrations in January 2006:
a) estimated daily sulphur dioxide emissions
b) average daily sulphur dioxide concentration in the air (detected at measuring point Park)

MODELLING DATA WITH ARTIFICIAL NEURAL NETWORKS

Development of an efficient forecasting and early warning system for providing air quality information towards the citizen becomes an obvious and imperative need [6]. Artificial neural network (ANN), shown in Figure 4, represents a mathematical model which contains several connected elementary units, called neurons [7]. ANN receives the input vector $I = [i_1, i_2, \dots, i_n]$, and generates appropriate output vector $O = [o_1, o_2, \dots, o_m]$. Input elements $x_1, x_2, \dots, x_r$ are multiplied by the corresponding weights $w_{1,1}, w_{1,2}, \dots, w_{1,r}$. The neuron sums up inputs and adds a bias b_i.

The argument of the transfer function is:

$$a_i = x_1 w_{i,1} + x_2 w_{i,2} + \dots + x_r w_{i,r} + b_i \tag{1}$$

while the neuron produces output:

$$y_i = f(a_i) = f\left(\sum_{j=1}^{r} x_j w_{i,j} + b_i\right) \tag{2}$$

This output represents an input to the neurons of another layer, or an element of the output vector from the neural network.

The ANN can be used for SO_2 concentration modelling. This task can be realized through the following steps:

- generating ANN with appropriate architecture
- ANN training with measured data
- modelling data with ANN
- comparison of the measured and modelled data

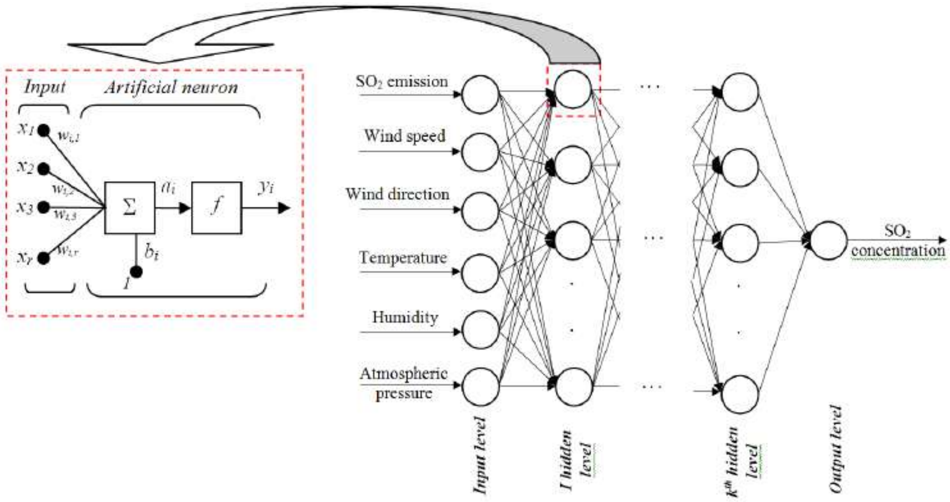

Figure 4. Artificial neural network for the prediction of SO_2 concentration

The basic architecture of the ANN is shown in Figure 4. The input layer of the ANN based model of SO_2 concentration has six neurons (SO_2 emission, wind speed, wind direction, temperature, humidity and atmospheric pressure). The input values are average daily SO_2 concentrations measured in the period from January to March of 2006 which were previously normalized. The ANN has just one output neuron for predicting the SO_2 concentration. The mapping problem is solved using the neural fitting tool.

The overall number of samples is 86, 60 samples are used for network training, 13 samples are used for network validation and 13 samples are used for network testing. The network has just one hidden layer, and the number of neurons in hidden layer is set to 20. The neurons in the hidden layer of ANN have the sigmoid transfer function, while the neuron of the output layer has the linear transfer function. The network is trained with Levenberg-Marquardt back-propagation algorithm. After the training phase, the ANN can successfully perform data generalization. ANN can predict the SO_2 concentration in the air for the input data set which was not presented in the training phase. Measured and predicted values of the SO_2 concentration are shown in Figure 5.

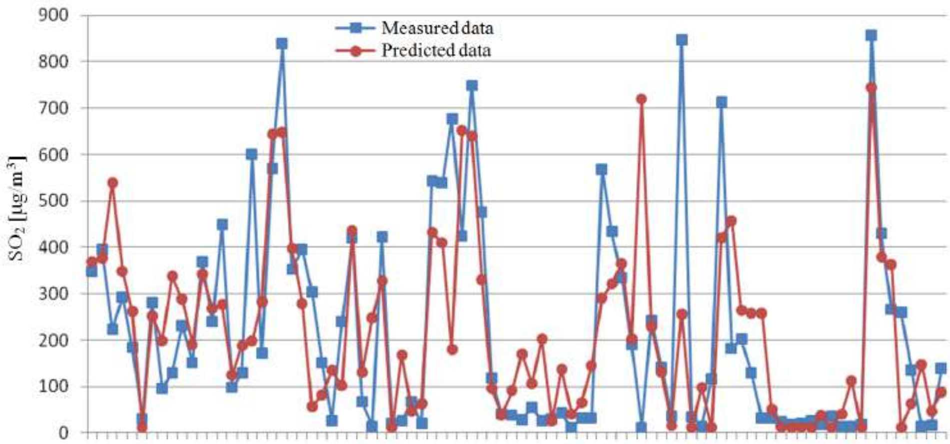

Figure 5. Measured and predicted values of SO_2 concentration in the air

Regression value (R) is the measure of the correlation between outputs and targets. After the training phase, the regression value of training, validation and testing set was approximately R=0.7. The reasons why R hasn't higher value are different. Firstly, there are a huge number of the influencing parameters on the SO_2 concentration in the air, and only few of them are taken in consideration in this study. Some of the influencing parameters are known, and some of them are unknown. Some parameters can be just normalized and used (temperature, for example), some parameters has to be primarily coded, then normalized and finally used for ANN modelling (wind direction, for example), while some of the parameters (which are maybe not less important) are hard or even impossible to present properly. Secondly, there is also a problem with uniquely mapping. Every set of input parameters should be mapped to the exactly one target value. Taking in consideration measured data, it can be noticed that there is some inconsistency. In some cases, there exists just one SO_2 concentration value which corresponds to a few numbers of input data sets. Similarly, there exists just one set of input parameters which corresponds to a number of SO_2 concentration values.

It is suggested that meteorological variables describing the stability of the atmosphere should be included in the model as well as time-series data from previous days. Additionally, inconsistency of input data could also be considered [8].

CONCLUSION

Forecasting of air pollution is very important task nowadays, due to the health effects caused by air pollutants in the urban areas. Primary goal of this work is the examination of the possibility of using the artificial neural network based system for predicting the air pollution. The real measured data during three months period of time was used for predicting of the sulphur dioxide concentration in the ambient air. Although ANN model has some advantages in comparison with the other analytical models (the relationship between input and appropriate output parameters could be established without strictly knowing of mathematical equations), many difficulties occurs during such modelling. Mentioned difficulties are especially caused by the inconsistent data, which occurs as result of changes in the meteorological conditions.

Acknowledgments

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FINAL FLOTATION WASTE KINETICS OF SINTERING

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ABSTRACT

In the copper extraction, especially during the process of flotation enrichment and the pyrometallurgical processing, the waste materials are being generated that represent huge polluters of environment. Deposits of final flotation waste (FFW) and discarded slag from the smelting furnaces transform large areas into degraded soil and they represent permanent source of water and air pollution.

To discuss the application of FFW in the manufacturing of new materials from the glass-ceramic group, were examined thermal properties whose knowledge is necessary for usage in the production of glass - ceramic. The paper presents the examination of kinetics of sintering FFW by measuring the change of sample contraction over time, in consequence heating on thermo microscope.

Key words: Final flotation waste, kinetics of sintering, glass-ceramic, application.

INTRODUCTION

The efficient industrial developments of one country are measured by the degree of protection of the environment as well as level of recycling usage – revalorization of the waste raw materials.

According to the data smelter in RTB Bor, the total amount of waste smelter slag deposited in the landfill is approximately 16-18 million tons. In addition to the deposited slag, depending on the capacity of concentrate copper smelter produces daily new 700 - 1000 tons of waste [1]. According to the fact that those are materials of ferro silicate composition, a possibility of use is of great significance, not only for reduction of industrial waste quantity but as the potential raw material for forming sintered glass-ceramics. Recycling of industrial waste material is very frequent subject of numerous works [2 - 11], in which a glass-ceramics of corresponding quality is being obtained by process of vitrification.

Vitrification process i.e. reduction in porosity by a viscous silicate-based liquid is the ultimate purpose of firing of many silicate systems. Viscous silicate liquid, being formed at firing temperatures has a role of a binder. For obtaining satisfying results, viscosity of liquid phase, has to be low enough that densification of the body has to be accomplished within given time period, without deformation under influence of gravitation force. Relative and absolute speeds i.e. sintering kinetics of these two processes (densification and deformation), are mostly defined by temperature, composition and grain size [12].

EXPERIMENTAL WORK

Thermal characteristics (sintering, softening and smelting interval) are determined by thermo microscope Carl Zeiss – Jena. Cube like shaped samples of 4 x 4 x 4mm size are pressed with 60 MPa pressure. Change of sample volume has been monitored and registered by the computer controlled digital camera (Canon PRO-1). Implying isotropy of dilatation, measuring surface of visible side of the testing body at the known to temperature, the volume change curves have been obtained in the function of temperature.

RESULTS AND DISCUSSION

From the diagram of the sample densification, during themperature rating of 12 ^{o}/min (Fig. 1 it is observed that interval of the sintering is between 940 °C and 1140 ^{o}C). The maximum volume change (13%) is achieved at a temperature of 1140 ^{o}C. Plastic deformation of the sample, start at 1160 ^{o}C. The sample is completely melted at 1280 °C.

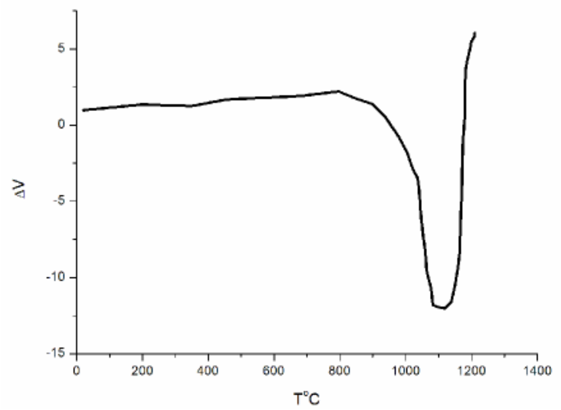

Figure 1. The diagram of the FFW volume's change depending on temperature

The diagram of sintering kinetics FFW (Fig. 2), show the change of the sample densification across the time during temperatutre rating of 1 °C/min. Points on diagrams are experimental data. Curves are differentials of sintering speed, that is, increment of density in unit of time dρ/dT in the temperature range of 900 – 1070 °C that fit properly by Gaussian distribution. Maximums of their sums provide integral of differential. Observed the two intervals sintering who are separated. First interval of sintering is between 920 and 965 ^oC with maximum at 940 ^oC for 14 minutes. Starting density is 2.7 g/cm^3. Second interval of sintering is taking place at the temperature between 1010 and 1050 ^oC with maximum at 1040 ^oC, 60 minutes later. At the temperature of 1050 ^oC sintering is being finished and maximum density of 4.2 g/cm^3 has been achieved. It is assumed that these two separated intervals are consequence of different reaction speeds, of the particles of different sizes. The aim was to maintain constant temperature during as long as possible time frame, so the time delay on specific temperature provides the biggest contribution to volume change. After 14 minutes maximum speed of sintering is reached by fraction of 1.4μm grain diameter and after 60 minutes maximum speed is being reached by fraction of grain diameter 4.3μm. Times intervals of 14 and 60 min are real whilst the granulations of 1.4μm and 4.3μm are theoretically calculated.

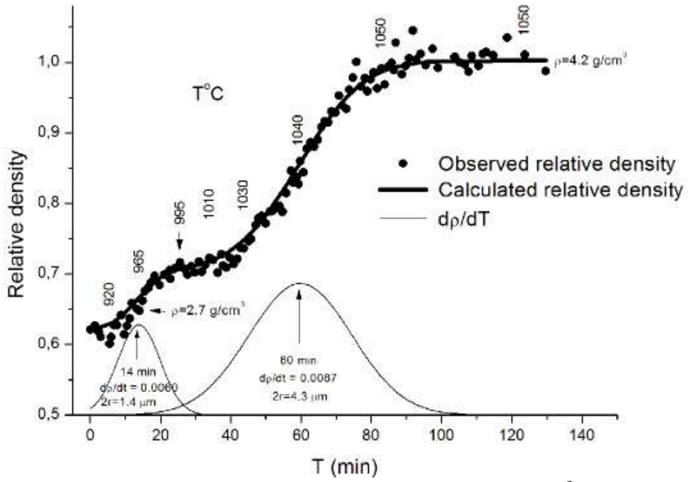

Figure 2. diagram kinetics of sintering FFW Bor (1^oC/min)

Liquid phase that came out of small grain fraction during first interval of sintering provides its contribution to starting of sintering of large grain size fractions. Reduction of first part of volume happens in first sintering interval, while second part of volume reduction comes from porosity of large grain fraction. Hence, sintering until beginning of second sintering interval is regrouping of particles since porosity of large grain fraction is not being changed. Inside large pores small grains are being mutually sintered but also react with large grains. Porosity between small grains during first interval of sintering is being minimized. When second sintering interval begins, reduction of volume starts by disappearance of pores between large grains. Contribution to the part of sintering is given by already existent liquid phase produced by the small grain. If there was no small fraction, sintering would have started later.

Having in mind that that two mutually segregated sintering intervals are a consequence of unequal speed of reaction of particles of different sizes, using Andersen method of decantation, two granulometric fractions have been separated up to 5μm and over 5μm. Two samples bodies of different granulometric fraction were prepared. On thermo microscope, shrinkage rate, times of sintering and plastic deformation have been experimentally analyzed at heating regime of 10 C/min. On Fig. 3 there is diagram of sintering kinetics of two granulations. It is obvious that grain size distribution below 5μm is being sintered at the temperature interval of 750 ^{o}C up to 990^{o} C, while the sample is being shrunk by 8%. Fraction over 5μm starts sintering at temperature of 1030-1040 ^{o}C and ends at 1115 ^{o}C. Shrinkage of the sample is 7%. Within temperature interval of 1115-1160 ^{o}C volume and density stay constant. Above 1160 ^{o}C plastic deformation (yeilding point) begins followed by increase of the volume.

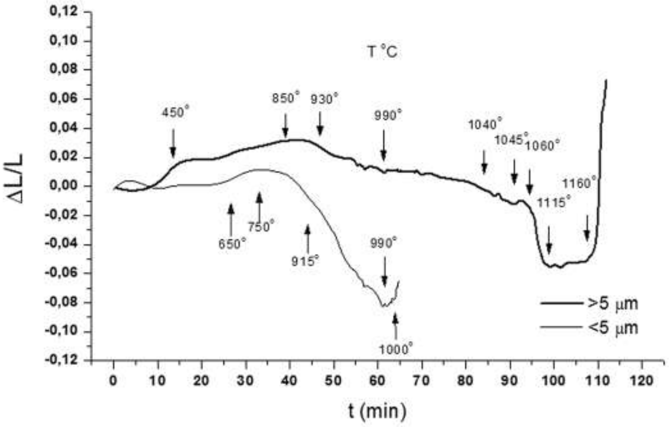

Figure 3. Diagram kinetics of sintering FFW Bor – two grain

Since it is all the same material, viscosity and surface tension are the same: and difference in sintering temperature is consequence of grain size. Smaller grains, are due to higher specific surface, more reactive which means that sintering can start at lower temperature.

CONCLUSION

Partition of sintering process of FFW are consequence of grain size distribution. It is obvious that with a proper selection and adjustment of grain size distribution the regimes of sintering can be predicted. With that, it is possible to add small grain aggregate that would act as "reinforcement bars" and FFW would be as binder. This combination of different materials can lead to laying out of different glass-ceramic material.

Kinetics of liquid phase development during FFW sintering, very much depends on grain size distribution. A good match of experimental results with theoretical model has been achieved.

Acknowledgements

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APPLICATION OF ZEOLITES IN REMEDIATION AND ENVIRONMENTAL PROTECTION

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ABSTRACT

The usage of zeolites depends on their physical and chemical properties and opportunities for economic exploitation. Natural zeolites have been widely used in the remediation of the environment. The most of these applications are based on their ion-exchange properties. It is also well-known that ion-exchange in the case of zeolites takes place among cations and only their modification can provide them with anion sorption properties.

The paper gives a brief overview of the use of natural zeolites and its modified forms in the separation of hazardous inorganic and organic species in soil, water and air systems.

Key words: zeolite, clinoptilolite, adsorption, heavy metals, environmental protection.

INTRODUCTION

Zeolites are crystalline, hydrated aluminosilicates of alkali and alkaline earth elements, which possess an infinite three-dimensional structure. They are characterized by the ability to lose or receive water and to exchange some of its constitutional cations without major changes in the structure. Up to day, it was identified about 40 species of natural zeolites, while the number of synthesized is significantly higher (approximately about 170) [1].

Zeolites are constituents of many rock complexes and are formed in various ways. The primary classification of zeolites to endogenous and exogenous is performed according to the forming conditions. Endogenous could be of magmatic or hydrothermal type, but they are of no practical significance. Exogenous zeolites are of volcanic-sedimentary and sedimentary origin, while certain subtypes of sedimentary deposits are the primary source of obtaining natural zeolites. Sedimentary deposits are associated with the formation and secondary modifications of different ages of this type rocks.

The most significant zeolites are: clinoptilolite ($Ca,Na_6(AlO_2)_6(SiO_2)_{30}\cdot 24H_2O$), mordenite ($(Na_2,Ca)_4Al_8Si_{40}O_{96}\cdot 28H_2O$), phillipsite ($((K_2(Ca,Na_2)_2Al_8Si_{10}O_{32}\cdot 12H_2O$), erionite ($(Na_2K_2MgCa_{1.5})_4Al_8Si_{28}O_{72}\cdot 28H_2O$), analcime ($Na_6(AlO_2)6(SiO_2)_{30}\cdot 24H_2O$) and chabazite ($Ca_2(AlO_2)_4(SiO_2)_8$).

Clinoptilolite is one of the most widespread zeolitic minerals in nature. The chemical composition of this mineral is usually accompanied by a pronounced change of the Si / Al ratio. As by the rule, clinoptilolite with low silicon (Si) content are enriched with calcium (Ca), but frequently contain barium (Ba) and strontium (Sr), while clinoptilolites with a high content of silicon (Si) contains sodium and potassium. The water content varies in the range of 17-24 molecules per elementary cell, depending on the cation which is present in the mineral. Clinoptilolites rich with calcium (Ca) have more water and less potassium (K) [2].

The ability to be modified is what makes zeolites of particular interest. The development of artificial zeolites begins in thirties of the last century by synthesis at high pressure and temperature. The synthesis of zeolites is important because it allows scientists and engineers to predict the characteristics of zeolite and produce hydrophobic zeolite with a specific pore size [3,4].

The main zeolite sites are streched all over the world: Bulgaria, Greece, Hungary, Italy, Romania, Slovenia, Slovakia, Serbia, Croatia, Turkey, Russia, China, Japan, Australia and many countries on the American continent. The most significant deposits in Serbia are located in the foothills of mountain Kopaonik (40 km from Kruševac, near Brus); in Kosovo; in the vicinity of Belgrade (place called Slanci near Smederevo); on the Fruska Gora hill and near Vrnjačka Banja touristic and spa center.

PROPERTIES AND APPLICATION OF ZEOLITES

Characteristics that directly affect the quality and the usage of zeolites are defined by the process of emergence zeolite minerals in nature. From the standpoint of purity, the content of pure minerals varies between 50 and 90 % in zeolite sedimentary rocks, better known as zeolite tuffs. The quality of the raw material and its further use is determined by the content of zeolite minerals in tuff. Sedimentary zeolite tuffs are usually soft, friable and light with bulk density of about 1,2-1,8 t/m^3. It is important to none that despite the mulal diversity among species of zeolitic minerals, the same type of minerals differs from deposit to deposit and should be examined individually before application.

The basic unit of zeolite structure is tetrahedron, whose center represens the atom of silicon or alluminium, while the vertices of thetrahedron are formed by four oxygen atoms. Each oxygen atom is shared by two tetrahedrons. In this way, all the tetrahedrons form the skeleton of zeolite. Replacement of Si^{4+} and Al^{3+} ions in tetrahedron causes an excess of negative charge which is compensated by monovalent or divalent cations (Na, K, Ca, Mg, Ba) distributed along with the water molecules in the pores of minerals. Cations in the pores are easily exchangeable despite of Si and Al in the structure of minerals, which could be exchanged only in exceptional circumstances.

Depending of the type, zeolites can be highly active adsorbents. Cations of alkali and alkaline earth metals of many zeolites can be easily replaced by heavy metal cations. Due to the existence of the system of channels and cavities, comparable in size with atoms, molecules and ions, crystalline zeolites may allow the passage to the particles not greater than the diameter of the input. Such structure allows these minerals to selectively adsorb only certain molecules or ions and to play the role of "molecular sieves".

The processes of ion exchange between zeolite and external environment can be occurred in a variety of conditions:

- ion exchange, between the zeolite and the solution, under normal pressure and the temperature up to 1000^{o}C;
- ion exchange in aqueous medium, at an elevated temperature and pressure (in the hydrothermal conditions);
- exchange of ions from the gaseous phase;
- exchanges ions from the melt phase;
- ion exchange between zeolite and solid phase.

Most of the physico-chemical properties of zeolites depend on the aluminum content in the zeolite. The selectivity of zeolite surface depends on the SiO_2/Al_2O_3 ratio. Aluminum-rich zeolites with low content of silica are hydrophilic adsorbing polar molecules and therefore are used as driers, while higher content of silica in the structure increases the hydrophobic character of zeolites.

Thermal stability of zeolite is dependable by the Si/Al ratio as well as the nature of cation. For example, the decomposition of the structure of zeolite NaX with a low content of SiO_2 (SiO_2/Al_2O_3=2.5) comes up at 660^{o}C. In the structural equivalent of NaY zeolite with higher content of SiO_2 (SiO_2/Al_2O_3=5) decomposition is occured up above 700^{o}C. Strong acids decompose zeolite with a low content of SiO_2 by dissolving aluminum ion in the skeleton which leads to distortion of the structure. This feature is used to dealumination of zeolite. Dealuminated NaY zeolite is structurally stable above 1000^{o}C [5]. Macro and micro pores in the structure of natural zeolite contain water, which is approximately 10-25% of their mass. It is possible to release zeolite of adsorbed water by calcination at 400 to 500^{o}C without disturbing their structure. Thus the liberated pores in zeolites are prepared for the adsorption of other molecules. The volume of micropores formed in this way depends on the structure of the zeolite and the number and nature of cations.

Zeolite is widely used in the purification of drinking and wastewaters, waste gas treatment, remediation of contaminated land, in prevention of harmful effects of radiation, in the chemical industry and in agriculture to improve the physico-chemical characteristics of the soil. Nowadays, zeolites are widely applicable in veterinary medicine, pharmacy, paper industry, in explosives production, polymers, rubber, paint, in the manufacturing of light construction and decorative materials, etc.

Application of Zeolites for Wastewater Treatment

Natural zeolites have no ability for adsorbing anions due to negative charge of aluminosilicate skeleton. Through the adsorption of surfactants, partial neutralization of negative charge of external surface of zeolite minerals is possible. The adsorbent with increased ability for adsorption of anions is obtained in this way but also, which is of the great importance, the capability of simultaneous adsorption of some cationic and organic contaminant has been achieved.

During the purification of waters contaminated with heavy metals, selectivity is an important criterion for the selection of proper sorbent material [6-10]. The selectivity and capacity of various types of zeolites to some heavy metal ions is presented in Table 1, under different experimental conditions.

Table 1. Sorption capacities and selectivity for heavy metals for selected zeolites [8]

Zeolite	SC^a/(mg/g)	Selectivity series	Experimental conditions
Clinoptilolite	2.4 (Cr), 1.5 (Co), 0.9 (Ni), 3.8 (Cu), 2.7 (Zn), 3.7 (Cd), 6.0 (Pb)	Pb^{2+}>Cu^{2+}>Cd^{2+}>Zn^{2+} >Cr^{3+}>Co^{2+}>Ni^{2+}	IMC^b (1-30 mg/L), pH (3-6), ZC^c (5g/L)
	101 (Pb), 11.7 (Cu), 6.8 (Cr), 5.58 (Fe)	Pb^{2+}>Cr^{3+}>Fe^{3+}>Cu^{2+}	IMC (10 mg/L), ZC (0.5-180g/L), pH (2-4)
	5.91 (Cu), 4.12 (Cr), 3.45 (Zn), 1.98 (Ni), 4.60 (Cd)	Cu^{2+}>Cr^{3+}>Zn^{2+}>Cd^{2+} > Ni^{2+}	IMC (100mg/L), pH (3-6), ZC (2.5-5g/L
Chabazite	3.6 (Cr), 5.8 (Co), 4.5 (Ni), 5.1 (Cu), 5.5 (Zn), 6.7 (Cd), 6.0 (Pb)	Pb^{2+}>Cd^{2+}>Zn^{2+}>Co^{2+} >Cu^{2+}>Ni^{2+}>Cr^{3+}	IMC (1-30 mg/L), pH (3-6), ZC (5g/L)
Zeolite X	549 (Pb), 109 (Cu), 162 (Cd), 70 (Ni)	Pb^{2+}>Cu^{2+}>Cd^{2+}>Ni^{2+}	IMC (20-2000 mg/L), ZC (2g/L)
Zeolite 13X	136 (Cu), 100 (Co), 86.3 (Ni)	Cu^{2+}>Co^{2+}>Ni^{2+}	IMC (1.5-3 mmol/L), ZC (20 g/L), pH (3.5)
Zeolite 4A	13.7 (Co), 41.6 (Cr), 50.5 (Cu), 9.0 (Ni), 30.8 (Zn)	Cu^{2+}>Cr^{3+}>Zn^{2+}>Co^{2+} >Ni^{2+}	IMC (100mg/L), pH (3-6), ZC (2.5-5g/L)
Zeolite NaP1	43.6 (Cr), 20.1 (Ni), 32.6 (Zn), 50.5 (Cu), 50.8 (Cd)	Cr^{3+}>Cu^{2+}>Zn^{2+} >Cd^{2+} > Ni^{2+}	IMC (100mg/L), pH (3-6), ZC (2.5-5g/L)

SC^a-Sorption capacities; IMC^b- Initial metal concentration; ZC^c- zeolite concentration.

Extraction of iron, lead, cadmium and zinc from mine waters by natural, untreated zeolites showed good results for lead, both in acidic and alkaline solutions, while the adsorption degree of zinc and cadmium ions decreases with the pH and with an a increase in the concentration of iron. Effectiveness of zinc and cadmium removal decreases with the increase in concentration of calcium ions while the removal of lead ions remains particularly untouched. Motsi and Rowson (2009) examined the influence of changes in the pH (from 2.5 to 4.5) on the adsorption of metal ions (Cu, Fe, Ni and Mn) from the synthetic aqueous solutions using clinoptilolite as an adsorbent. It has been found that adsorption degree of heavy metal ions from the solution increases with increasing of pH initial value. At lower pH values, clinoptilolite preferably adsorbs hydrogen (H^+) ions from the solution, which is represented by the decrease of adsorption capacity. The increase in the initial pH from 2.5 to 3.5 resulted in an increase of adsorption capacity up to 49%, 38% i 20% for Mn^{2+}, Zn^{2+} i Cu^{2+} ions respectively [6].

Besides natural zeolites, the adsorption studies were performed on modified zeolites using aqueous solution of NaCl and CH_3COONa. Pre-treatment of zeolite with NaCl and $CaCl_2$ aqueous solution leads to an increase in the speed of the immobilization of heavy metal ions, and thereby does not decrease the selectivity of the zeolite in multicomponent solutions. Regeneration of both, natural and modified zeolite is satisfactory achieved by treating with 2M NaCl solutions [7].

Natural zeolites of clinoptilolite type are used for the removal of NH^{4+} ions from wastewaters and ammonia from the air (e.g. the livestock farms), wherein the later can be used to produce ammonium phosphate fertilizer or by thermal treating could be regenerated and re-used for the same purpose.

Zeolite tuff is used for decontamination of wastewaters to remove Cs and Sr radioisotopes [10]. Approximately 500,000 t of zeolite was spent to construct the protective layers and decontamination of land in Chernobyl. It was also suggested the formation of filter with clinoptilolite tuff for the extraction of radionuclides from drainage waters in the Chernobyl nuclear power plant.

The Application of Zeolites for Soil Remediation

As ion exchangers, zeolites are used in sanitation and neutralization of landfills and because of their affinity to ammonia ion lather could be used as a source of nitrogen. In the mining industry the biggest problem are ash landfills of power plants and flotation tailings. These degraded areas of land contain significant amounts of heavy metals such as Pb, Cu, Zn, Cd, Co and a negligible content of biogenic elements like N, P, K and organic components, representing sterile area for vegetation. These heterogeneous materials disseminated by wind and water, pollute surrounding fertile land, and therefore represent an even greater environmental problem.

In the purpose of reclamation of such areas, the application of zeolites in order to improve physico-chemical properties of the soil are tested on multi sites in Serbia [2].

Flotation tailing, created during ore processing in Brskovo plant, is located along the river Tara, near Mojkovac. Heavy metals, mostly zinc, lead, copper and traces of nickel and cadmium are detected in tailings. After detailed characterization of tailings, the experiments were carried out in semi-controlled conditions (greenhouse) and on flotation tailing site. In both variants grass mixtures were grown with NPK fertilizer, zeolite, bentonite, lime and compost which have contributed to: the best coverage and enchantment of ground (up to 35%); to the highest yield of dry grass mixtures and to the lowest concentration of lead, copper and zinc. In the area of approximately 16 hectares on the territory of flotation tailing of Copper Mine in Bor researches were conducted with the aim to cover pyrite tailings which daily pollute the town. The investigations have included experiments in greenhouse and field conditions. Experiments were carried out with or without earth layer using supplements like NPK fertilizer, zeolite, manure and lime in various proportions in order to find optimal conditions. In the treatments where besides mineral NPK-fertilizers, lime, zeolite and manure were added considerable increase in grass yield (from 41% to 302%) has been achieved compared to the control sample. In this way, the assumption that the use of reclamation materials based on zeolite, with the selection of appropriate crops, can successfully contribute to the biological reclamation of completely sterile area is confirmed again.

The studies were conducted on the ash pan of Nikola Tesla thermo-electric power plant in Obrenovac, where grass-legume mixtures treated by different combinations of NPK-fertilizers, zeolite and phosphogypsum were grown. At the end of the experiment, the best performances were achieved in variants of fertilization with NPK-fertilizer and zeolite with statistically highly significant increase in yield of 220% compared to the control sample.

The Application of Zeolites for Air Purification

The adsorption on zeolite has a limited application in the treatment of soil and water, but the technology is widely applied to the air pollution control in industry. The zeolites can be used for the treatment of vapors which contain the emissions of Nox, CO_2 and for most chlorinated and non-chlorinated VOCs (*volatile organic compounds*) [11,12]. The hydrophobic zeolites can also be used for the effective treatment of the solution with a high boiling point. The ability of zeolites to adsorb high humidity, their resistance to combustion, efficiency in the removal and destruction of VOC` s at low concentrations and ability of regeneration, zeolites shows advances in some systems than other adsorbents and takes an important role in the protection of the atmosphere. Experimental data shows that, on temperature below 40^oC and humidity lower than 80%, efficiency of continual rotary zeolite absorber could be above 90%. Based on high Si/Al ratio, zeolite ZSM-5 has proved to be very efficient. This type of zeolite is effective as sorbent for organic molecules even at low concentrations, high humidity and high temperatures.

CONCLUSION

Natural zeolites have characteristics that allow their widespread application in environmental protection as well as in many other areas. The sorption capacities of natural and modified zeolites cannot be compared with synthetic ion exchange materials (resins) whose composition, structure and properties are exactly defined. Their advantage over these materials lies in their wide availability all over the world, as well as in low cost. These are the main reasons why researches are still conducting the experiments in order to improve their properties or to find new areas of application in the field of environmental protection. It is of particular importance to obtain long-term stable modified zeolites, as well as to improve their sorption capacity. Finally, the consideration of the treatment, disposal or regeneration of the contaminant-loaded zeolitic forms will also definitively increase their environmental application possibilities.

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ANODIC BEHAVIOUR OF AgCu50 ALLOY IN THE PRESENCE OF CHLORIDES AND BENZOTRIAZOLE

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ABSTRACT

The presence of chloride ions in concentrations larger than 0.01 mol dm^{-3} significantly intensifies anodic processes at AgCu50 alloy.In order to slow down this reactions it was looked into the possibility of using benzotriazole known as an effective corrosion inhibitor for copper. This paper shows influence of benzotriazole in a wide range of concentrations on anodic processes as well as the influence mechanism and the formation mechaninisms of copper and silver oxides and chlorides. It was determined that benzotriazole concentrations larger than 0.005 mol dm^{-3} lead to nearly complete alloy passivation at these investigated cloride concentrations.

Key words: AgCu50 alloy, benzotriazole, electrochemical oxidation, chlorides, cyclic voltammetry, open circuit potential.

INTRODUCTION

Silver-copper alloys are widely used for making jewelry, kitchen utensils, decorative products, coins and medals, as well as to make electric contacts and solders in the industry. Organicinhibitorsare extensivelyused to protectmetalsand alloysfrom corrosionin different media. Among them, the most studied is effectiveness of azoles for corrosion protection of copper and its alloys [1]. The best-knowncorrosion inhibitorof copper andits alloysfrom the groupof azolesisbenzotriazole (BTA). It can be said that it is an anodic corrosion inhibitor of copper whose mechanism of action involves chemisorption, on the copper surface, governed by the Langmuir isotherm [2, 3] whereupon occurs the formation of Cu(I)BTA complex [4, 5, 6].

Benzotriazole is organic compound form azoles group which is composed of benzene and the triazole ring with chemical formula of $C_6H_5N_3$. Based on thecharacteristics of the BTA, inhibition efficiency in particular environment can be explained. BTAcan be foundin three formsdepending on thepHvalue of the solution[4]. In strong acidic environment it is in protonated form $BTAH^{2+}$, in neutral and weak alkaline environment is found in form of BTAH while in strong alkaline medium it is found in a form of BTA^-.

Thermodynamic conditions shown in E-pH diagrams predict the potential range in which the presence of chloride ions with activity of ≥ 0.078 [Cl-] allows the corrosion of copper to occur in near-neutral solutions without the formation of copper oxide. Also, in acid solutions, the potential at which copper dissolves in the presence of chloride ions is reduced to more active values [4].

Tromans and Sun [4] have showed that Cu-BTA protective layer can be formed on non-oxidized copper surface in a solution containing benzotriazole and chloride ions. Based on theelectrochemicalexperiments,they suggestedthe following mechanismof inhibition:

$$Cu + BTAH = (Cu\text{-}BTAH)_{ads}$$
$$nCuCl^-_2 + nBTAH = (Cu\text{-}BTA)_n + nH^+ + 2nCl^-$$
$$(Cu\text{-}BTAH)_{(ads)} + (Cu\text{-}BTA)_n = [(Cu\text{-}BTAH)\text{-} (Cu\text{-}BTA)_n]_{(ads)}$$

Subject of this paper is oxidation behavior of AgCu50 alloy in 0.1 mol dm^{-3} NaOH in the presence of 0.01 mol dm^{-3}NaCl, as well as inthe presenceof various concentrationsof benzotriazole.

EXPERIMENTAL PROCEDURES

The research in this paper include following experiments:

- measurement ofthe open circuit potential for AgCu50alloy and for pure metals Ag and Cu in 0.1 mol dm^{-3} NaOH;
- measurement ofthe open circuit potential for AgCu50alloy and for pure metals Ag and Cu in 0.1 mol dm^{-3} NaOH + 0.01 mol dm^{-3} NaCl in the presence of BTA (0.00005; 0.0001; 0.0005; 0.001; 0.005 and 0.01 mol dm^{-3});
- recordingpotentiodynamicvoltammograms forAgCu50alloy and for pure metals (Ag,Cu) in 0.1 mol dm^{-3} NaOH + 0.01 mol dm^{-3} NaCl in the presence of BTA (0.00005; 0.0001; 0.0005; 0.001; 0.005 and 0.01 mol dm^{-3}).

Voltammograms were recorded in a potential range from-1.6Vto 1V*vs.*SCE at a sweep rate of 20 mV s^{-1}. The experiments described in this paper were conducted at 25 ± 0.5 °C.

In theelectrochemical cell filled with the working solution were immersed: reference electrode (saturated calomel electrode - SCE), working electrode (Ag, Cu and AgCu50) and counter electrode (platinum sheet 1 x 2 cm).

Working electrodes have been made from the refined metals (Ag, Cu) with purity of 99.99%, and their mixture in the portions of 50% wt. of Ag and 50% wt. of Cu, by smelting in quartz furnace at a temperature of 1250 °C, casting and subsequent cooling. Castings were than treated further with an aqueous solution ofHNO_3(1:1) to remove the oxides formed while cooling and after that they were subdued todrawingandrollingprocedures to obtain wires of dimensions Ø = 1 mm and h = 150 mm. There after the wires were annealed at 600°C for 30 minutes. The working surface of the electrode represents a vertical intersection of the wire that's 1 cm long and 1 mm wide.

Before each experiment, the electrode was mechanically polished with abrasive paper and then by using felt soaked in suspension of distilled water and alumina (0.5 μm). After polishing working electrode surface is rinsed with distilled water and alcohol.

The system for electrochemical measurementsconsisted of hardware (PC, AD-DA converter NI-6251 produced by National Instruments and analog interface) and software for excitation and measurement (LabVIEW 8.2 platform - National Instruments, and application software) both fully developed by Technical Faculty in Bor [7]. The investigations have been performed in 0.1 M NaOH by cyclic voltammetry and open circuit potential measurement.

RESULTS AND DISCUSSION

Open circuit potential measurements

Results of open circuit potential measurement as a function of time for Cu, Ag, AgCu50 in 0.1 mol dm^{-3} NaOH + 0.01 mol dm^{-3}NaCl are presented in Fig.1, while Figure 2 shows results of the same measurements in presence of 0.001 mol dm^{-3}BTA. Stabilized value of open circuit potential for the alloy is between the potentials for copper and silver. After the addition of BTA all the three potentials reached stable value much faster than in solution without benzotriazole. In presence of BTA potentials of the pure metals, copper and silver, shifted to more negative values, while the open circuit potential for the alloy remained almost the same (about 0.21 V *vs*. SCE).

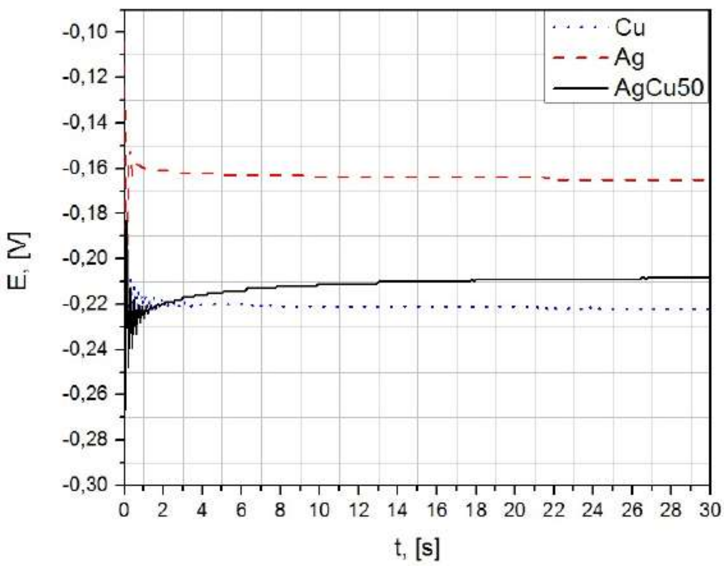

Figure 1. Potential as a function of time for Cu, Ag and AgCu50 in 0.1 mol dm^{-3} NaOH + 0.01 mol dm^{-3}NaCl

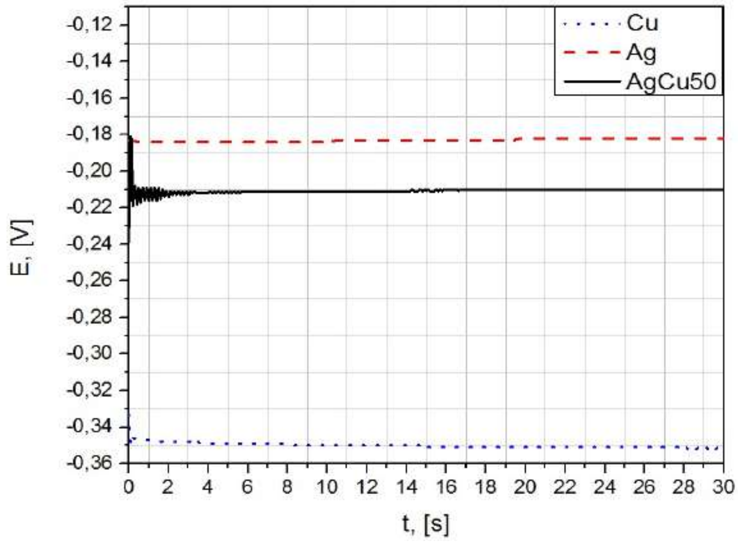

Figure 2. Potential as a function of time for Cu, Ag and AgCu50 in 0.1 mol dm^{-3}NaOH + 0.01 mol dm^{-3}NaCl + 0.001 mol dm^{-3}BTA

Cyclic voltammetry

Cyclic voltammograms obtained in 0.1 mol dm^{-3} NaOH with addition of 0.01 mol dm^{-3} NaCl at 20 mV s^{-1} scan rate for pure copper, pure silver and AgCu50 alloy are presented in Figure 3.

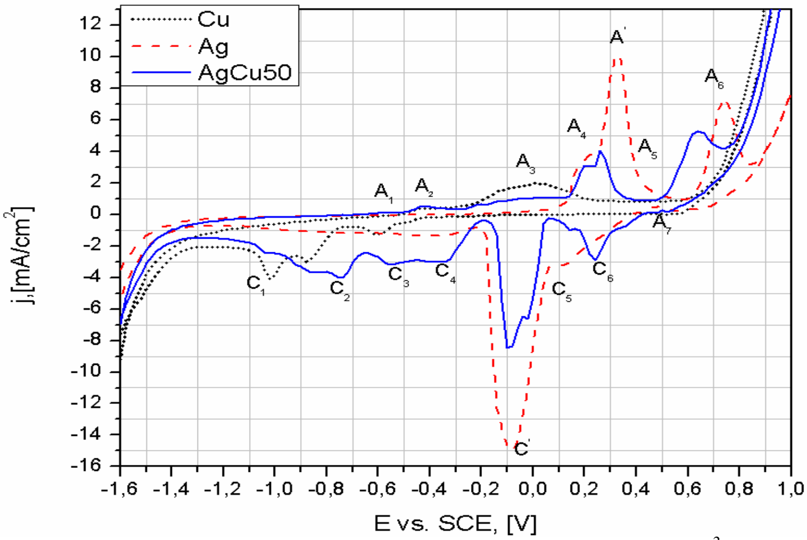

Figure 3. Electrochemical behavior of Cu, Ag, AgCu50 in 0.1 mol dm^{-3} NaOH with addition of 0.01 mol dm^{-3} NaCl at 20 mV s^{-1} scan rate.

By analyzing voltammograms in Figure 3, it can be concluded that there are six current peaks in all voltammograms (A_1, A_2, A_3, $A^{'}$, A_5, A_6). Each current peak is associated with a particular electrochemical reaction. By comparing researches related to the oxidation of the pure silver and pure copper [8,9,10] it can be concluded that in these systems in alkaline solution OH^- particles are being adsorbed on the metal surface, so that the peak current A_1 corresponds to the adsorption of OH^- ions by following reaction:

$$Ag/Cu + OH^- = Ag/Cu(OH)_{ads} + e^-$$

Current peaks A_2 and A_3 correspond to the formation of copper oxide. Based on listed literature it can be concluded that current peak A_2 corresponds to the formation of Cu_2O, while current peak A_3 corresponds to the formation of copper oxide CuO[11,12]. According to literature the current peaks A_4, A_5 and A_6 are attributed to the electrochemical reactions of silver oxides formation. Current peak A_4 corresponds to the formation of oxide Ag_2O type one, while the current peak A_5 occurs in the formation of oxide Ag_2O type two, a current peak A_6 represents the formation of oxide AgO [11,12,13,14]. At chloride ion concentrations higher than 0.001 mol dm^{-3} and potential where A_4 occurs, new current peak $A^{'}$ appears which represents the formation of silver chloride AgCl according to the reaction:

$$Ag + Cl^- \rightarrow AgCl + e^-$$

The effect of the concentration of BTA on the electrochemical behavior of AgCu50 alloy was examined in the concentration range of 0.00005 - 0.01 mol dm^{-3} BTA. Obtained cyclic voltammograms are presented in Figure 4.

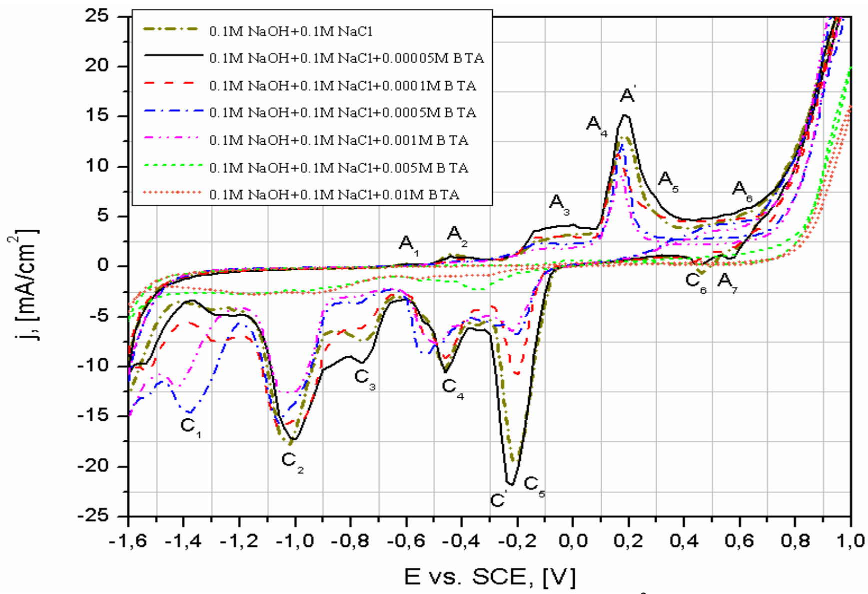

Figure 4. Electrochemical behavior of AgCu50 in 0.1 mol dm^{-3} NaOH with addition of 0.1 mol dm^{-3} NaCl with and without addition of (0.00005-0.01 mol dm^{-3}) BTA at 20 mV s^{-1} scan rate.

At the lowest examined concentration of 0.00005 mol dm^{-3} BTA acts as an corrosion activator, which is in accordance with the rule that solution should always contain sufficient amount of inhibitor, which can be determined by research. With the increase of benzotriazole concentration, the inhibition is achived by filming of Ag-Cu alloy surface with the CuBTA and AgBTA complexes. The processes of formation metal oxides and chlorides present in alloy occur simultaneously with formation of CuBTA and AgBTA complexes until the whole surface is covered by them.

CONCLUSION

The presence of chloride ions in concentrations larger than 0.01 mol dm^{-3} significantly intensifies anodic processes on AgCu50 alloy. In order to slow down these reactions, it was looked into the possibility of using benzotriazole known as an effective corrosion inhibitor for copper. It was determined that benzotriazole in concentrations larger than 0.005 mol dm^{-3} lead to nearly complete alloy passivation at all investigated chloride concentrations.

On cyclic voltammograms of AgCu50 alloy in 0.1 mol dm^{-3} NaOH in the presence of chloride ions it was registered one additional current peak,which doesn't appear on voltammograms without Cl^- ions, and it was ascribed to the formation of silver chloride (AgCl). Due to intensification of anodic processes, current peaks appear with higher current density values. At the lowest examined concentration of 0.00005 mol dm^{-3}, BTA acts as an corrosion activator, which is in accordance with the rule that solution should always contain sufficient amount of inhibitor, which can be determined by research. With the increase of benzotriazole concentration, the inhibition is achived by filming of Ag-Cu alloy surface with the CuBTA and AgBTA complexes. Oxides and chlorides of both metals present in the alloy are being formed simultaneously with formation of CuBTA and AgBTA complexes until the whole surface is covered by these complexes.

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PREPARATION OF SOLIDIFYING BACKFILL FOR ENVIRONMENTAL PROTECTION

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ABSTRACT

If there is a request to totally excavate a particular layer without ore depletion together with permanent preservation of the earth's surface deformation then it is mined by underground mining methods with filling the cavities with solidifying backfill with engineered characteristics. For this purpose, the research carried out for the selection of backfill materials, binders and mounting.

Key words: Solidifying backfill, selection of backfill materials, binders, mounting.

INTRODUCTION

The main objectives of mining by methods with filling of cavities are: increase and full utilization of deposits without depletion of ore, excavation of deposits in complex mining and geological conditions, preservation of ecological factors in living environment, improvement of ergonomic and safety work conditions and recirculation of waste rocks [1-4].

To achieve these objectives it is necessary to install in excavation sites backfill material of appropriate physical and mechanical characteristics, especially in terms of achieving the required compressive strengthand permissible deformation after installing in the excavation sites. Backfill strength is satisfactory (normative) if it is possible safe opening of artificial (backfill) massif with designed mining rooms and digs, and if it ensures the preservation of earth's surface and facilities above deposits from deformation. On the massif from backfill material act gravitational and tectonic (static) and from blasting works (dynamic) forces. Mass of backfilled excavation may be subjected to deformations due to pressure, tensile, shear, bending in uniaxial, biaxial and volume stress condition. For choice and control of required strength backfill material, with regard to the roles to be met, independently from the character of the load, strength of backfill material is determined according to required strength of the uniaxial pressure.

Required backfill material strength is determined by one or more of factors:

a) stability (holding) vertical open sides

b) horizontal open ceilings,
c) allowed deformation of the earth's surface,
d) the possibility of moving equipment on the backfill surface etc.

Mass of from backfill material and the surrounding rocks, in certain circumstances, form a complex spatial system backfill-rock. The main structural elements of such system -rocks of roof, and floor and backfill area, are very different.

Calculation of backfill strength and deformation characteristics,is based on the knowledge of the stress-deformation characteristics of natural rocks and artificial (from backfill)massif in the area of excavationand the nature of their interaction, and is reduced to solving of the three tasks.

1. Finding a load on the mass of backfilled excavation
2. Determination of stress in backfill area in as an integral element of the rocks system (rocks backfill area).
3. Determination of the necessary strength of backfill, resulting from the required coefficient of reliability (security), for a particular stress condition, with the impact of other technological factors at excavation of the deposits.

The load to an artificially massif of backfill in excavation depends: of the physical-mechanical characteristics of surrounding rocks, stress in them, geometry of backfilled excavation, (size, depth and inclination), and physical-mechanical characteristics of backfill, as well as the role that construction of backfill material meets during the further exploitationand at termination of deposits exploitation.

At complete excavation of deposits (Excavation Site with the previous filled excavation), in the roof of deposit, near the excavation, establishes a zone of reduced pressure (disburdening), and in ore massif in front of advancement excavation, appears zone of high support pressure. With the increase of the width of the excavated areaand filled area, roofing rocks and backfill in a mire area behave like the surrounding rocks and permissive support, until backfill does not receive the entire load of pillars of overlying rocks. The load at the excavation comes from rocks of roof, which partly relies on the backfilled part of the excavation, and partly to the ore massif. Dimensions disburdening zone are proportional to the deformation characteristics of the backfillε. A Backfill deformation characteristic depends on the type of backfill and its installation. At$\varepsilon \leq 3\%$ movement of the leaning rocks is performed by bending without cracking and fragmenting. At$\varepsilon \geq 3\%$in the roof occurs cracking and de-lamination of rocks.

The procedure of selecting of backfill materials with required strength when applying the method of excavation with back fillingof excavation area at complete obtaining of deposits and protection of the earth's surface and objects from damage is performed based on tests and calculations derived in the design of excavation. If it is found that with normal dry or hydraulic one-component backfill do not achieve the required characteristics in terms of strength and deformation of backfill, then it must be applied specific multi -component backfill, with the addition of binders for hardeningwith special method of installation to achieve higher density, strength and favorable deformation characteristics.

SOLIDIFYING OR CURING BACKFILL

Under the terms of solidifying or curing backfill should involve features of backfill materials composed of multiple components,which, by embedding in empty excavation bymechanically and pneumatically inserting in the loose state, or hydraulic lining in form of paste and sludge, after a certain time standing in excavation,under the influence of added binders, solidifies, i.e.hardens, until create a solid, hard monolith, with required designed deformation characteristics and strength.

For the production and installation in Excavation Site of satisfactory hardening backfill, it is necessary to choose a suitable backfill material that serves as a solid base for filling of excavation and increases the density of the mixture, because in the mixture of about 1 m^3 participates, 9 to 0.95 m^3. The basic features that backfill material for the filling should have are: the material should have a firmness greater for 10-15% of normative required strength of backfill, should not be soluble in water,to have low coefficient of volume increase in moist environments, does not contain toxic impurities and that its obtaining is cheap and its transport to the excavation. Coarseness of filling material depends on the way of transport and installation in empty excavations. It is characterized by with coarseness module. Materials for filling are most often: crushed rock materials, natural sands, waste rock from the disposal sites,flotation barren mud, slag and ash from thermal power plants and slag from metallurgy.

Binders

For hardening of backfill in excavations, to backfill material for filling excavation should add the appropriate amount of binder or binders. Binders are added to the backfill material during installation in Excavation, under stirring with backfill material,at hydraulic or pneumatic filling,at mechanical installation of dry backfill materials in excavation site,for solidification of embedded mass injection of backfill in excavation site is performed. The most commonly used binders for the preparation of curing backfill are: various types of cement, ashes from metallurgical plants, ashes from thermal power plants, plaster, water glass, limestone and clays.Besides the binders for the specific properties required of backfill, to backfill are added:Activators that increase the activity of a hydraulic binding materials by breaking the hydrated membrane around the kernel of the active phase and accelerate the setting of water and hydrated lime, or retarders if is necessary to the previously drain harmful salts from the backfill.

Water

Water is a necessary ingredient for getting hardening, solidifying filling material whether it is used in the hydraulic transport of filling material or it is added to the backfill material together with a bonding material and acquisition agents. For the preparation of a solidifying backfill clean water is used without the dissolved acids, salts and the sludge, which may be aggressive in concrete. Many mining waters are not suitable for use if they are acid or contain a salt up to 5 g / l. The pH value of waters to create a solidifying backfill should be about 7. The amount of water added with fill depends on the water-cement ratio, which does not need to be high because with high water-cement factor decreases the activity of binding agents.

LABORATORY STUDIES FOR THE PREPARATION OF SUITABLE MIXTURES

To fill the excavation with designed hardening backfill, first, in the laboratory are identified including quantities: from a selected base material for backfill, binders of various quality and price and water to make a mixture,which will after solidification in excavation, achieve the required and satisfactory deformation characteristics. For the solution of this problem are carried out studies on test cubes 10x10x10 cm,which are cast from selected materials for backfill with adding of different amount of binder of various quality and water. Treatment is twice to five cubes of the same composition in a series of five of various quantitative compositions. During hardening of cubes,on some of them is Investigate speed of hardening.As the cubes are divided into two groupsthen remaining cubes can serve as a control if encounters corrupted cubes. Upon hardening of cubes after 28 days, survey has been conducted on strength and deformation characteristics.The research results are classified in tables and based on them is performed analysis of the research results. In order to independent researchers could successfully process and discuss the results of this analyses, here is given that procedure.

Research for preparation solidifying backfill in the world are often carried out on mixtures of various backfill materials, Cement of different brands other bonding materials and water.It is found that the changes in strength of concrete $\delta_b$made of the backfill with adding cement etalons δ_c,varies depending on the amount of added cement by the empirical formula:

$$\delta_b = a q_c^b \delta_c$$

where are:

a, b, - empirical coefficients that depend on the applied etalons, brand of cement MPa,
q_c - quantity of cement added to backfill material, kg/m^3
δ_c -brand of cement with water-cement ratio v/c = 1and consumption 400 kg/m^3, Mpa.
δ_b - strength of backfill cubes Mpa.

Determination of coefficients a and b in empirical formula, is done based on the results of tensile tests on cubes at uniaxial pressure. They are constructed by adding a certain amount of cement, known brand, and research results are classified into tables to obtain the mean values of backfillstrength $\delta_{bi}$from amount of added cement q_{ci}. Determination of coefficients a and b, in the empirical formulais carried out by applying the theory of minimum squares, according to the following procedure:

$$\log \delta_b = \log a + b\log q_c + \log \delta_c ;$$

If we introduce a substitution to express the functional dependence:
$a = \log a + \log \delta_c$; $x = \log q_{ci}$; $\delta_{bi} = yi$, then we obtain : $yi = a + bxi$

This function represents a straight line trend with unknown coefficients a and b, which may be determined based on the theory of minimum squaresfrom relation in which data are entered from tables.

$F^2(a,b,x,y) = \Sigma\ (yi - a - bxi)^2$ min. meaning that we should find the first derivative of the Functions yi and xi

$-2\Sigma(yi - a - bxi)= 0$; $-2\Sigma(yi - a - bxi)xi$; which implies:

$\Sigma yi = na + b\Sigma xi$; $\Sigma yixi = a\Sigma xi + b\Sigma xi^2$

These two equations contain two variables: a and b, which is easy to determine by the method of substitution,and their values are obtained from finite relations:

$$a = \frac{\Sigma yi - b\Sigma xi}{n}; \qquad b = \frac{\Sigma yixi - \Sigma yi\Sigma xi}{2\Sigma xi^2}$$

After obtaining of empirical function it is necessary to determine the standard error and correlation coefficient.

Table 1. The data of experimental research with data for processing of the obtained results

br	q_{ci}	δ_{bi}	Xi = log q_{ci}	Yi =log δ_{bi}	Xi^2	Xi .yi
1						
2						
3						
4						
5						
Σ	n =5		Σxi	Σyi	Σxi^2	ΣxiΣyi

When applying other binding substances than for comparison of backfill prices interesting to determine cement equivalent, i.e. the ratio of a binding material and cement in m^3 backfill that provides equal strength of backfill under the same hardening time.

$Ec = q_v/q_c$ kg/m^3

And these studies are conducted on standard cubes, and are important, because based on them binding agent can be selected which can be cheaper than use of cement, or may be selected the brand cement.

DENSITY OF BACKFILL MATERIAL IN EXCAVATION AND METHODS TO INCREASE IT

Density of the particle installation of solidifying backfill plays an important role in filling technology. Higher density of built-backfill in Excavation Siteis achieved by using a basic backfill material composed of particles of different coarseness with a higher share fine fractions and a dynamic way of installation. So, pneumatic insertion of backfill in excavation provides higher density of built-backfill from mechanical and manual feed. By the magnification of backfill density increases its strength, decreases the rate of water filtration And the required amount of cement necessary for hardening of backfill materials. At the same time is increased the amount of filling material for excavation of specific volume, but with growth of filling costs. Density of installation of backfill materials depends on its granulometric composition, humidity, and size of pressure in excavation and vibrations in blasting or vibrator during installation of backfill.When filling excavation with hardening backfill, in order to preserve the earth's surface and objects within exploitation field, it is necessary to establish the functional dependence of strength of hardening backfill from its installation density, and with it the need for of the vibrator in its installation. These researches are also conducted in the laboratory of the mine in a similar way of examining of strength on the series cubes constructed by vibrating of materials of different granulometric composition to achieve density γ_i .

Numerous researchercorrelations between of strength of backfill excavation and its density have expressed by potential trend:

$\delta_b = Ae^{b\gamma}$ Mpa

where are:

A i b -corresponding coefficients,

γ - density, specific mass, t/m^3

Based on the data obtained from the research of strength of hardening backfill depending on its density of installation, tabela 2 is formed. In it is added columns for data processing and determination of coefficients A and b in empirical function:

$\delta_b = Ae^{b\gamma}$ where are: $\delta_{bi}= yi$; $\gamma_i = xi$; and $yi = Ae^{bxi}$ A

$yi = Ae^{bxi}$; $\ln yi = \ln A + bxi \ln e$; $\ln e =1$; $\ln A = a$; $\ln yi = y$; $y = a + bx$

Logarithmic transformation by natural logarithm of this trend and by introducing a substitute for the logarithms is obtained form of the straight-line trend for which is already, Based on the theory of correlation and least squares,given solution for coefficients A and b in the previous example, where for obtained value a,for coefficient A should apply inverse logarithm.

Table 2. The data for determination of coefficients a and b, as a function of backfill strength from density

br	δ_{bi} = yi	γ i = xi	lnYi = ln δ_{bi}	yi γ i	γ i^2	$\delta_{bi}\gamma$i
1						
2						
3						
4						
5						
Σ	n = 5		Σyi = Σ ln δ_{bi}	Σ yi γ i	Σ γ i^2	Σ δ_{bi} Σγi

CONCLUSION

Before a final decision on the selection of materials for the preparation of hardening backfill should be carried out extensive research to select the best ways of obtainingand installation of solidifying backfill of required strength and deformation characteristics in excavation site. We should investigate the possible equivalent that can be replacement if its price is lower.

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VENTILATION AIR METHANE RESOURCE POTENTIAL OF "SOKO" COALMINE, SERBIA

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ABSTRACT

With estimated coal reserves of approximately 64 million tons of coal "Soko" is probably the most significant underground coalmine in Serbia. Unfortunately, tectonic and geo-morphologic characteristics of the deposit do not permit the application of high-productive mining methods so the average annual productivity of coal is 150 000 t/year. Besides that, the presence of methane additionally complicates the working conditions. The presence of methane presents the constant threat to mining safety creating potentially hazardous environment. Ventilation system increases the safety but results in an environmental hazard. Methane is one of the most dangerous greenhouse gases and "Soko" daily releases nearly 4 500 $m^3$of methane into the atmosphere without treatment. On the other hand, methane is an important energy source and the aim of this paper was to estimate the total volume of methane in the "Soko" coal deposit based on the data from the methane monitoring system logs. As a result, the paper suggested that any efforts to prevent or utilize methane emissions can provide significant energy, economic and environmental benefits.

Key words: coalbed methane, safety, environment, hazard, utilization, energy.

INTRODUCTION

Underground coalmine "Soko" is located some 12 km east of Sokobanja, Serbia. Coal extraction from the "Soko" mine started in 1922 and there are no data on estimated coal reserves from that time. After the WWII "Soko", among other mines, became an important resource for the growing economy of former Yugoslavia and it was necessary to explore the deposit. The exploration operations continued periodically up to today and according to the latest elaborate on coal reserves [1] the reserves are estimated to 64 000 000 t.

The coal seam thickness is 25 m average, and the dip is 30÷40o resulting in the horizontal thickness of up to 70 m. Geologically, the coalbed is intensively disturbed with the number of longitudinal and transverse faults dividing the deposit onto several blocks. From the aspect of lithology, the coalbed has a highly pronounced superposition, i.e. alternate thin seams of marlstone, clay and sandstone with coal seam embedded between them.

These unfavorable lithological and geological conditions prevent the application of high-productive mining methods such as longwall. Instead, a low productive drill and blast, roof caving method is applied [2]. The mining operations are simultaneously undertaken attwo levels, with one stope in operation at each level. The vertical distance between levels is 9 m and the horizontal offset between working stopes is 20 m with stope on the upper level in advance. Average annual production of "Soko" coalmine is 150 000 t.

Additional problem to already complicated mining condition is the constant presence of methane in the mining environment. The methane is trapped inside the pores and micro cracks in the coalbed and surrounding rocks but also forms high pressure gas pockets. When coal is disintegrated in the course of mining operations, methane slowly emanates and contaminates the working environment. This creates potentially hazardous situation and the danger of methane combustion and detonation is constantly present. On January the 16th 1998, Serbia was struck with its second largest mining disaster when methane explosion in "Soko" took 29 lives. To prevent hazards and increase safety the "Soko" ventilation system is designed to deliver 2 650 m3/min of air to the mine. This amount of air is sufficient to dilute the ventilation air methane (VAM) content well below the hazardous limit of 4,5 % and keep the methane content below the Serbian regulatory limit of 1% [3] in the exhaust ventilation air. In addition to the ventilation system design a number of gas detectors are strategically positioned in the mine corridors and are coupled into single methane monitoring system. Gas detectors continuously monitor the methane content in the mine air and all the data are sent to dispatch command centre. The data are stored in the methane logs on the computer hard drives and can be accessed for further display or analysis. Typical form of methane log for one day is given in table 1. Alarm threshold of the system is set to methane content of 1% and any exceed of this limit sets the alarm on and the system automatically cuts off the electric power supply to the endangered area. Methane monitoring system and ventilation fans have an independent power supply. All this enables the workers to retreat to the safe zone and prevents the appearance of any spark that could ignite the methane.

Table 1. Typical form of methane monitoring system log

Table 1. Typical form of methane monitoring system log						
Date:	Start	**Dec. 02.** Time 07:00:00		Event CH4 [%]		
	End	**Dec. 03.** Time 07:00:00				
Location:		**VH-170**				
Time		**State**	**Excess**	**Time**	**State**	**Excess**
07:00:00		0,14	-	09:19:57	0,05	-
08:43:49		0,05	-	20:58:39	0,14	-
08:47:04		0,19	-	21:13:03	0,05	-
08:47:11		1,22	ALARM	23:10:55	0,08	-
08:47:18		1,46	ALARM	04:11:09	0,16	-
08:49:06		1,59	ALARM	04:13:17	0,08	-
08:49:20		0,62	-	04:22:17	0,19	-
08:49:29		0,14	-	04:25:53	0,11	-

Ventilation system combined with methane monitoring system increases the safety but results in another hazard, environmental. The exhaust ventilation air, carrying methane, is released into the atmosphere without any treatment. Methane is one of the most dangerous greenhouse gases and remains in the atmosphere for approximately 9-15 years. It is over 20 times more effective in trapping heat in the atmosphere than carbon dioxide (CO_2) over a 100-year period [4]. A combustion reaction of methane and oxygen results in creation of carbon dioxide and water.

Considering that, simple burning of methane would result in environmental benefit since carbon dioxide is less harmful greenhouse gas.

$CH_4[g] + 2\ O_2[g] \rightarrow CO_2[g] + 2\ H_2O[g] + ENERGY$ (a)

In addition, methane is an important energy source. Controlled combustion of ventilation air methane (VAM) could yield in significant amount of heat energy which can be used as such or be transformed to electric energy. Depending on the amount of methane this energy can be used in mine facilities or distributed to other users. In any case, efforts to prevent or utilize methane emissions can provide significant energy, economic and environmental benefits.

METHANE MONITORING DATA

The first step in any action on methane utilization is the assessment and computation of methane quantities. The aim of this paper was to compute the amount of methane released into the atmosphere and to estimate the amount of methane trapped in the coalbed. The basis of these calculations were the data from the methane monitoring system for the period of two months and the data on coal production for the same period. An agreement was reached that representative data on methane are the data received from the last sensor in exhaust ventilation air. The sensor is positioned in the exhaust ventilation branch and gives data on cumulative methane emission from the entire mine.

As shown in table 1, raw data from the methane monitoring log show the date of the measurement, position of the sensor, start time of the event, event state and eventual excess state.

The daily methane monitoring starts at 7:00 AM and ends at 7:00 AM next morning to correspond to three working shifts. The date of measurements shown in methane logs is the date of monitoring start. Position of the sensor given in table 1, VH-170 is the ventilation corridor (VH-1) at the level K+170 m (170 m above sea level).

Start time of the event is the moment of the change in methane content in mine ventilation air. The raw data do not show the end time of the event but it is not necessary since the end time is equal to the start time of the next event. During the time period between two events methane content remains constant or the changes are below the resolution of the system.

The event state is the methane content in the mine ventilation air during a period of time. The value is given in volumetric percent. Threshold of the system is 0,00% and resolution is 0,01%.

Excess state column is a descriptive column related to any irregularities in the system but most commonly excess state is related to the alarm state. Lower bound of alarm is set to 0,75 % CH4 and the upper bound is 1%.

VAM EMISSION CALCULATIONS

The raw data on methane concentration as shown in table 1 do not give the values of methane quantities. To compute the methane volumes these data were rearranged and coupled with the airflow value as shown in table 2. Due to limited space, table 2 gives the principle of methane volumes calculations only for one day.

Table 2. The principle o methane volumes calculation

Date:	Start	**Dec. 02.** Time 07:00:00		Event: CH4 [%]			
	End	**Dec. 03.** Time 07:00:00					
Location:		**VH-170**					
Start		***End***	***Δt***	***Δt***	***c_{CH4}***	***QAIR***	***VCH4***	***QCH4***
			(hh:mm:ss)	*s*	*%*	*m^3/min*	*m^3*	*m^3/s*

Start	End	Δt (hh:mm:ss)	Δt s	c_{CH4} %	QAIR m^3/min	VCH4 m^3	QCH4 m^3/s
07:00:00	08:43:49	01:43:49	6 229	0,14	2 650,00	385,16	0,06
08:43:49	08:47:04	00:03:15	195	0,05	2 650,00	4,31	0,02
08:47:04	08:47:11	00:00:07	7	0,19	2 650,00	0,59	0,08
08:47:11	08:47:18	00:00:07	7	1,22	2 650,00	3,77	0,54
08:47:18	08:49:06	00:01:48	108	1,46	2 650,00	69,64	0,64
08:49:06	08:49:20	00:00:14	14	1,59	2 650,00	9,83	0,70
08:49:20	08:49:29	00:00:09	9	0,62	2 650,00	2,46	0,27
08:49:29	09:19:57	00:30:28	1 828	0,14	2 650,00	113,03	0,06
09:19:57	20:58:39	11:38:42	41 922	0,05	2 650,00	925,78	0,02
20:58:39	21:13:03	00:14:24	864	0,14	2 650,00	53,42	0,06
21:13:03	23:10:55	01:57:52	7 072	0,05	2 650,00	156,17	0,02
23:10:55	04:11:09	05:00:14	18 014	0,08	2 650,00	636,49	0,04
04:11:09	04:13:17	00:02:08	128	0,16	2 650,00	9,05	0,07
04:13:17	04:22:17	00:09:00	540	0,08	2 650,00	19,08	0,04
04:22:17	04:25:53	00:03:36	216	0,19	2 650,00	18,13	0,08
04:25:53	07:00:00	02:34:07	9 247	0,11	2 650,00	449,25	0,05

The amount of methane in the exhaust ventilation air, i.e. the amount of methane released into the atmosphere is calculated according to equations

$$V_{CH_4i} = \frac{Q_{AIR}}{60} \cdot \frac{c_{CH_4i}}{100} \cdot \Delta t_i \text{, (m}^3\text{) and } Q_{CH_4i} = \frac{Q_{AIR}}{60} \cdot \frac{c_{CH_4i}}{100} \text{, (m}^3\text{/s)}$$

where:

V_{CH4i} - volume of methane during the i^{th} event

Q_{AIR} - air flow, (m^3/min)

c_{CH4i} - methane content in exhaust ventilation air during the i^{th} event, (%)

Δt_i - i^{th} event duration, (s)

Q_{CH4i} - methane flow during the i^{th} event

Event duration time Δt_i is calculated as

$$\Delta t_i = t_{i+1} - t_i \text{, (hh:mm:ss converted to s)}$$

Where:

t_{i+1} - i^{th} event end, (hh:mm:ss)

t_i - i^{th} event start, (hh:mm:ss)

The results of methane volumes calculations i.e. the cumulative daily volumes of methane (CDVCH4) released into the atmosphere are given in table 3.

Table 3. Cumulative daily volumes of methane

Date	*VCH4*	*Date*	*VCH4*	*Date*	*VCH4*	*Date*	*VCH4*
	m^3		m^3		m^3		m^3
1	7 773,54	17	4 223,62	1	6 439,65	17	5 056,43
2	9 921,60	18	4 197,60	2	2 856,17	18	4 917,90
3	10 303,20	19	4 215,90	3	4 208,59	19	6 356,68
4	5 406,01	20	4 197,60	4	1 144,80	20	4 417,73
5	3 969,16	21	4 197,60	5	2 135,69	21	4 242,90
6	4 960,36	22	4 979,07	6	2 846,31	22	5 266,26
7	3 786,03	23	5 342,40	7	3 902,88	23	5 068,92
8	4 437,89	24	4 297,10	8	4 848,26	24	5 769,70
9	2 209,34	25	4 197,60	9	4 197,60	25	5 342,40
10	4 580,95	26	4 197,60	10	3 728,51	26	5 754,21
11	5 308,29	27	4 244,11	11	4 197,60	27	7 220,08
12	3 052,80	28	5 442,29	12	3 052,80	28	4 873,37
13	3 052,80	29	5 342,40	13	1 908,00	29	4 231,13
14	1 908,00	30	5 358,44	14	4 120,46	30	4 391,97
15	2 565,13			15	4 875,33	31	4 635,34
16	4 207,45			16	4 596,54		
	TOTAL 141 875				**TOTAL 140 812**		
	Daily average 4 630 m³						
	Yearly estimate 1 689 950 m³						

ENERGETIC POTENTIAL OF "SOKO" VAM UTILISATION

A combustion reaction of methane and oxygen results in creation of carbon dioxide and water with the release of significant amount of energy.

$$CH_4[g] + 2\ O_2[g] \rightarrow CO_2[g] + 2\ H_2O[g] + ENERGY$$

With net calorific value (NCV) of methane of 35,80 MJ/m3 (50,01 MJ/kg)[6,7,8], a stoichiometry combustion of estimated yearly volume of VAM from the "Soko" mine would release 60 500 210MJ of energy. With NCV of coal in "Soko" of 16,83 MJ/kg [10] this amount of energy is the equivalent to the energy of 3 600 t of coal. In other words, with current productivity, the energetic potential of yearly amount ofVAM equals the ten days coal production. Other, but not the least significant benefit from "Soko" methane utilization is environmental benefit. Stoichiometry combustion of VAM would convert methane into environmentally less harmful carbon dioxide and water. Average CDV_{CH4} of 4 630 $m^3$is a small amount compared to similar methane sources in the world but, for a small country such as Serbia and especially for the Sokobanja municipality being a famous spa center and ecologically clean municipality, methane emission from "Soko" coalmine is a major environmental impact and classifies "Soko" as a major polluter. Having this in mind, any attempt of methane recovery and utilization is a step toward the preservation of Sokobanja and Serbia environment.

CONCLUSIONS

VAM energetic potential of Soko underground coal mine being equal to 10 days coal production does not seem significant. However, having in mind that VAM is an energetic potential available at almost no cost it should be seriously considered. In addition, combustion of VAM would result in less environmentally hazardous carbon dioxide and decrease pollution levels.

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TESTING THE EFFICIENCY OF EXCHANGE FERTILIZER MIXTURES AFTER MECHANICAL ACTIVATION

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ABSTRACT

In this paper the effect of mechanical activation of composite mixtures of natural clinoptilolite (Cp) and phosphate rock (PR) on solution P, Ca, K, Na, Mg concentrations was investigated. It was observed that the addition of Cp increases the PR dissolution but insufficiently for direct use of the ore. A subsequent mechanical treatment of the Cp/PR mixtures improves solubility of the PR and solution P, Na, Mg concentrations released were of their optimal values required for plant growth. Solution K concentration after activation, however, decreases below the optimal limit, while Ca levels remain unchanged.

Key words : clinoptilolite, phosphate rock, mechanical activation.

INTRODUCTION

At the location Lisina, near Bosilegrad in Eastern Serbia, has been confirmed amount of about 95 million tones of PR mineral resource, with an average content of 9% P_2O_5. Thus, Lisina represents the only major PR deposit in continental Europe of great strategic significance. The PR is the primarily raw material for producing water - soluble P (WSP), but it can be applied directly under certain conditions. Direct application of PR (DAPR) has been suggested as economical alternative to expensive commercial WSP [1]. But, the efficiency of PR is limited due to its poor solubility, and it may be suitable for direct application only under specific circumstances.

The addition of zeolite has a positive impact on increasing the efficiency of PR [2]. Due to their high cation exchange capacity (CEC), water retention and adsorption properties, zeolites are widely-used multi-purpose soil amendments [3].

Modification of the properties of PR by mechanical activation is one of the known directions taken in the mechanochemistry of inorganic materials [4, 5].

The main aim of this research was to determine how mechanical activation affects the release of P, Ca, Na, K and Mg nutrient cations from the Cp/PRmixtures of different composition. Throught the batch experiments, a comparative examination of mechanicaly activated (MA-Cp/PR) and non-activated (Cp/PR) substrates will show whether the test mixtures are adequate sources of nutrients required for plant growth.

MATERIAL AND METHODS

The zeolite tuff (K-Cp), from deposit Baia Mare, Romania and phosphate rock (PR), apatite from ore deposit "Lisina" Bosilegrad, Serbia, were used in the experiment. Selected characteristics of the Cp and the PR samples are presented in Tables 1 and 2. The CEC of the Cp using EPA Method No. 9081 was 158.2 meq/100g of zeolite (out of which Ca^{+2} 92 meq, K^{+} 51.5 meq, Na^{+} 8.85 meq and Mg^{+2} 5.84 meq).

Table 1. Selected chemical characteristis of the clinoptiloite (Cp) used in the study

Oxide	SiO_2	Al_2O3	Fe_2O_3	CaO	MgO	TiO_2	Na_2O	K_2O	loi
mass %	63.60	11.81	1.74	7.35	0.69	0.40	4.40	0.169	9.81

Table 2. Selected chemical characteristis of the phosphate rock (PR) used in the study

Oxide	P_2O_5	SiO_2	Fe_2O_3	Al_2O_3	TiO_2	CaO	MgO	Na_2O	K_2O	S	V	loi
mass %	9,72	52,29	3,39	3,57	0,45	18,04	0,32	0,16	2,76	0,3	0,011	4,87

The two groups of several batch-experiments were performed to investigate the solubility and ion-exchange relationships between Cp and PR. In the first group the purified Cp fraction (50 µm to 100µm) and the PR coarse silt frations (< 37 µm) were used. Second group contained the MA-Cp/PR mixtures of the same composition as the first group. Mechanical activation was performed using a vibrating ring-mill (KHD, Humboldt Wedag, AG), for a period of 30 s per sample to avoid sticking. The both groups of mixtures were assembled in the three different ratios of Cp and PR; 5:1 10:1 and 15:1 and each system initially contained 4g of PR. The mixtures replicated three times were placed in a 300 ml volumetric flask to which was added 200 ml of distilled water. Samples were shaken on a rotary shaker for 72 h at 220 rpm. After draining, the resulting solutions were examined on the contents of Ca, K, Na, and Mg using the atomic absorption spectrophotometer technique. Solution P concentration was determined using a colorimetric technique.

RESULTS

The distribution of solution P, Ca, K, Na and Mg concentrations, after 72 h of shaking the PR, the Cp/PR and the MA-Cp/PR mixtures are shown in Figure 1.

Solution P concentration in the soil adequate for a variety of crops ranges from 0.2 to 0.3 mg L^{-1} [6]. The P concentrations in the solution were between 0.20 and 0.26 mg L^{-1} in the Cp/PR mixtures and between 2.86 – 3.20 mgL^{-1} in the MA-Cp/PR mixtures. These results show that the mechanical activation increases the concentration of readily available phosphorus in the residual solution of the mixtures by a factor of 10-15. With the increase of zeolite share in the mixture the quantity of phosphorus in the solution slightly inreases (Fig 1).This finding is in accordance with the results of Yusupov et al. [5] where the Cp/PR mixture of similar composition were used.

Typical soil solution Ca concentrations necessary for high yield of agricultural crops has been reported to be from 8 to 45 mg L^{-1} and should not be lower than 14.8 mg L^{-1} [6]. The solution Ca concentrations increase with an increase in Cp/PR ratio and vary between 14 and 24 mg L^{-1} regardless of the mechanical treatment (Fig.1). These results indicate sufficient amount of Ca can be supplied by the Cp/PR substrates.

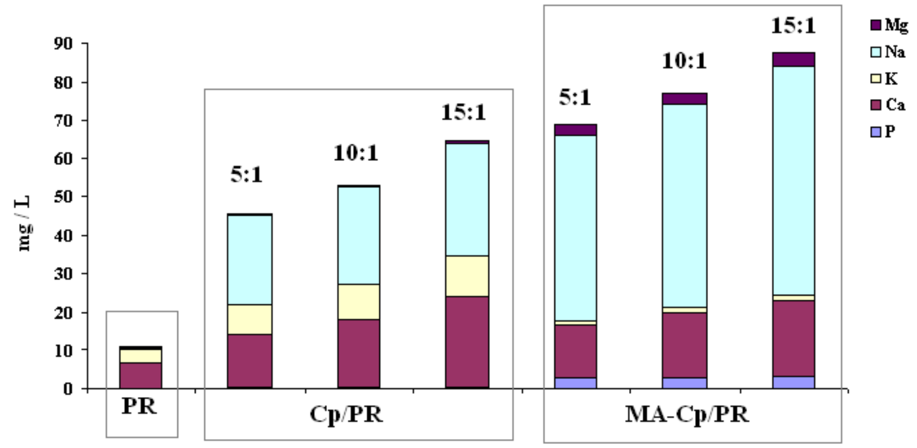

Figure 1. Solution P, Ca, K, NA and Mg concentrations released from the PR alone and different exchange-fertilizer substrates after 72h

The optimum soil solution K concentrations are in the range between 8.6 and 60.0 mgL^{-1} [6]. The K values found in the solution of the Cp/PR were between 7.87-10.34 mg L^{-1} or near the lower of the optimal range. The highest concentration of K in the solution was detected in the Cp/PR mixture with the maximum Cp abundance (Fig 1). In contrast to the observed trend in P, mechanical activation significantly reduces the concentration of K, which varies from 1.13 up to 1.35 mg L^{-1}. It is known that many clinoptilolites have great affinity or K [2]. Increase of the Cp specific surface area after mechanical activation probably induces a consequent adsorption of K by the Cp, which results in an overall decrease of K in the residual solution.

The growth response to Na significantly varies among plant species [7]. The typical Na concentration in the soil solution is on average 2.3 –23 mg L^{-1}. The Na concentrations found in the solution of the Cp/PR and the MA-Cp/PR were between 23-29 mgL^{-1} and from 48 to 59 mg L^{-1}, respectively.

Optimal concentration of Mg in soil equilibrium solutions is about 0.94 mg L^{-1} [9]. Solution Mg concentrations in this study ranged from 0.45 to 0.94 mgL^{-1} in the Cp/PR mixtures and from 3.18 to 3.52 mgL^{-1} in the MA-Cp/PR mixtures. The obtained result indicating that the ample Mg and Na will be supplied by the both test substrates.

CONCLUSION

It is shown on the example of exchange – fertilizer mixtures of PR from Lisina deposit and natural Cp that the structural breakage during the mechanical activation determines the solubility of PR. It is found that ion exchange interaction of Cp with PR improves PR dissolution and after mechanical activation in particular the P, Na and Mg concentrations in the residual solutions increases. Solution Ca concentrations of the Cp/PR and the MA-Cp/PR mixtures remain of similar values and displaying slight linear growth with increasing the share of zeolite in the mixture. The K values found in the solution of the Cp/PR were near the lower of the optimal range. After mechanical activation, the K concentration in the solution additionally decreases probably due to adsorption of K by Cp.

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THE ROLE OF INFORMATION-ALARM CENTER IN CONTROL OF GAS VENTILATION PARAMETERS IN THE PIT OF RMU "SOKO"

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ABSTRACT

The problem of gases emission in the Mine Soko is very strong, and that in the dual form; first in terms of risk for workers employed in the pit of Soko Mine (gases are explosive and toxic) and second in terms of emission of greenhouse gases (CH_4 and CO_2). Here is presented monitoring and results of automatic remote control for the purpose of Mine security, but also result of methane and carbon monoxide emission, unfortunatelly without indicators of carbon dioxide emission from the pit of Mine Soko.

Key words: automatic remote control, methane, carbon dioxide.

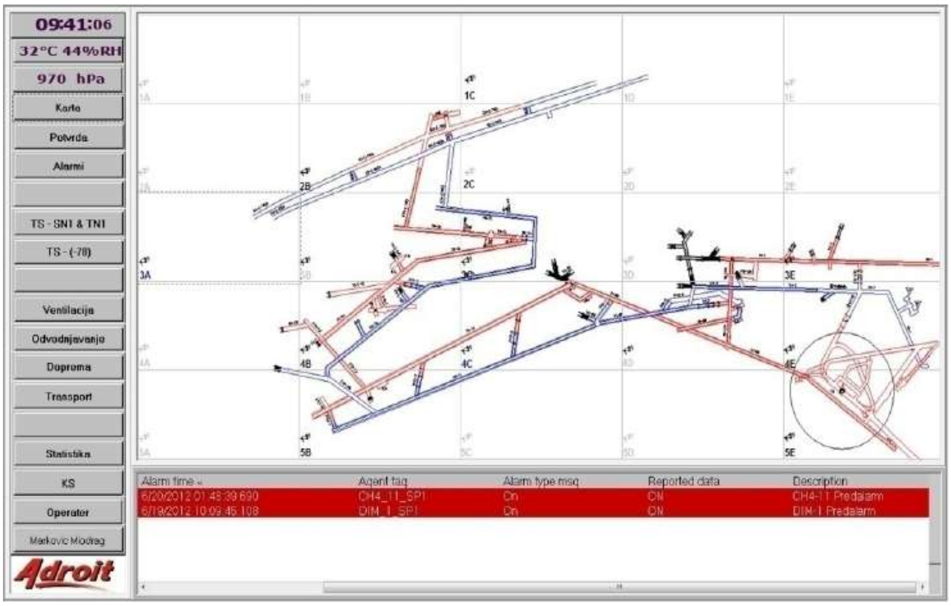
INTRODUCTION

Coal exploitation in RMU "Soko" is being done with relative methane stability from 15,75 to 33,31 m^3CH_4/t and absolute methane stability 4 to 5 m^3 CH_4/min. Beside methane, which is being continuously separated from the coal in the exploitation process, this layer is characterized by bursts of gases, coal and rock materials under pressure.

MONITORING OF HARMFUL AND DANGEROUS GASES EMISSION INTO THE AIR FROM THE PIT RMU "SOKO"

In this paper we will present the results of monitoring and the monitoring parameter emission from the pit into the air, using the system for automatic gas control of ventilation parameters and software for control, collection and analysis of the measured parameters.

- Monitorig of gas state in the pit RMU „Soko", is being done by installation of system for automatic remote control (ARC) of gas-ventilation and fire parameters type Sieger and Trolex, manufactured in England.
- By ARC system continuously measuring and archiving of ventilation, gas and fire parameters, as well as automatic disconnection of electricity in parts of the pit which is detected exceeding the allowed values of methane is done.
- System ARC consists of a devices installed in the dispatch center and in the pit, and of the accompanying installation as well.



The room of IAC (the Information and Alarm Center) has:

- The installed electronic equipment (a server computer and fitting equipment), that is used for recieving, processing and display of controlled parameters in a pit;
- The workstation, that is used to download data from the server and allows monitoring of parameters in real time;
- The workstation is connected to two LCD monitors that have:
  - The LCD 1: The subsystem of automatic remote control of ventilation, gas and fire parameters and the subsystem for alarm and oral communication;
  - The LCD 2: Technological parameters of subsystems of remote control of the devices operations in a pit and on an external facility;
- A computer with a printer that is used for overview and printing diagrams and shift reports. There is also „*Docking station server*" installed – the application for maintance of portable instrumentsa and archiving data, as well as „*Smalloger*" application – that is used for listening to conversations recorded within the subsystem of loud speaking .

Measuring instruments installed in a pit:

- ✓ Measuring instruments for measurement of the concentration of methane, *Trolex* TX6383 and TX6363 types;
- ✓ Measuring instruments for measurement of the concentration of carbon monoxide, *Trolex* STX3241 type;
- ✓ Measuring instruments for measurement of an airspeed, type *Trolex* TX5920 type;

- ✓ Measuring instruments for measurement of the main ventilator depression, *Sieger BP-2* type;
- ✓ Measuring instruments for measurement of differential pressure, *Sieger BP-2* type;
- ✓ Measuring instruments for measurement of flue gases, *Sieger – FIDESCO* type;
- ✓ Measuring instruments for measurement of the concentration of oxygen, *Trolex STX3241 type*;

The analysis of the occurrence of high concentrations of methane indicates the fact that increased concentrations of methane related to certain moments in the technological process of exploitation, in which methane is suppressed (mostly) from the chamber of excavation and previous works in the floor corridors, which could be seen in the following two examples:

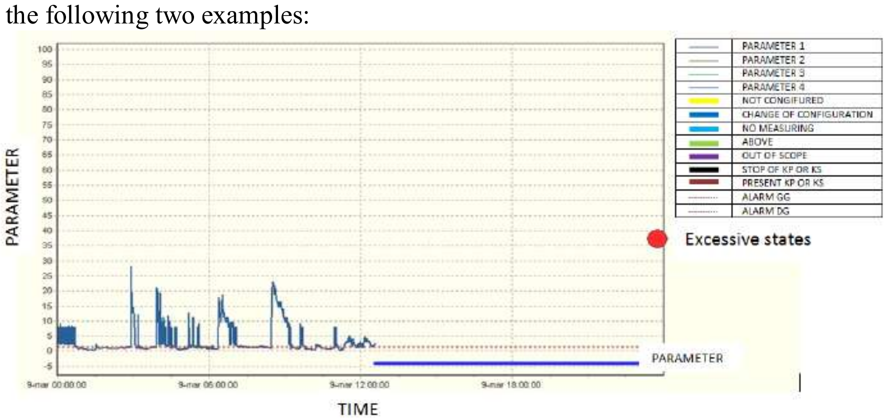


Diagram of methane concetration moving on excavation work site on the floor EH-78i during excavation demolishing (july 2013.)

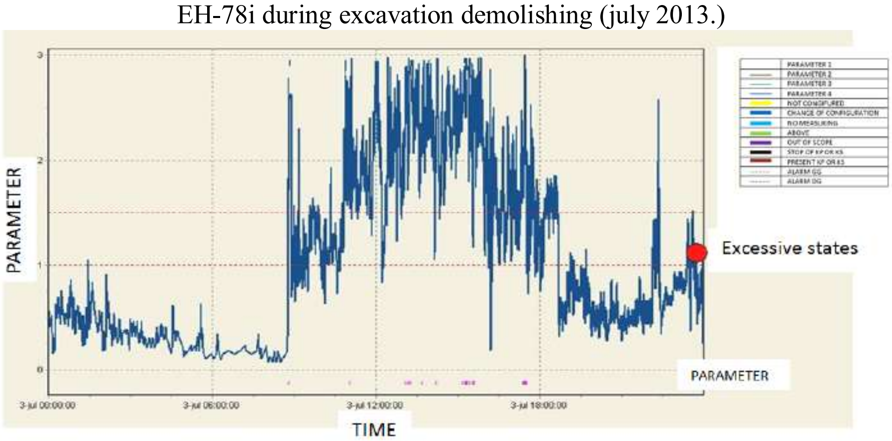


Diagram of methane concetration moving on excavation work site on the floor EH-78i during excavation demolishing (july 2013.)

- The devices perform a countionuous measurement and the results are forwarded to SCADA software.
- SCADA has a task to process, display and archive the measurement results.
- Launching the software it is possible to analyze the gas state of a pit for any period of time.
- Data are stored permanently.

By automatically measuring the concentration of methane in the output air stream of the Soko Mine pit and according to other ventilation the emissions of total amount of metal is monitored, and that is presented in the following diagram:

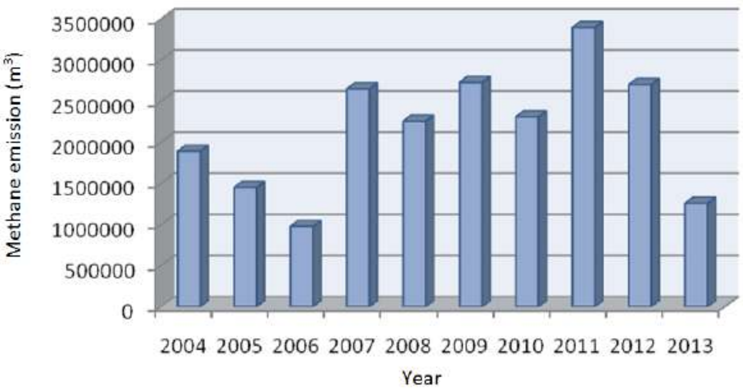
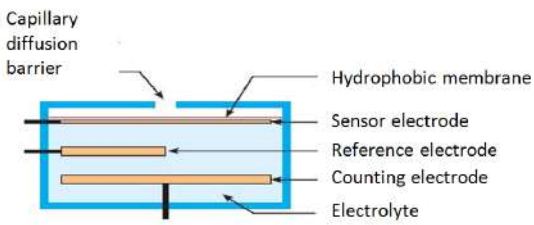


Diagram of methane emission from the pit of „Soko" Mine in the air between the years 2004 and 2013

- Carbon monoxide emission monitorig is accomplished by *Trolex STX3241* typed measuring instruments.
- Controlling carbon monoxide device operates on the electrochemical principle using the electrochemical sensor.
- A gas that comes in contact with the sensor passes through a small capillary-typed hole first, and then diffuses through *hydrophobic barrier*, and finally reaches the surface of electrode.
- This approach has been adopted in order to allow the proper amount of gas to react at the sensor electrode and to produce sufficient electrical signal – an impulse.



- Electric impulse is converted into a numerical value of the concentration of carbon monoxide, that is expressed with *ppm (particles per milion)*, which is loaded on the display of device in a pit and in a dispatcher center on the ground. The devices measure continuously, and the results are forwarded to SCADA.

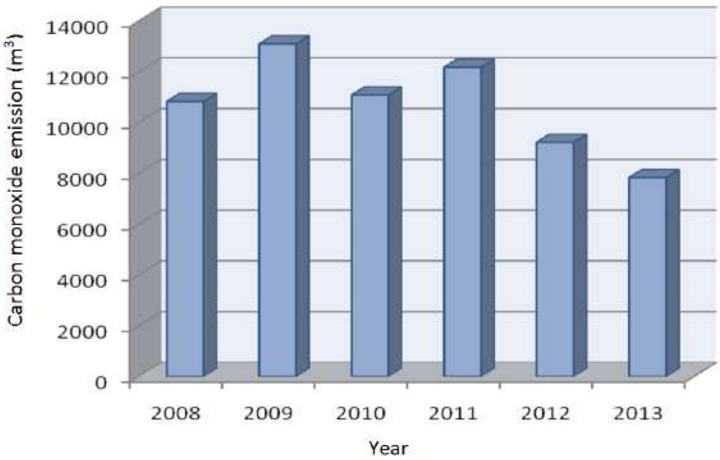


Diagram of carbon monoxide emission from the pit of „Soko" Mine in the air between the years 2008 and 2013

CONCLUSION

- Continuous monitoring of harmful and dangerous gases emission in the air, beside the local influence of coal exploitation on environment on the area of Sokobanja community has a national importance to provide full register of pollutants, which is recorded and updated in the Agency for environmenatl protection of Republic of Serbia;
- The implemented system for automatic gas-ventilation and fire parameters in the *Soko* Coal Mine has achieved remarkable results in terms of safety and health of miners.
- The lack of such a system of continuous monitoring of harmful and dangerous gases is that there are information about carbon dioxide missed, which is the most important gas with the greenhouse effect, and it is known that the *Soko* Coal Mine pit extracts CO_2 in significant amounts.
- The Annex A of the Kyoto Protocol (December 1997) to the United Nations Framework Convention on Climate Change (UNFCCC) defines the following gases wih the greenhouse effect (GGHE): - carbon dioxide (CO_2), methane (CH_4) aerated water (H_2O), nitrogen dioxide (N_2O), and ozone(O_3).

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WORLD'S WATER RESOURCES ARE EXHAUSTIVE SERBIA AND MONTENEGRO SPECIAL REVIEW

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ABSTRACT

Last century's rapid industrialization generated increase of production and offer of goods, creating prerequisites for growth of social standard, wealth and national income. In this speedy race, technology and development of production processes should enable a more rational utilization of natural resources while acting economically, as well as to adapt to everyone's needs.

Key words: water, natural resources, environment, development of technology, environmental protection, Agenda 21.

INTRODUCTION

Growing harmful effects of polluted environment, the environment itself becoming aggressive, started causing great economic losses, and are threatening not only human population and spreading a range of diseases caused by this activity, but also diminishing the durability and value of many materials, including water. These circumstances generate higher expenses for maintenance, resolving the problems of waste water and losing large areas for production. Being polluted downwards from a certain spot, a river became impossible to use for agriculture or industry without huge costs, and not even to mention the effect it had on tourism and recreation possibilities. These problems appeared and are most expressed in highly developed industrial areas, and it was there that very strict norms were set in order to protect the environment using most efficient measures.

It is only in the course of this year that four hurricanes, one after another, devastated within five weeks the areas of the Caribbean and the American State of Florida; disastrous storms in the Western Pacific, successive drought seasons in the Southeast of the US (as well as in Serbia), fires and floods in Australia within the distance of 500 km are just among first consequences of climate changes and heating of the atmosphere. The worst is that all those changes implied casualties.

Eminent environmental experts from all over the world emphasize that the late climate changes are just an introduction to "what is yet to come"?! Namely, the atmospheric carbon dioxide concentration, as a result of fossil fuel combustion (primarily petroleum), increased as much as 30% compared to pre-industrial period. Carbon dioxide produces a kind of layer that maintains the health of sun rays and causes the phenomenon of heating of the atmosphere, while the global sea level rose for 3 centimeters, only in the past ten years.

Since the beginning of the 20th century, water needs have increased for about 15 times. At the end of the 70's and the beginning of the 80's, the world population was using around 120 liters of water per day for their needs, i.e. 190 km^3 per year. It is estimated that the total yearly water needs will reach around 6,000 km^3 by 2015, out of which 450 km^3 per year will be used for household consumption.

Drinking water constitutes only 2% of the total water area in the world, in other words, this is the water that can be adapted to human needs, after being subject to certain "adjustments" (such as disinfection etc.). Additionally, major "pure" areas include both poles, while a minor part relates to water resources on the continents. We will use the example of Kuwait, a small country surrounded by deserts and salty seas. For the needs of its population, using the method of chemical water desalination, this country produces 25,000 tons of drinking water yearly. The production process by the means of desalination is very expensive, which makes it usable only for rich countries such as Kuwait or Saudi Arabia. Then, what are countries of Africa and Asia, not having such wealth, likely to do? They must turn to rich countries for help. And that is a never-ending story.

The same context shows us a rather interesting example of the United Arab Emirates. Namely, in the Emirates, 90% of water is produced using desalination. Given the geographic position, the Emirates have an evident need for water. This country's population consumes 350 liters per person on daily basis. World's global average is 250 liters. Most recent agricultural arrangements with this Arab country may also be very attractive in the sense of potable water. This can be achieved by constructing small hydroelectric power stations, more precisely by placing water basins at the end of the outermost power station, the water of which will be treated by ozonization and minor modifications using disinfection agents, if needed.

In particular, there is, already at present, an emerging problem of unequal distribution of water resources, on the one hand, and an impaired quality of water, on the other. Unfortunately, all of this is a consequence of man's activities.

Therefore, correct understanding of the environmental crisis requires establishing relationships and interactions between economy and ecology, in the context of production capacities and technological accomplishments, as a determinant. Hence, the assumption that economic growth in balanced state, conceived as meeting of environmentally justified needs on the one hand, and elementary social needs on the other, can represent the basic parameter of further development of socio-economic relations in global sense; it can also affect establishing proper civilization norms.

The environmental condition in our country is significantly threatened. Pollution is clearly differentiated per region and is unequal. One of the characteristics is that the extent of threat has an exponential growth and is directly dependent on the level of industrial development of the area in question.

Analyses to date, done for the needs of the Serbian water management body, have shown that out of the entire quantity of water flowing through Serbia, only 9%

originates from the territory of Serbia while 91% is transition water. On the other hand, it is worth mentioning that Montenegro is one of the most water-abundant areas in the world. Although it occupies a considerably smaller area than Serbia, Montenegro benefits from approximately the same potentials. Average annual water outflow from all watersheds in this country is 44 $l/s/km^3$. A slight problem is that the water outflow is remarkably misbalanced; this is why in springtime, the melting snow carries a great risk of causing runoffs and floods.

The total water quantity used for water supply in Serbia is around 750 million m^3 on annual basis. The share of groundwater is 80%, i.e. ground water from different water-bearing media (alluvial, as the most common ones) constitutes around 600 million m^3. Their capturing is done using water capturing devices – mostly wells, while capturing sources is done for about 145 million m^3.

Montenegro uses karst aquifers for more than 90% of water supply, with the exception of cities of Herceg Novi, Pljevlja, Podgorica and Ulcinj, obtaining water from other sources as well. Current minimum exploitation capacities of Montenegrin karst aquifers in draught period are $3.85 m^3/s$.

At the territory of Serbia, groundwater is used in 80% of cases for the needs of drinking water supply in inhabited areas.

In Vojvodina, an exclusive way of water supply is utilization of groundwater, while the Kosovo basin is supplied with surface accumulations in the amount of 10% (accumulations and river currents), and the rest comes from groundwater.

Experts from the Republic of Serbia foresee that around 45 m^3/s will be necessary for the needs of Serbian population by the end of 2020's.

The most significant groundwater sources and potentials are located at the territory of Central Serbia (60%), around 33% at the territory of Vojvodina and 7% in Kosovo and Metohija.

Additionally, in every second, the quantity of 80,000 liters of water flows out of mountain watersheds and snow-melts into brooks and rivers in Serbia. Chemically, this water is entirely pure, which, with minor or no modification at all, can be marketed abroad. Equally, it is known that every year there are 30,000 deaths more than births. In this respect, Serbia will not experience problems with lack of water. It is unequally distributed in our case as well. One of the biggest watershed currents at the proximity of Kuršumija (Lukovska Banja) has not been placed in exploitation yet, while its capacity can supply the entire region, including the City of Niš.

Table 1. Total capacities of existing ground water sources in Serbia

No.	district and city	exploitation of groundwater from a water-bearing medium alluvial	al.dilute	neorg.	karst	chink	T o t a l (l/s)
1	Severnobački	0	755	0	0	0	755
2	Srednjebanatski	0	648	0	0	0	648
3	Severnobanatski	0	779	8	0	0	787
4	Južnobanatski	396	557	51	0	0	1.004
5	Zapadnobački	150	294	183	0	0	627
6	Južnobački	908	537	189	0	0	1.634
7	Sremski	160	340	296	0	0	796
8	Mačvanski	1.078	0	0	030	0	1.108
9	Kolubarski	85	0	0	267	0	352
10	Podunavski	730	0	0	0	0	730
11	Braničevski	530	0	0	90	0	620
12	Šumadijski	320	0	15	26	0	361
13	Pomoravski	205	0	430	150	0	785
14	Borski	65	0	60	90	0	215
15	Zaječarski	110	0	0	525	0	635
16	Zlatiborski	212	0	0	379	0	591
17	Moravički	380	0	0	0	0	380
18	Raški	260	0	0	100	17	377
19	Rasinski	290	0	25	50	0	365
20	Nišavski	440	0	0	381	0	821
21	Toplički	0	0	25	75	0	100
22	Pirotski	5	0	0	715	0	720
23	Jablanički	55	0	350	0	0	405
24	Pčinjski	455	0	0	39	0	494
25	Kosovski	185	0	60	0	0	245
26	Pećki	0	0	140	860	0	1.000
27	Prizrenski	30	0	0	375	0	405
28	Kosovskomitrovački	86	0	0	30	0	116
29	Kosovskopomoravski	55	0	0	0	0	55
30	City of Belgrade	5.736	0	210	0	0	5.946
31	Vojvodina	1.614	3.910	727	0	0	6.251
32	Centralna Srbija	10.956	0	1.115	2.917	17	15.005
33	Kosmet	356	0	200	1.265	0	1.821
Republic of Serbia		12.926	3.910	2.042	4.182	17	23.077

Source: Materials for drafting a Water management basis of the Republic of Serbia

The necessary quantities of high-quality water by 2021, according to experts' estimates, will be in the range of:

Vojvodina	22.48 m^3/s
Central Serbia	46.46 m^3/s
Kosovo	5.35 m^3/s
Republic of Serbia	76.25 m^3/s.

Researches have shown that, out of 29 districts and the City of Belgrade, the estimated amounts of groundwater exceed the necessary amounts of high-quality water only in 10 districts. It is interesting that only in three districts this excess does not come from water-bearing media in the area of alluvial plains, where it is more than 12 m^3/s.

The excess amount of 3.4 m^3/s at the sources of Zlatibor, Pirot and Metohija is achieved by the possibility of capturing karst aquifers.

Moreover, by 2021, the deficit of necessary quantities of high-quality water in Vojvodina will be around 0.55 m^3/s, in Central Serbia 6.59 m^3/s, in Kosovo and Metohija 1.96 m^3/s and in the Republic of Serbia as a whole 9.10 m^3/s. Are we threatened by thirst?!

The biggest water supply system in Serbia is the Belgrade system. This is, at the same time the oldest system, set up already in 1892. At present, the quantity of approximately 7 m^3/s is used for the needs of the city and its agglomeration, out of which 6 m^3/s from groundwater coming from alluvial deposits of the Sava Riber from the Makiš, Ada Ciganllija, Novi Beograd and Boljevci sources. Nowadays, the Belgrade water supply system provides around 8 m^3/s of drinking water, out of which, purified groundwater constitutes around 5.5 m^3/s, while the quantity of 25 m^3/s is provided by purification of the Sava River water.

The Belgrade source encompasses 99 wells with horizontal drains and 46 pipe wells, around 200 km of main discharge pipeline (400–1.400 mm profile), three installations for groundwater treatment and supporting facilities. Current water needs, due to extensive industry, do not display realistic values, but in the near future, the lack of drinking water in the amount of 1m^3/s is to be expected. Construction of the above mentioned installation at the Makiš will resolve this problem.

Mid-term plans in Serbia have set the basics for the implementation of environmental protection activities as well as those in water supply area. It seems sufficient to mention the fact that separate ministries at the level of the Republic have been set up to deal with and try to resolve environmental issues. Concretely, resolving the water issue in an institutional manner is formalized in the Law on Waters, Law on Environmental Protection, Law on Protection of Water Supply Sources, Rulebook on Designation of Sanitary Protected Zones etc.

There are some opinions that the proposed legal solutions have not been adequately set and not implemented in concrete circumstances. For example, the Rulebook governing the area of protection of water supply sources does not state who is responsible for designation of sanitary protection zones etc… Putting a water supply source under protection is a very complex and responsible task, so any kind of random designation of sanitary protection zones can be of great harm. This is particularly pronounced for all surface currents, in the area of preservation and securing the prescribed category of current.

Global technological power centers are emphasizing stronger integrations at the national level and within multinational corporations that react efficiently to top technological challenges. Simultaneously, these processes in environmental protection include elements of monopoly, protectionism and mechanisms for maintaining supremacy over developing countries, because, in order to preserve a high level of environmental protection, particularly with water, purchasing equipment etc. from developed countries is a must. Technological studies of world's leading researchers identify development programs in the following areas:

- ***Energy*** (energy and new biological processes, energy saving, solar energy, industry and ocean energy);

- ***Materials*** (ceramics, mixtures and metal substitutes, anticorrosion procedures and waste material recycling, conservation of materials, using sea ores, cosmic technology and mineral resource research);
- ***Biotechnology*** (industry and renewable resources, genetic engineering, industrial procedures and enzyme engineering, forest resources and biological engineering);
- ***Agricultural and food industry*** (soil fertility and chemical industry – technology, culture and microbiology, livestock feed and chemical products, water supply and new technologies, new technological procedures and conservation, ocean resources and new technologies);
- ***Processing industry*** (photochemistry, production procedures and laser technology, industry and robotics, modular fabrication);
- ***Transport and communications*** (transport and photo batteries, vehicles and new technologies of transport management, voyages and cosmic technologies, satellites);
- ***Health*** (computer-based diagnostic and health care services, health improvement and disease prevention technology, sanitary policy and health data system, surgery and new technologies).

When considering the entire problematic of global environmental protection, and in particular, water current protection, it can be said that there are results being achieved in this area, but that they are insufficient. The most expressed problems of lack of water (drinking water, especially) in summer months jeopardizes considerably not only the standard of living, but the elementary existence itself, as well. Therefore, man's activity must be conceived in the way as:

1. Produce such goods that will not pollute environment after use;
2. Distribution centers should be formed in areas that do not interfere with environment;
3. In price policy, neutralization of harmful effects on environment during and after use of water should be included in the selling price, as an anticipation;
4. Using the means of promotion, it is necessary to inform, direct, motivate and educate consumers not to use environmentally harmful products and, which is most important, educate all consumption segments by raising the awareness on the necessity to protect and improve the environment.

Practically, accepting all the initiatives in terms of reconceptualization of market as an institution and setting environmental requirements as well as subsystems within marketing activities will make it possible for basic environmental protection criteria to be met, provided that normative (legal) acts are enforced. The previous statement that our country does not have an environmental protection strategy in force supports our strivings to start creating and implementing it as soon as possible.

Recently, there have been many talks about Agenda 21, used for manipulating in order to privatize water resources as much as possible and put everything under control of highly developed countries. The European Union went a significant way ahead in order to create these conditions; namely, ethics and reason have been put in question since the adoption of the Decision that water does not fall within the human rights sphere any more, which is a direct threat to those nations who do not have enough water or are remote to water sites. Water is a common good and cannot be taken care of solely by sanitary engineers. Unless a strategy of preservation of water currents in the world is defined, thirst will emerge as a global threat, bringing catastrophic consequences.

WATER SITES IN THE WORLD, TYPES, PRODUCTION AND CONSUMPTION

Water sites in the world are characterized by unequal distribution. Out of the total water potential in the world, 97.5% is the share of salty water. This percentage includes also 1% of salty groundwater. Out of that percentage, two thirds of water are iced water and the rest is liquid surface water and groundwater. About 60,566,592,999 liters of water are produced in the world every day. As already stated, this kind of production is mostly present in the countries of the Arab Gulf. As for the production price, it was due to the perfection of technology that it became close to the freshwater production. Namely, wholesale price of water in South California for 3,875 liters was $7 in 1990. Already in 2010, thanks to modern technological accomplishments, the price approached the one of freshwater – approximately $5 for the s quantity. A slightly bigger difference is perceivable at present, due to the increase in prices of energy and materials used for production.

"Researchers are now working on at least three new technologies that could cut the energy required even further. The closest to commercialization, called forward osmosis, draws water through the porous membrane into a solution that contains even more salt than seawater, but a kind of salt that is easily evaporated. The other two approaches redesign the membrane itself— one by using carbon nanotubes as the pores, the other by using the same proteins that usher water molecules through the membranes of living cells." (Source: Tom Pankratz, Global Water Information Service, International Water Association, Mark A. Shannon, University of New York).

"None of the three will be a solution for all the world's water woes. Desalination inevitably leaves behind a concentrated brine, which can harm the environment and even the water supply itself. Brine discharges are especially tricky to dispose of at inland desalination plants, and they're also raising the salinity in parts of the shallow Persian Gulf. The saltier the water gets, the more expensive it becomes to desalinate."

The degree of humidity on Earth has not changed. The water, drunk by the animals at that time (dinosaurs, for example), millions of years ago, is the same water falling down as rain. But, will that be enough for our world, becoming more and more populated?

Responsible institutions in the world are monitoring water needs as they do for population growth .Thus, World Fund for Environment and Wildlife Protection; State Hydrological Institute of Russia; Geological Institute of the United States of America, New York; Center for Environmental Systems Research, University of Kassel, Germany; National Snow and Ice Data Center (NSIDC), University of Colorado, USA, are quantifying the data on world's water and point out at the following: 69.9% or 24.36 mio trillion liters of water is trapped in ice (glaciers, snow covers and permafrost). 118,639 trillion liters or 0.3% is in rivers and swamps. This quantity includes water in plants, animals and atmosphere.

There is not more than 35 mio trillion liters of freshwater in the word, which is about 2–2.5%. We have less than 1% of water remaining for cultivating crops, cooling electric power plants and providing drinking water for households and personal hygiene.

Furthermore, 30.1% or 10.55 mio trillion liters is below the surface, within soil or in aquifers absorbing water from the surface. On all continents, aquifer water flows away faster in comparison to the natural renewal speed. Nowadays it frequently occurs that big icebergs, after breaking off a glacier in the North and the South Pole, float freely in the ocean or in the sea. For example, an iceberg from the Antarctica can float and melt for years, as noticed by experts, releasing its reserves of freshwater into the sea. Molecules of this water will eventually evaporate, condense and return to the Earth in the form of precipitations. This represents one additional source of water, but the environmental balance is disturbed by increased melting of both Poles.

Two thirds of water are used for food production in the world. With the total population growth at the rate of 83 million per year, water needs will keep rising until we change the way of using water.

For example, the population of the United States of America, as a developed country, use around 380 liters of water on daily basis. Millions of impoverished countries survive with less than 19 liters a day. 46% of people in the world have no running water in their households. Women in developing countries walk 6 km on average to bring water home. In 15 years, 1.8 billion of people will live in areas with extreme water scarcity. (National Geographic Srbija, issue 42-10).

More examples. We will mention additional data we came across in our research: the weight of the artificial lake "Three Gorges" in China will bow the Earth's axis for around 2 cm. The longest water tunnel, supplying New York, is 130 km long and has the capacity of 35 mio gallons of water per day (1 gallon = 3.785 liters)

The *Itaipu Dam* construction in South America cost $18 billion and was carried out in 17 years. Construction of dams forces almost 80 million people all around the world to change the place of residence.

MODERN TENDENCIES OF WORLD POPULATION GROWTH

There is an increasing tendency of population growth. Wealth in the world is unequally distributed, so the population growth trend is more common in poor countries than in rich ones. Despite all the precaution in environmental protection, however, Earth's atmosphere is being overheated and sudden climatic changes are occurring. All of this causes negative effects in the production of basic supplies, which presumes their insufficiency on the long run. Last century saw a large problem of nourishment of the population, while in the 21st century, the problem of using water resources will come up, besides unresolved food issues. The battle for improving the quality of life is a permanent task of all structures on our planet. The ones disturbing the already misbalanced environment must invest more in its revitalization and its restoration to the original, non-polluted state. Globalization, as an omnipresent process, may delete economic barriers and boost the well-being of developed countries, but it may not annihilate the cultural heritage of certain nations, which can be the main factor of opposing to the destruction of environment. While this combat is still taking place, countries with most prominence in economic development are looking for a strategy that would enable them to fit in the global division of labor. Or, more precisely, small countries or developing countries, will extend their markets to the extent that the most powerful countries allow them to.

In the aforementioned circumstances, the world population tends to grow remarkably: it rose from 6 billion in 1999 to 6.9 in 2010. According to forecasts of institutions such as the UN, the OECD, the World Bank, EBRD, World Health Organization, this pace of growth means that there will be around 8.5 billion of people in the world by 2025. Developing countries constitute almost 99% of these growth figures. This confirms our previous statement – developing countries will be the main factor of population growth, whilst developed countries' population will decline. We will mention the example of Germany, where experts foresee that by 2050 the age structure of the population will include almost 30% more of those aged 60 and above.

On the other hand, major initiatives have been launched in the environmental protection domain. Namely, a number of rich people invest their resources to help the menaced population in the world; at the same time, there is a rising number of those who directly involve in protection of flora and fauna. Due to the consequences of damages made to the atmospheric layer, the so-called "Greenhouse effect", a Fund has been established to finance projects and their scientific accomplishments. Around $3 billion will be allocated to environmental protection. These funds have been and will be generated from income and profit in airline and railroad transport by companies such as "Virgin". The profit gain from the group's transport business, encompassing about 50% of the company's entire business or the first 400 million of dollars, will be allocated to research, development, production and distribution of bio-gas as well as to projects aimed at reducing the emission of harmful gases to the atmosphere.

Researches done by international experts point out that the emission of harmful gases to the atmosphere, most often from factories and cars, caused the rise of temperature in the world within the past 1000 years for 0.6 degrees Celsius. The total value of funds collected for the elimination of harmful gas threat is about $ 5.7 billion (World Bank data, as stated by Richard Branson this year in New York).

The stated data entail the conclusion that developing countries will experience the largest population growth and this will be a challenge for world's economy and resources, which are currently, exhaustive. This is also supported by the fact that the United Nations have requested a $3.5 million support from rich countries to provide assistance for about 27 million people in 29, mostly African, countries.

Table 2. Current and 2050. World population

Country	Population in 2009 (mio)	Country	Estimated population in 2050 (mio)	%
China	1,311	India	1,628	45.09
India	1,122	China	1,437	9.06
USA	299	USA	420	40.40
Indonesia	225	Nigeria	299	121.40
Brazil	187	Pakistan	295	77.70
Pakistan	166	Indonesia	285	26.60
Bangladesh	166	Brazil	260	39.03
Russia	142	Bangladesh	231	39.20
Nigeria	135	DR Congo	183	-
Japan	128	Ethiopia	145	-
Serbia	**9.5**	**Serbia**	**8.5**	**-10.50**

Source: UN, EBRD, World Bank. (Approximate data for Kosovo and Metohija included for Serbia).

On the other hand, let us take a look at the unique case of Japan: at present, there are more than 20,000 persons aged above 100 in this country. According to the mentioned data, there will be one person aged above 65 per two working-age persons by 2025 in this country. This will be the highest percentage of social dependence compared to any other industrially developed country.

A fact of particular concern is that in 2025 Serbia will have no more than 8.5 million inhabitants, in other words, it will have a negative population growth rate (-10.50%).

BASIC CHARACTERISTICS OF DEMOGRAPHIC STRUCTURE IN SERBIA

There are 8–9 million inhabitants in Serbia, including Kosovo and Metohija, out of which 48% males and 52% females. Additionally, 14% of the entire population live in rural areas, out of which 29% (ca. 1 million) are poor, with daily income inferior to $2.

The population growth of ex-Yugoslavia, subsequently Serbia and Montenegro, and in the end, Serbia, had a constant birth rate decline, with regional differences. In 1951, the population growth rate was 12.6‰, in 1981 it was 7‰ and finally 1.4‰ in 1998. There has been a noticeable negative population growth in Central Serbia since 1992, and since 1989 also in Vojvodina. According to the last population census in 1998, the population of Kosovo and Metohija increased 2.7 times compared to the 1953 census·

If we compare the data from other parts of the country in the same period (1953 as the basis), we can establish that the population in Serbia increased for 42.6%: Central Serbia for 28.6% and Vojvodina for 15%.

However, when considering the data from later, approaching the 21st century, a remarkable birth rate decline in Yugoslavia and Serbia, at present, are revealed by researches. Namely, natality in 1951 was 25.9‰, 16.3‰ in 1981, and 12.1‰ in 1998. The birth rate decline was differed in regions, so, in Serbia went down from 16.2 in 1981 to 12.0 in 1998.

In Central Serbia, it went down from 13.2 in 1981 to 9.3 in 1999 and in Vojvodina from 13.7 in 1981 to 9.5 in 1998. While the birth rate for Kosovo and Metohija was 30.2‰ in 1981, it changed to 19.6 in 1998, i.e. 19.6 live-borns per 1000 people in the stated examined period.

The mortality of Serbian population was in constant decline until 80's, after which a rising tendency was noticed. The mortality rate in 1981 was 9.2‰, while in 1988 there were 10.7 deaths per 1000 inhabitants. In the examined period, the mortality rate rose to 14‰.

Unlike negative trends of "aging" and mortality, much has been accomplished to reduce infant mortality, which has a long-term declining tendency. The data below show the following values:

Table 3. Infant mortality rate per year in %

1951	1981	1992	1993	1994	2006	2010
130	34.3	21.7	21.9	18.4	14.3	12.4

Source: SGJ and SZS per year.

Infant mortality decline was a result of, primarily, socio-economic conditions at that time and strengthening the preventive health care practice.

Additionally, demographic structure of the population is also threatened by a considerable number of migrations to abroad. At the moment of research, there are two or three generations of our citizens abroad, therefore, the established data have very strong and indicative importance in planning and producing a strategy for their potentials returns to their home country, some of them after retirement or due to paperwork problems such as work permits etc.

To be specific, when speaking about citizens of Serbia on temporary work abroad and members of their families, out of the total of 395,943 citizens, 328,795 come from Central Serbia. At the same time, in each of 25 Serbian districts in total, migrant workers are more and more numerous. Compared to the 1991 population census, the one from 2002 shows that the number of citizens of Serbia on temporary work abroad and members of their families went up for more than one third. This increase is a result, as indicated by researches, of challenging economic situation in the past decade. Statistical data show that the number of migrant workers from Belgrade increased for 7,357 people in the interval between the two censuses. The most significant increase of migrant workers is in the districts of Pčinja (20,757), Raška (15,588) while the Zlatibor District is at the third place with 13,381 people.

In the same context, it is also worth mentioning that more than 300,000 people above the age of 60 currently live in Belgrade.

WATER PURIFICATION

This should be one of the most important tasks of modern civilization and technical accomplishments. At this point, we would like to remind of the fact that that around 80,000 persons in Angola were infected with cholera about ten years ago. This is one of the hardest diseases of gastrointestinal tract (intestine infection) caused by consumption of contaminated water. Many of the affected died due to late reporting to the doctor, which disabled timely intervention to prevent the bacteria from spreading. From medieval times until 18th century, cholera was fatal and claimed numerous victims.

In the past years, a wide-range absorbents obtained by processing industrial materials with great efficiency in absorbing water polluters (ammonium, hard metals, diverse organic polluters etc.) have been studied and put into use. Probably, it has never occurred to anyone to introduce zeolites in polluted rivers of Timok, Rzav etc. and prevent environmental disasters that took place. Or, simply, before releasing the waste water into rivers and lakes, it should have been subject to zeolite treatment. Our chemists have a far broader knowledge of the subject matter than they were given the position and role in the new value system as far as environment is concerned.

Concretely, the abilities of zeolites as ionic modifiers make it possible to produce water from seas and oceans, by desalination and demineralization. Kuwait obtains around 25,000 tons of pure water using these methods.

But phosphates in still waters, less than in current ones, produce algae and other water consumers of oxide, so this is a great threat to flora and fauna and its destruction. Reducing the standard values of phosphates in detergents has become a common process, but its complete elimination is impossible at this stage, since zeolites cannot replace phosphates thoroughly as an efficient washing agent. Or, if there is willingness to detoxify soil and waste disposals, it is hard to imagine the quantity of this mineral in the processes necessary to make good use of such areas. Moreover, different tests have been conducted in the military domain as well. Our information follows this order: if zeolites absorb toxic materials, if they absorb the excess radiation, they can be a good protective shield from nuclear radiation. This is an assumption. Therefore, taking all of the abovementioned into consideration, an additional attractive material has been made available to civil engineering, in the function of its development. Natural minerals could be a kind of protection from unwanted radiation of any source. It is possible to think of it as protection in civil engineering for cladding houses, military buildings etc.

The imposing conclusion is that possibilities of exporting this mineral are immense. Despite limitations that this is a strategic material, the profitability of production and processing indicates that the relation between production costs and world market price has 56% of profitability. While examining further investments in opening mines and costs of such an investment, it turns out that the entire investment pays off in two years of exploitation. With Europe-level income, not more not less…

Pilot-researches of placing this mineral at the European market indicate that on the monthly basis around 1000 tons (or more) are necessary for the needs of fine medicine production only (highest quality), which is 15,000 tons of this ore annually and the financial effect of € 7 million in total income, i.e. about € 3.6 million of net profit.

Zeolites will be the most wanted product in the future, both in our country and in the world. It is necessary to form teams of marketing and educational profiles as soon as possible, in order to be ready for the future expansion in consumption of this mineral. This is supported by the fact that researches are already being carried out in the military sector.

Researches of international experts point out that the emission of harmful gases to the atmosphere, most often from factories and cars, cause the rise of temperature in the world within the past 1000 years for 0.6 degrees Celsius. The total value of funds collected for elimination of harmful gas threat is about $ 5.7 billion (World Bank data, as stated by Richard Branson this year in New York).

CONCLUSION

1. Mid-term plans in Serbia have set basics for the implementation of environmental protection activities as well as those in the water supply area. It seems sufficient to mention the fact that separate ministries at the level of the Republic have been established to deal with and try to resolve environmental issues. Concretely, resolving the water issue in an institutional manner is formalized in the Law on Waters, Law on Environmental Protection, Law on Protection of Water Supply Sources, Rulebook on Designation of Sanitary Protected Zones etc.
2. There should be permanent work on education of the entire population, from primary school to academic studies. Faculties dealing with the subject matter have already appeared, but this is still insufficient.
3. Serbian legislation must comply with the EU legislation and accept its standards.
4. Such goods should be produced that will not pollute environment after use;
5. Distribution centers are to be established in such areas that do not interfere with the environment;
6. In price policy, neutralization of harmful effects on environment during and after use of water should be included in the selling price, as an anticipation
7. Using the means of promotion, it is necessary to inform, direct, motivate and educate consumers not to use environmentally harmful products and, which is most important, educate all consumption segments by raising the awareness on the necessity to protect and improve the environment.

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10. National Snow and Ice Data Center (NSIDC), University of Colorado, USA

BIOSORPTION OF HEAVY METALS FROM WATER BY MODIFIED AGRICULTURAL BY-PRODUCTS

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ABSTRACT

Low cost agricultural by-product corn cobs (OK)and apricot shells(LJ) in raw and modified form have been used as potential biosorbents of copper, lead, aluminum and cadmium ions from water. In order to increase biosorption efficiency both biosorbents were modified in several ways: washing with acid (WOK, WLJ); after acid washing treatment, materials were treated with base (WOKNA, WLJNA); just treated with base (OKNA, LJNA);after acid washing and treating with base, finally materials were treated with citric acid (WOKNACA, WLJNACA).Experimentswere carried out in batch system. Biosorbents modified with base and citric acid showed significantly better results in comparison with raw material and materialwashed with acid.

Key words: biosorption, corn cobs, apricot shells, heavy metals, modification.

INTRODUCTION

Rapid industrialization and technological advances caused problems such as heavy metals pollutions. Biggest heavy metals polluters of environment are paper industries, metal plating, mining operations, battery manufacturing etc. [1].Danger of heavy metals bioaccumulation in the food chain and their toxicity are important environmental and health problems.Some heavy metalsare essential nutrient for living organism. However, it has be proven that excess of many heavy metals such as copper, lead, cadmium, etc. cause cellular dysfunction and eventually cell death.For toxic metals removing from wastewaters different conventional techniques were used including chemical precipitation with lime, oxidation-reduction process, chemical coagulation and flotation, and effective but very expensive techniques such as ion-exchange, reverse osmosis, ultra-filtration, electrolysis etc. [2-6].Difficult process handing and high cost of operation, production of sludge or potential toxic by-product are the main disadvantages of these techniques.

Biosorption is an effectivetechnique for removal of heavy metals from aqueous solutionand become an alternative to conventional techniques of wastewater treatment, due to its low operating coast, environmental friendly nature and high sorption efficiency. Nowadays, many agricultural wastes including rice straw, rice bran, wheat shells, soybean hulls, sugarcane bagasse, peanut and walnut shells, apple residues have been investigated as potential biosorbents[7,9,10,13,15,17]. Main constituents of these materials are cellulose, hemicelluloses andlignin. The functional groups present in these materials have affinity for metal uptake: hydroxyl groups of cellulose and different polar functional groupsof lignin, such as alcohols, aldehydes, ketones, acids, phenolic hydroxides and ethers.

The modification of agricultural waste materials has been extensively investigated [7-16]. Biomaterials have been modified by chemical and physical treatments: rice husk treated with epichlorohydrin, NaOH and $NaHCO_3$ [9]; saponified, acid-extracted and base-extracted sugar beet pulp [10]; maize stem, rye straw and rice straw modified with NaOH[11]; chemically and physically treated barley husk and wheat straw [12]; peanut shells modified with phosphoric and citric acid [13]; and soybean hulls modified with citric acid [14-16].

The purpose of this study was to use low coast and locally available agricultural wastes corn cob (OK) and apricot shells (LJ) as a biosorbents of copper, lead, aluminium and cadmium ions from aqueous solution. This study investigated the effect of few chemical treatments (HNO_3, NaOH and citric acid) in order to improve biosorption capacity for both materials.

MATERIALS AND METHODS

Materials

Corn cobs were obtained from Maize Research Institute, Serbia. The apricot stones were obtained from Juice Factory "Vino Župa" Aleksandrovac.Both biomaterials were air dried at room temperature for a few days.Kernels were removed from apricot stones and apricot shells were used for further experiments. Dried biomasses were ground (KHD HumboltWedag AG) and <1 mm fraction was chosen for the biosorption tests. Samples were stored in dry plastic containers.

Stock solutions were prepared by dissolving precise amount of $Cu(NO_3)_2{\times}3H_2O$ (p.a. grade) in distilled water. Coppersolutions with different concentrations were prepared by dilution of the stock solution. Using pH meter (SensIon MM340), pH value was adjusted to the requiredvalueswith 0.1 M HNO_3 and 0.1 M NaOH solutions.

Treatment type

Raw native biomaterials (OK and LJ) were investigated to determine their efficiency in removing different heavy metal ions from aqueous solution. In order to increase biosorption efficiency biosorbents were modified throughfew steps:

1. Biosorbents were mixed with 0.3M HNO_3 in ratio: 1:5. Mixture was shaken at 250 rpm and then washed with distilled water and dried at 50°C for 24 h – WOK, WLJ.
2. After acid treatment (step 1) biosorbents were modified with 0.1 M NaOH in ratio 1:20. Mixture was shaken at 250 rpm for 2 h and then washed with distilled water. In addition,distilledwater was added in same ratio and mixture

was shaken for a further1 h at 250 rpm. At the end mixture was washed and dried at 50°C for 24 h – WOKNA, WLJNA.

3. Biosorbents were modified just with base treatment (step 2) without any acid washing – OKNA, LJNA.
4. Biosorbents were mixed with 0.6 M citric acid (CA) in ratio: 1:5. Mixture was shaken at 250 rpm and heated on 60°C for 2 h, then washed and dried at 50°C. After that modified sorbent was heated on 120°C for 90 min and finely it was washed and dried in oven – WOKNACA, WLJNACA.

Batch experiment

The batch experiments were conducted at 303 ± 1K. The biomasses (10 g/L) were added into Erlenmeyer flasks containing the 50 ml of different metals solution (0.5 mM), which were shaken at 250 rpm for 120 min.Afterward, the mixture was filtrated and the metals concentration was analysed by Atomic Absorption Spectrometer (PerkinElmer, model AAnalyst 300). Blank tests were performed using the same conditions but without biosorbents.The biosorption efficiency of Cu(II) was calculated using the following equation:

$$R(\%) = \frac{\left(C_i\text{-}C_{eq}\right)x100}{C_i}$$

where:C_i and C_{eq}(mg/L) are the initial and final equilibrium metal ion concentration, respectively.

RESULTS AND DISCUSSION

Alkaline treatment with NaOH is common technique to modified lignocellulosic materials since it is able to hydrolyze cellulose and remove impurities such as natural fats and waxes from cellulose surfaces thus revealing chemically reactive functional groups like –OH [17].In addition, during the treatment the covalent bond between components in lignocellulose materialbreaks, hydrolyzing hemicellulose and depolymerizing lignin [18]. Alkaline treatment has impact on molecular properties of cellulose, causing changes in crystallinity and orientation of fibrils in cellulose fibers [19].

Citric acid modification of NaOH treated biosorbents showed sorption enhancement of metal ions.Process of heating was used to convert citric acid into citric acid anhydride.Cellulosic hydroxyl groups with citric acid anhydrideforms an ester linkage and thereforeintroducecarboxyl functional groups to the cellulose. More carboxyl groups increases the biosorption capacity of these materials.Heat treatment could also result in cross-linking between two cellulosic molecules[15, 20].

Biosorption efficiency(R) of untreated and modified corn cobs and apricot shells forcopper, lead, aluminium and cadmium ions are summarized in Table 1.

Table 1. Biosorption efficiency (R) of untreated and modified biosorbents for heavy metals ions

	Cu	Pb	Al	Cd
	R (%)			
OK	57,14	69,78	37,68	68,77
WOK	30,18	47,06	24,00	25,24
OKNA	99,41	98,90	94,20	99,60
WOKNA	100,00	100,00	86,18	99,29
WOKNACA	86,80	99,10	100,00	61,16
Lj	49,91	55,49	49,28	9,88
WLj	41,45	62,50	28,63	28,30
LjNA	100,00	99,01	100,00	99,60
WLjNA	100,00	100,00	94,63	99,93
WLjNACA	81,71	98,09	83,12	59,22

The results showed that different ways of modification have a significant influence on biosorption efficiency. Untreated biosorbent (LJ) and acid washed biosorbent (WLJ) have a poor biosorption efficiency compared with base treated biosorbent (LJNA). Fig. 1 shows that biosorption efficiency of apricot shells increased 44.51, 43.52, 50.71 and 89.72 % for Cu, Pb, Al and Cd removal, respectively after treatment with NaOH. It can be seen that biosorption efficiency of washed apricot shells increased 58.55, 37.50, 66.71 and 71.63 % for Cu, Pb, Al and Cd removal, respectively and 40.26, 35.59, 54.82 and 30.92 % for Cu, Pb, Al and Cd removal, respectively after treatment with NaOH only and after treatment with NaOH in combination with citric acid, respectively.

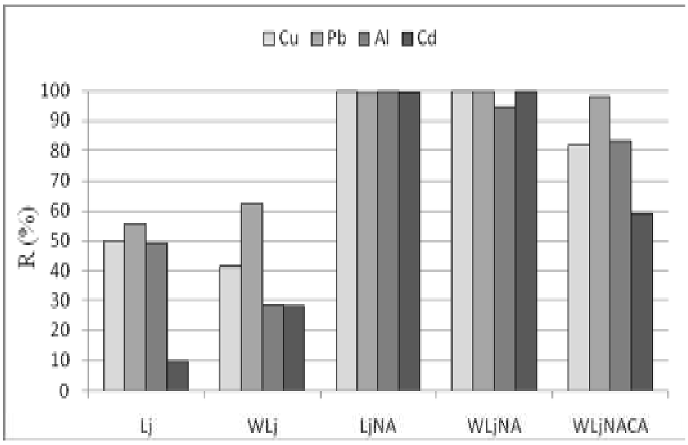

Figure 1. Biosorption efficiencyof different heavy metal ions by raw and modified apricot shells

Results for raw and chemical treated corn cobs are presented in Fig.2. There is noticeable similarity between results among corn cobs and apricot shells due to lignocellulosic nature of both materials. Only corn cobs modified with citric acid (WOKNACA) makes difference in case of biosorption of aluminium.

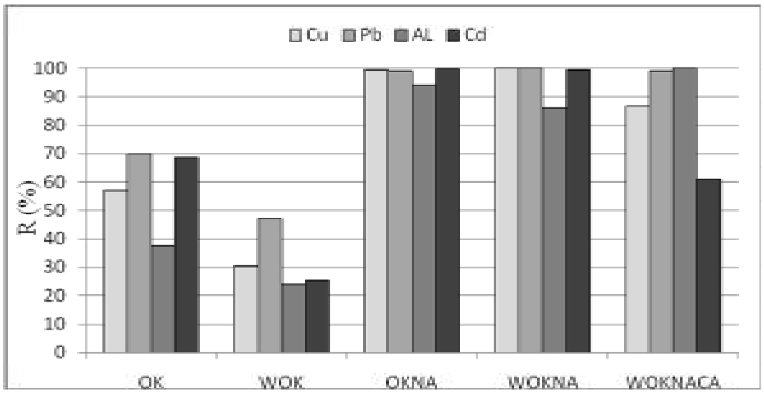

Figure 2. Biosorption efficiency of different heavy metal ions by raw and modified corn cob

Fig. 2 showed that biosorption efficiency of corn cobs increased 42.27, 29.12, 56.52 and 30.83 % for Cu, Pb, Al and Cd removal, respectively after treatment with NaOH. It can be seen that biosorption efficiency of washed corn cobs increased 69.82, 52.94, 62.18 and 74.36 % for Cu, Pb, Al and Cd removal, respectively and 56.62, 52.04, 76.00 and 35.92 % for Cu, Pb, Al and Cd removal, respectively after treatment with NaOH only and after treatment with NaOH in combination with citric acid, respectively.

CONCLUSION

This paper deals with the biosorption of different heavy metals ions from water by agricultural lignocellulosic waste materials which are generated in large quantities. Corn cobs and apricot shells were investigated and results showed that they have different biosorption efficiency for copper, lead, cadmium and aluminium.

Biosorption efficiency was increased after treatment of biosorbents with NaOH and citric acid. The biosorption efficiency for copper increased from 40.26 to 56.62 %; for lead was increased from 35.59to 52.04 %; for cadmium was increased from 30.92 to 35.92 %and for aluminium was increased from 54.49 to 76 %for corn cobs andfor washed corn cobs, and washed apricot stones, respectively.

Modification of biosorbents with NaOH gives the best results. The biosorption efficiency for copper was increased from 42.27 % for corn cobs to 69.82 % for washed corn cobs; the biosorption efficiency for lead was increased from 29.12 % for corn cobs to 52.94 % for washed corn cobs; the biosorption efficiency for cadmium was increased from 30.83%for corn cobs to 89.72 % for apricot shells; the biosorption efficiency for aluminium was increased from 50.72 % for corn cobs to 66.00 % for apricot shells.

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„METERIS“ LANDFILL WASTEWATER

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ABSTRACT

This work presents the results of testing the quality of filtrate in sanitary landfill "Meteris" after treatment, i.e. before discharge and discharge into the sewage system. The aim of this study was to examine the quality of waste water, and to assess the effectiveness of collection and selection of treatment of waste water, based on the obtained results. The study was conducted in March - May 2013, and include the physical, chemical and microbiological analysis. The waste water from the plant tanks was transported and released into the city sewage system, which means that they must be the quality of urban wastewater. Tests have shown that the quality of waste water meets the provisions of the Regulation on maximum permissible concentrations of hazardous substances - MPC , for engaging in the city's sewers. This means that in a landfill in Vranje physicochemical and microbiological process leachate wastewater is satisfactory, as can be seen from the percentage reduction in the basic parameters of their quality.

Key words: Sanitary landfill, leachate wastewater.

INTRODUCTION

In terms of ecological, sanitary-epidemiological, technological, urban, construction, hydrological and energy, solid waste management represents very complex and highly heterogeneous materials whose disposal is one of the major problem of civilization. Waste management covers the whole range of measures to promote and facilitate the prevention of waste at its source, separate collection, recycling and other methods of recovering materials from waste, reliable and environmentally sustainable final disposal of waste. [1]

Public company "Komrad " in Vranje is a company whose main activity is removing and disposing garbage, hygiene and greenery. In Vranje municipal and Vranje Spa waste is collected and disposed of 1113,000 households, which is total of approximately 60,000 inhabitants, (data from 2006.). In addition, the amount of inert industrial waste is from 1178 registered manufacturing and trading companies and shops. So to the landfill "Meteris" daily postpones incompact urban and inert industrial waste of 220.40 m^3, or 74.52 m^3 of compressed waste.

In landfill usually generated wastewater called leachate waste water (filtrate) which is collected with drainage channel system and taken to the pool for wastewater treatment. Purification of waste water is carried out by the aerator in the pool. Purified water is used on the landfill as a way to prevent burning of garbage at landfill. In winter, any excess water is transported by tanks and discharged into the public sewer system of Vranje [2].

GENERAL CONSIDERATIONS

The "Meteris" sanitary landfill for urban solid waste was designed by the Institute "Kirilo Savić" (Belgrade) and it is built according to the project in 2002. with the task to dispose waste of Vranje city and Vranje spa. Area where the landfill is situated isn't one of the protected zone. In this area has no permanent plant and animal species, so it is suitable for a place to landfill site. Landfill is constructed with cassette for waste disposal, which method represents an efficient use of space and the prevention of soil pollution.

Waste on landfill should be spreads, compresses and reduces the volume of waste, the air should release to prevent the burning of waste. Waste is covering by soil daily, which provided the project.

Quantity of filtrates on landfill depends of the amount of atmospheric precipitation, depending on climatic conditions. The actual composition of the filtrate is very difficult to predict because it depends on the waste composition, temperature and moisture content, fluid path, the thickness of the landfill waste decomposition stage, the possibilities inter layers to absorb and eliminate pollution and the quality of water that infiltrates into the landfill.

Waste which does not belong into the category of hazardous waste, inert industrial waste and communal waste is disposed on sanitary landfill "Meteris". Based on the morphological structure of these two categories of waste it is calculated density of waste. During the initial period of waste disposal, the water content of the waste is increased and reaches a maximum value of the absorption. When the maximum value is reached, the leachate forms continuous flow. Time of arrival of the water trickling through to the bottom of the landfill and the delay time period is relative to the precipitation and depends on the type of waste and the capability of moisture absorption. Precipitation and water from manipulation areas, internal roads are collected in peripheral canals by the road and further are discharged into the surrounding terrain. In order to provide better and faster collecting of leachate, landfill body is projected in the cascades, which are staggered with respect to one to another in a north-south direction. The lowest part of the landfill in the first cascade, placed the drain collector is used to collect and faster implementation straining filtrate in the plant for wastewater treatment.

Biodegradable organic matter, chemical processes of oxidation and dissolution of organic and inorganic materials in the waste, forms leachate with chemical characteristics. For example, the reaction between the organic acid and the metal ions generate metals and salt, a carbon dioxide aqueous medium after the dissolving effect of the calcium and magnesium, which causes an increase in the hardness of leachate. Also, growth of bacteria in the landfill affects lots of conditions, such as humidity, which is a prerequisite for the survival of bacteria. Content of moisture which is nearly equal to the saturation is the ideal condition, but lower moisture content below 55-60%, is a limiting factor for the biological activity of the microorganisms, and it is reason why it is necessary periodically to wet the landfill, especially in drought periods. Changes in precipitation and temperature results in large fluctuations in the composition of the leachate. In the literature we meet with the following average organic pollution leachate of waste water can be taken for value of 10,000 mgO_2 / l for BPK_5, microbiological contamination in 1ml of filtrate 1.5 million bacteria, of which 34,000 intestine [3,4].

TEHNOLOGICAL PROCESS OF LEACHATE

Having regard to the local conditions and the contemporary international practice of collection, treatment and final disposal of leachate, on landfill "Meteris" was chosen solution with a partial biological treatment of leachate, and on-site.

Leachate (drainage) water is collected on the lowest part of the landfill in the collection pit. There are mixed more technical water from the car wash and disinfect vehicles and sanitary sewage from the facility for staff and facilities for washing and disinfecting vehicles. Technical water previously passed through the separator grease and oil from the sands of lead, which is separated particles of sand and petroleum products. From the collection pit wastewater is transpose by gravity collector to wastewater treatment plant. These are the most common aerated lagoons, where aerobic bacteria with sufficient dissolved oxygen, break down the organic matter attendees in water. In aerated lagoon it realized completely mixing and due to the increased turbulence caused by hydraulic aerators, prevents the deposition of silt and secured a permanent increased turbidity, which prevents the growth of algae. Partially treated waste water transferre out of the lagoon, carrying suspended biomass and it is a completely different character than the one in bio aeration pool or sedimentation can be sorted out. Content of organic matter in the water that comes from the aerated lagoon was reduced by approximately one third compared to raw sewage. The content of soluble organic matter in the purified water is reduced several times compared to the incoming wastewater. From the aerated lagoon water is transferred to the sump pump where it is separated and deposited organic matter, where it is sludge stabilization and isolation of treated wastewater. The sump is set vertical pipe to the sludge precipitated and performed diffusion of purified water to the surface of the sump. The sump is gravitationally deposited silt, and the water is transferred to the collecting shaft of treated wastewater in dispensing tanks into the city sewage. The fuel filter is the process of stabilization at the bottom of the precipitated sludge, which degrade and mineralize as much as 50% of separated sludge, so that it only applies mud pumps periodically (a few times a year) and transfers to a landfill where it is mixed with solid waste disposed and covered with an inert material.

If the methods of treatment are applied to waste water in landfill, leachate can reach to quality of water that is required for the discharge of sewage system. From the collecting shaft treated water continues to tank, transports and discharge to the nearest city sewerage. Usually, in sewage treated leachate mix urban waste water, leads to the urban waste water plant. [5,6]

MATHERIALS AND TESTING METHODS

The quality of leachate waste water originates from the landfill "Meteris" are examination in the internal laboratory National Institute of Public Health in Vranje, which is accredited for these tests, in accordance with the regulations. Sampled and tested wastewater are taken from the aeration lagoon and collecting sump as a two-hour summary composite. The samples were examined physicochemical and microbiological parameters: temperature, pH, turbidity, suspended solids, consumption of potassium permanganate, BPK5, HPK, dissolved oxygen, chlorides, sulfates, nitrates, nitrites, and the presence of coliform bacteria per 100 ml of sample, sulphite clostridia, and the total number of microorganisms in 1 ml of sample.

Tests were conducted throughout the hydrological year, but due to limited space in this paper there are presented only the results of physicochemical tests-and the most important parameters during the spring period 2013. [7,8,9] Also was determined and the degree of purification of waste water seepage from the landfill "Meteris" examination of waste water before and after bio aeration and sludge lagoons. Testing the quality of effluent are presented in this paper. Results are discussed in relation to the Ordinance on Hazardous Substances MDK for discharging in to sewer system of Vranje. [7,11]

RESULTS AND DISCUSSION

Results of testing of raw water and water before and after the aeration lagoon sediment and are shown in Table 1 as well as the effects of the treatment stages. This paper presents only the relevant parameters, both for the quality of waste water, and for evaluating the effectiveness of purification: HPK, BPK5 and dissolved oxygen. Summarizing the results of samples, the biological treatment process of wastewater leachate on landfill "Meteris," we conclude that treated waste water quality satisfies conditions and criteria regulated to discharge to city's sewers.

During the test period treated leachate was brown to dark brown in color, with the smell of rot and feces. The water temperature was 16 to 200C, ph value was 8,14 to 8,41 and the electric conductivity was 74.4 to 103.5 μScm-1st the minimum value of the dry residue (at 1050C) was 266 mg / l and the maximum 616 mg / l. $KMnO_4$ ranged 27.65 to 38.5mg / l. The amount of nitrate and nitrite was all the time in the lawful limits (<30 mg / l). A very high degree of purification can be seen in the percentage reduction of the basic parameters of quality and reduction of suspended solids, ammonium ions, BPK_5 and HPK. The effect of treatment by the reduction of BPK_5 values go up to 99%. Histogram display (Fig 1 and 2) confirms the same figures.

The effectiveness of treatment is very high, and the order, the largest in aeration lagoon and lowest in sedimentary basins, which is understandable because the rate of oxidation decreases towards the end segments of the system and increases the concentration of dissolved oxygen. Dissolved oxygen due to abundant aeration showed high levels of 3.5 mg/l to near 7.0 mg/l in all lagoons, and gives the concentration of suspended solids and the percentage of their treatment can be tolerated, and lower values of dissolved oxygen, which causes airborne and energy balance in the flow of air.

Suspended solids affect dissolved oxygen so as to intense aeration quickly shoot down so that the concentration of dissolved oxygen is an indicator of the success of the flotation process. The quality of process in bio aeration lagoons includes microbiological status or level of reduction in the number of coliform bacteria. Based on this analysis, presented in this paper limited due the number of pages, ions we cannot display an obvious significant decline in the number of coliform bacteria so that micro-biological quality of the water in the lagoon sediment completely corresponds to a given quality of freely engaging in sewers system.

Table 1. The results of analisys of leachate waste water in the purification system

Serial Number	The parameters	Units of measure	MAC of flows into the city s.	Filtrate	Aeration lagoon in put	Aeration lagoon out put	Deposition lagoon in put	Deposition lagoon out put
Sampling 02.04.2013.								
1.	pH		6,5-8,5	7,4	7.5	7.4	7,2	7.6
2.	Suspended materials	mg/dm^3	400	269	58	36	28	16
3.	Ammonium ion	$mg\ N/\ dm^3$		76	19.3	17.6	15.3	15.3
4.	Dissolved oxygen	$mgO_2/\ dm^3$	do 6			4.2		6.7
5.	BPK_5	$mg\ O_2/\ dm^3$	4	240	17.0	16.7	6.5	5.0
6.	HPK (from $KMnO_4$)	$mg\ O_2/\ dm^3$	40	356	56.6	51.6	35.0	28.8
7.	Removal BPK_5	%			93	2	61	23
Removal of BPK_5 raw water / sediment output from the lagoon,%							98	
Sampling 16.04.2013.								
1.	pH		6,5-8,5	7.6	7.4	7.5	7,6	7.7
2.	Suspended materials	mg/dm^3	400	298	36	29	22	9
3.	Ammonium ion	$mgN/\ dm^3$		78	14,3	14,3	14,1	14,3
4.	Dissolved oxygen	mgO_2/dm^3	do 6			4,4		7,0
5.	BPK_5	mgO_2/dm^3	4	150.0	18,0	16,7	4,5	3,0
6.	HPK (from $KMnO_4$)	mgO_2/dm^3	40	341.0	48.6	46.6	36.0	29,9
7.	Removal BPK_5	%			88	7	73	33
Removal of BPK_5 raw water / sediment output from the lagoon,%							98	
Sampling 30.04.2013.								
1.	pH		6,5-8,5	7.8	7,5	7,8	7,6	7,8
2.	Suspended materials	mg/l	400	298	8	16	38	6
3.	Ammonium ion	$mgN/\ dm^3$		80	17,3	16,3	14,6	14,6
4.	Dissolved oxygen	mgO_2/dm^3	do 6			3,5		6,8
5.	BPK_5	mgO_2/dm^3	4	280.0	18	16,7	7,8	4,0
6.	HPK (from $KMnO_4$)	mgO_2/dm^3	40	389.0	59,6	59,6	40,0	32,0
7.	Removal BPK_5,	%			93	7	53	49
Removal of BPK_5 raw water / sediment output from the lagoon,%							99	

CONCLUSION

Based on all the above the leachate wastewater of the urban sanitary landfill "Meteris" in Vranje, can be concluded that in the process of collection, treatment and final disposal, the chosen solution with the partial biological treatment on-site landfill brings the quality level of quality utility wastewater, where the leachate is transported by tanks and discharge into the city sewage system. In this way, it's meet the standards defined by the Regulations on technical and sanitary conditions for the freely discharge waste water into the sewage system.

Value of reducing BPK5 which goes up to 99%, reduction suspended substances are very high, ammonium ions and HPK has also high degree of efficiency, which is evidence of good management in landfill. The effectiveness of treatment is greatest in aeration lagoon and lowest in sedimentary basins, which is understandable, because the rate of oxidation decreases towards the end segments of the system and increases the concentration of dissolved oxygen. Dissolved oxygen due to abundant aeration shows the high levels of 3.5mg / l to near 7.0mg/l in all lagoons.

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REMOVAL OF COPPER IONS FROM AQUEOUS SOLUTION BY WHEAT STRAW AND BEECH SAWDUST

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ABSTRACT

The paper presents the results of adsorption of copper ions from synthetic solution onto wheat straw and beech sawdust. Physical and chemical characterization of the adsorbents was performed. Kinetic studies indicated that copper adsorption followed the pseudo-second order model for both adsorbents. The maximum adsorption capacity was 5 mg g^{-1} for wheat straw and 4.5 mg g^{-1} for beech sawdust. The adsorption equilibrium fallows Langmuir adsorption model for both adsorbents. The results show that beech sawdust and wheat straw can be used as a cheap, natural adsorbents for the adsorption of copper ions from aqueous solution.

Key words: wheat straw, beech sawdust, copper ions, adsorption.

INTRODUCTION

Many industrial plants release heavy metals with their wastewaters and solid wastes heavily polluting the environment. These are primarily the extractive and metallurgy processing plants of non-ferrous metals, electronic industry, electroplating and metal finishing plants, and many others [1].

Despite the existence of numerous conventional technologies for heavy metal ions removal from wastewaters as: chemical precipitation, ion exchange [2], adsorption [3], different membrane techniques [4], direct electrowinning [5], further researches were made with the unique aim of getting more economically and more environmentally sus-tainable technology that could provide the lowest level of heavy metal ions in a treated effluent that will be low enough to be safely discharged in a surface water stream. 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].

The biosorption, as a possibility for substituting the commercial adsorbents, has been and still is the subjects of scientists with the aim of replacing commercial adsorbents by maybe less efficient but much cheaper natural sorbents.[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. Because of this, these adsorbents are known as "low-cost" adsorbents.

The aim of this study was to investigate the adsorption ability of wheat straw and beech sawdust for the adsorption of copper ions most frequently present in mine waters.

EXPERIMENTAL

Materials and methods

A series of the adsorption experiments were performed by using $CuSO_4$ stock solution (0.2 gCu^{2+}/L in distilled water). From this solution lower initial concentrations were then prepared, depending on the experiments that should be carried out. The used chemical was AnalaR purity.

Wheat straw and beech sawdust was used as an adsorbent in this study. The adsorbents were 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 and beech sawdust were weighed, then this weight was rinsed with 200 ml of distilled water, dried again at 90 ^{o}C and used for further characterization or in the adsorption experiments. No chemical pretreatment of wheat straw and beech sawdust has been performed. The concentrations of considered heavy metal ion during experiments were determined using a PerkinElmer - 403 atomic adsorption spectrophotometer. In order to characterize wheat straw and beech sawdust, the wheat straw and beech sawdust were burned and the ash was analyzed. The amount of ash after burning wheat straw was 6.2 %, and after burning beech sawdust was 2.06 %. The results are presented in Table 1.

Table 1. Chemical characterization of wheat straw and beech sawdust

Oxides (%)	SiO_2	CaO	K_2O	P_2O_5	Al_2O_3	MgO	Fe_2O_3	SO_3	Na_2O	TiO_2	MnO
Wheat straw	36.36	6.83	28.62	3	0.29	3.25	0.57	16.12	4.14	0.017	0.11
Beech sawdust	34.08	22.39	4.56	1.17	4.73	3.32	3	24.76	1.51	0.18	0.13

The adsorption of Cu^{2+} ions on wheat straw and beech sawdust – Experimental procedure

Adsorption experiments were carried out in a batch reactor with a stirrer in order to keep the adsorbents in suspension. Stirring of the suspension was performed with a magnetic stirrer, at a constant speed of 300 rpm. Beech sawdust and wheat straw, previously rinsed with water, has been used as adsorbents in all experiments. As the aqueous phase a synthetic solution of copper with a constant and known initial concentration of Cu^{2+} ions was used. Beech sawdust and wheat straw (weight 1 g), was brought in contact with 50 ml of the copper solution in the batch reactor, for different times, and maintained in suspension by stirring. After a certain time, the suspension was filtered and the filtrate was analyzed on the concentration of remained Cu^{2+} ions. From the mass balance the amount of adsorbed copper was determined. The adsorption capacity and its change with the process time were then calculated by using the equation (1):

$$q(t) = \frac{C_i - C(t)}{m} V \tag{1}$$

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).

In order to obtain evidence concerning the adsorption of copper ions on beech sawdust and wheat straw, a series of the equilibrium experiments were performed by mixing equal quantities of adsorbents (1 g) with equal volumes of solutions (50 ml) containing different concentrations of metal ions in the range from 5 to 200 mg dm^{-3}. The mixtures were stirred at 300 rpm for 60 minutes; then filtered and the filtrates analyzed for the remaining part of the metal.

RESULTS AND DISCUSSION

Kinetics of adsorption

Kinetics of metal ion adsorption onto natural adsorbents has been considered by many scientist and several kinetic models were suggested [8-10]. Since the earlier findings including ours [7,11-12], about the adsorption kinetics using both sawdust and 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 [7].

To describe the kinetics of adsorption of Cu^{2+} ions onto wheat straw and beech sawdust, the second order kinetic model of adsorption was used, described by the following equation:

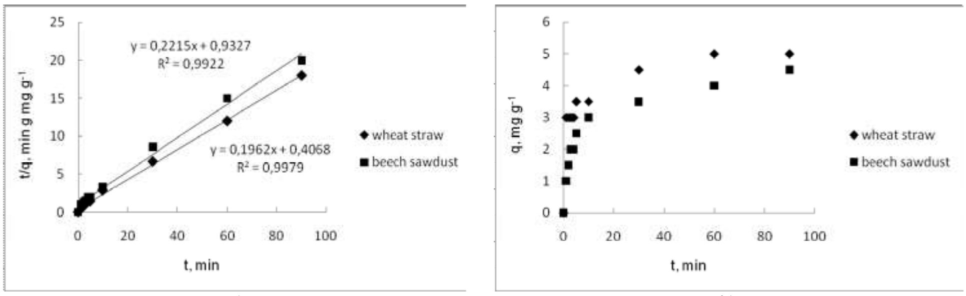
$$q(t) = \frac{q_e^2 k_2 t}{(1 + q_e k_2 t)} \tag{2}$$

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 1a. 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} in the case of wheat straw and 4.5 mg g^{-1} in the case of beech sawdust). Linearizing the curve from Figure 1a 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 adsorbents as shown in Figure 1b. The regression coefficient is close to unity for both adsorbents, confirming a good fit of the experimental results with the considered second order kinetics model of adsorption.



a) *b)*

Figure 1. a) Change of adsorption capacity with process time;
b) pseudo second order kinetic model

Adsorption isotherms

The equilibrium between an adsorbate immobilized on the active sites of an adsorbent and the adsorbate remaining in aqueous phase is usually presented by adsorption isotherms. In order to describe the adsorption characteristics of low-cost sorbents, experimental equilibrium data are most frequently modelled by the relationships developed by Freundlich and Langmuir [13].

In this paper experimental data are fitted with Langmuir adsorption isotherm model. The adsorption isotherm results are shown in Figure 2 (left column). Linear Langmuir plot is presented in the right column next to the isotherm. According to the regression coefficient R^2 = 0.9914 for wheat straw and R^2 = 0.9987 for beech sawdust, the experimental results provide a very good fitting to the Langmuir model for both adsorbents.

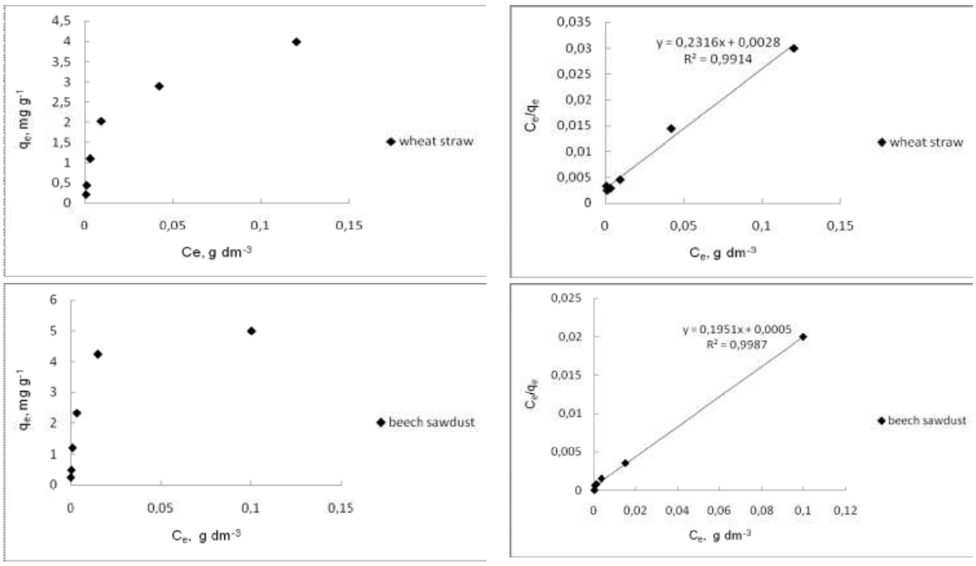


Figure 2. Adsorption isotherm (left) and linear Langmuir plot (right) for wheat straw and beech sawdust

CONCLUSIONS

The results presented in this paper shows, that beech sawdust and wheat straw can be successfully used for the adsorption of copper ions from aqueous solutions. Maximum capacity, corresponding to equilibrium saturation of adsorbents, is 5 mg g^{-1} for wheat straw and 4.5 mg g^{-1} for beech sawdust. Kinetics of adsorption follows the pseudo-second order reaction model for the adsorbents. The adsorption isotherm fits with Langmuir isotherm model for both adsorbents. The results show that beech sawdust and wheat straw can be succesfully used as a cheap, natural adsorbents for the adsorption of copper ions from aqueous solution.

Acknowledgement

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ENERGY EFFICIENCY USING EXPERT SYSTEMS

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ABSTRACT

Measurement and numeric control (digital) systems have mainly imposed in the last decades because the technological revolution within electronic components domain. It is thus obtained a bigger accuracy in numeric information processing by facilitating the direct connection with computer, a higher work speed and an increased automation degree of the process. It was accomplished an original „on-line" management system in closed circuit with gradual command of heating electric power and self-adaptive control with PID behavior of temperature. The hard structure is made of a command unit with thyristor connected to an electronic device specialized on its interface with an electronic computer.

Key words: expert system, equipment, energy efficiency, furnace, temperature.

INTRODUCTION

The expert systems (figure 1) are numerical structures of regulating and automat control using an operation system, a programming environment and a series of execution organs that fulfill promptly the commands of the expert systems.

An expert system undertakes a human problem of which solutions can be logically determined by a natural deductive system (natural system based on a series of solid knowledge) and codes it with the help of a computer. It results in this manner a software component that interprets the logical solution and transforms it into a codes solution. If all this process takes place in its expected order, then one can foresee the expected results.

Knowledge accumulation – specific for the field (in the shape of rules and laws), gathered by an expert and associated with the problem.

Database – relevant information, history, statistics, components, coefficients etc.

Analysis, command – analysis the rules, laws together with the actions of the user for the determination of the new conditions of identification of the possible solutions. The system will react in the field of the problem being based on the data base and using the input data from the **final user.**

The user interface – ensures the link between the expert system and user and designed in such a manner than to offer explanations of the system actions.

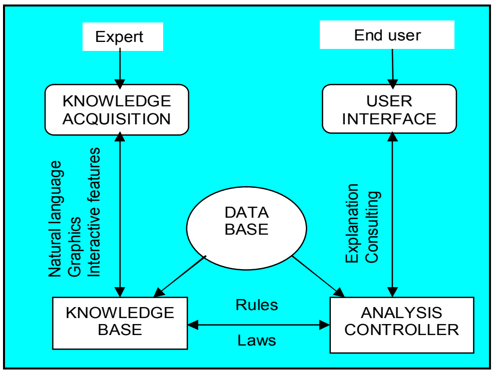

Figure 1. The expert system.

EXPERT SYSTEM TECHNIQUES FOR ENERGY EFFICIENCY INCREASING

In the figure 2 is shown the block scheme of on expert system to control a heating system is given; it is supplied at the industrial power network 380V, 50Hz and it has as a measurement parameter the temperature.

The power source SP can be constituted in a steady state convertor type M3, ensuring a three phase supplying of the thermal system with a continuum voltage.

IBM – PC represents a personal computer, compatible IBM, that has the role of numeric regulator and achieves it by the software component.

The **parallel programmable interface IPP** has as a purpose the expanding of the number of outputs available on the parallel standard interface LPT of a computer compatible IBM-PC. Given the necessity of existence of two parallel parts of 8 bytes, for data exchange with the block D/A and A/D, as well as a part for commands, for configuration the system, one can use a specialized circuit in the INTEL family.

The **block of digital-analogic conversion D/A** has as a purpose the supplied at its output of an electric signal (voltage or current), proportional with the numeric expression received at the output. In this case, through the foreseen channel in the block scheme, the block D/A receive from the IBM-PC system a numeric value and supplies at the output a continuum voltage ranging between 0-10V, necessary for the command of the power source SP.

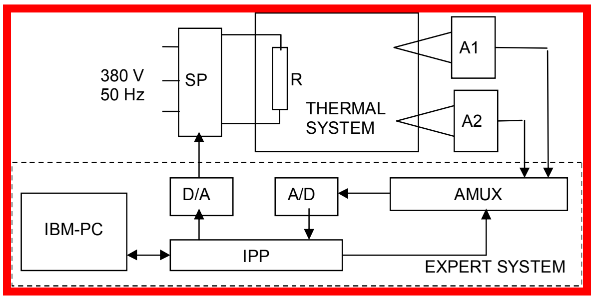

Figure 2. The expert system for heating system programming.

The **block of analogic-digital conversion A/D** supplies at the output a number in binary representation, proportional with the analogical measure from the output. The convention A/D supposed the superposition of the input signal at two operations: sampling and quanting. The first operating defines the temporal aspect of the conversion and the way of taking the sample and the second defines even the way of obtaining of the numeric equivalent of the analogue measure.

The **block of analogic multiplexing AMUX** has the role to enable the reception of ware electric signals on a single channel, it actually achieves a time partitioning of the input channel of the block A/D. The analogic multiplying operating needs commutation devices to direct the useful signal on a desire channel. In a simple variant the analogic swich can be assimilating with a rotative switch with a position or with an ensemble of n swiches one being closed during the other stay opened.

Measurement amplifiers A1, A2 – the majority of the expert system working with analogic dates work with high level tension signals (0..5V, 0..10V), but not always the transducers used (in the case of measuring some non-electrical measures) can supply such signals. It appears the necessity of amplifying the signals supplied towards the expert system up to values compatible to these it is able to read as input data. For solving this problem the measure amplifiers are being used. The practical implementing of the measurement amplifies has at the basis the operational amplifiers that is capable to ensure a big gain in a wide range of frequencies and as characterized by symmetric output, amplification and input impedance very big.

EXPERT SYSTEM TECHNIQUES FOR FURNACES ENERGY EFFICIENCY

The expert system is made on the basis of an original mathematical model theoretically and experimentally obtained. The mathematical model respects and combines static and dynamic behavior of an industrial furnace and the model of a temperature regulator with PID behavior.

Measurement and numeric control (digital) systems have mainly imposed in the last decades because the technological revolution within electronic components domain. It is thus obtained a bigger accuracy in numeric information processing by facilitating the direct connection with computer, a higher work speed and an increased automation degree of the process.

It was accomplished an original "on-line" management system in closed circuit with gradual command of heating electric power and self-adaptive control with PID behavior of temperature. The hard structure is made of a command unit with thyristor connected to an electronic device specialized on its interface with an electronic computer.

The calculus program is based on an original mathematical model theoretically and experimentally obtained. The mathematical model respects and combines static and dynamic behavior of an electric furnace and the model of a temperature regulator with PID behavior. That is why the model can be used for any other furnace than the one used during experiments. As any theoretical model, it has a lot of coefficients whose identification can be made only experimentally in order to respect the constructive functional particularities of the installation.

The expert system assures the self-adjusting parameters of the temperature regulator with PID through the indicial response method of the furnace. Taking into consideration the experimental knowledge necessity of the furnace constructive functional characteristics it was made the first experiment to determine its indicial response. The gradual command of heating power was realized by using thyristor commanded in phase angle. In this case the relation between power and command angle Ψ is:

$$P=\frac{U_s^2}{R}\left(1-\frac{\psi}{\pi}+\frac{\sin 2\psi}{2\pi}\right) \tag{1}$$

The variation of command angle of π radians corresponds to a variation of U_{com} command tension from the exit of digital-analogical converter of 10 V thus, U_{com} = 0 V corresponds to the angle ψ= π (rad), and U_{com} = 10 V corresponds to the angle ψ= 0 (rad).

Mathematical model correspnd to to following steps:

I. Parameters initialization:
1°. Consign temperature (CONSEMN) (°C)
2°. Proportionality band (BP) (%): 5% … 40%
3°. Hysteresis (HISZ) meaning max $|\theta_{measured}(t) - \theta_{programmed}(t)|$): 2°C … 5°C
4°. Initial power applied to furnace (EF) (%): (60 …80) x P_{MAX}/100
5°. Time (TIME), (min)
6°. Sampling quantum (K): 10 … 15 seconds
7°. Estimate time (TIME_ESTIM) of T_u and V_{MAX} parameters: 3 … 4 min
8°. Admitted maximum deviation (ABATERE) meaning:
max $|\theta_{măsurat}(t) - \theta_{estimat}(t)|$: 1…3°C

II. The furnace is at ambient temperature thus we apply an initial power equal to that which was adjusted at aforementioned point 4° (EF).

III. When the furnace temperature θ(t) has the value:

$$\theta(t) \geq CONSEMN - \frac{75}{100}\, x\ BP\ x\ CONSEMN \tag{2}$$

We find B point by decreasing for five times the value of temperature range, value which is experimentally determined for temperature tangent variations not bigger than 1°C/min.

In order to estimate temperature:

$$BETA[q]=DREAPTA[numar]+ qx\left(\left(DREAPTA[2\,x\,numar]-5\,x\,ECART\right)-DREAPTA[numar]\right)/\,numar \tag{3}$$

where q index is varying from 0 to a maximum value= number.

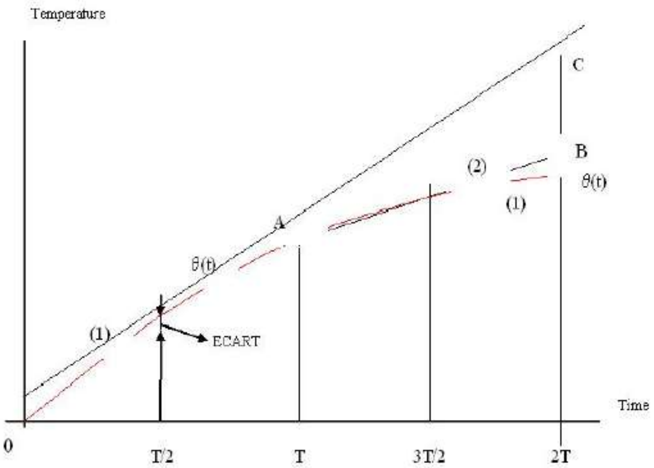

Figure 3. Graphical representation of the estimation model of temperature evolution.

According to research methodology presented the expert system for energy efficiency increasing of heat treatments installations for steel alloys realized on determination base through experimental methods of theoretical mathematical models parameters. These demonstrate the complexity of the construction and functioning of these installations. This expert system assures the accuracy and uniformity of temperature within charge.

CONCLUSION

In order to obtain the precision of temperature (imposed by the technological demands) it was replaced the panel within the furnace with an original leading system and the uniformity of temperature in charge was realized an auxiliary heating device closed muffle type where the pieces were placed. The necessity of using an auxiliary heating device came from the conclusions of the experiments made with the initial heat treatment installation no-load and on load that showed the existence of some high temperature differences unallowable for steel alloys especially at the furnace arch and base of hearth.

Choice criteria for muffle form and material start from the phenomena of the complex heat transfer within the furnace, the furnace construction (useful space and heating elements disposal), the treated charge type (alloy, shape and dimensions for the pieces, pieces laying in the auxiliary heating device), the characteristics of used metallic materials (high alloyed refractory steels) such as mechanical strength at high temperatures, resistance to creep, refractoriness, thermal conductivity. There of it was used the auxiliary heating device of T20CrNi370 austenitic alloy – SR-EN 6855-98.

From the dependency analysis between the view factors value between two parallel surfaces where there exist heat transfer through radiation and the distance size between that surfaces it results that the muffle walls must be as closer as possible to the heating elements (mounted in the walls).

The expert system contains a hard structure and a specialized soft. Both were realized by taking into consideration the specific of the used installation (furnace power, thermocouples type, the indicial response of the furnace) and they form an on-line self adaptive leading system in closed circuit with PID temperature adjusting.

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THE POSSIBILITY OF USING BURLEY TOBACCO STALKS AS BIOMASS

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ABSTRACT

This work represents a significant contribution in the field of potential use tobacco stalks as biomass. The aim of this study was to determine the chemical composition of the Burley tobacco stalks, in order to predict optimal using possibility. Special emphasis is given to the energy potential, through the prediction a high heating value (HHV), based on the lignin and ash content. The results of these experimental studies indicate that the Burley tobacco stalks can be used as a raw material for the production pure protein and cellulose, as well as a certain amount can be used in the purpose of thermal energy, through the production of biogas, bio-ethanol, pellets or briquettes, affording an environmentally acceptable and energy-valuable products. The special significance of this research is the fact that there are no data of the chemical composition of Burley tobacco stalks from the Republic of Serbia.

Key words: biomass, tobacco stalks, Burley, HHV.

INTRODUCTION

Optimization of production of any agricultural crops, including tobacco, involves the utilization of the entire amount of potential biomass. It should be noted that agriculture is one of the most important activities in the Republic of Serbia, since it accounts for about 10% in the formation of GDP. 10.9% of the population is engaged in agriculture. Furthermore, agriculture generates large amounts of waste that represents a significant biomass potential. It has been estimated that total of 12.5 million tons of biomass is produced in Serbia each year, of which is about 1.7 million tons in the remains of agricultural production. A large share of agricultural waste in the Republic of Serbia makes corn stalks and corn cobs, different types of straw (wheat, barley, oats and soybeans), and then sunflower remains (1). Tobacco stalks, which are classified according to the categorization into green tobacco waste (2), also make a significant part of the biomass in Serbia. Every year, after the harvest of leaves, a large amount of tobacco stalks remains on the field. A smaller amount (1/4) is usually plowed, while larger quantities are disposed as waste or burnt on the field, which leads to a waste of resources and environmental pollution. Given the share of large leaf tobaccos in total tobacco production in the country (over 85%), stalks may represent an easily accessible and cost-effective raw material, from which it can be obtained a whole range of products by final industrial processing (3). The results of available researches showed that stalks and other tobacco waste could be used in various products, in the production of pulp and paper, organic acids (citric, malic, oxalic acid), nicotinic acid, bioethanol, biogas, as well as inorganic fertilizer (4, 5, 6, 7, 8, 9, 10). It is interesting to note that in addition to lignin, tobacco contains relatively high concentrations of cellulose. The highest content of cellulose is found in tobacco stalks, even 35-40% of dry matter (11). Such a chemical composition is suitable for the production of biofuels. Therefore, if they are used as a raw material for briquetting, either alone or in combination with other available crop residue, tobacco stems could be used as biofuel (11). The use of lignocelluloses biomass for biofuel production will be inevitable in the near future, when it is expected that the liquid fossil fuels will have to be replaced by renewable sustainable alternatives (12). In addition, due to the high content of cellulose, stalk is an important raw material in the production of paper, cardboard, textiles, cotton, flax and other vegetable fibers (13, 8). Also, the tobacco stalks may be used for the production of pesticides. Since it is biodegradable, it is an attractive alternative to synthetic pesticides and fertilizers. It is also used for compost production for mushroom cultivation and decorative plants (14, 15, 16, 2).

According to data of the Statistical Office of Serbia for 2011, large leaf tobaccos are cultivated on 5937 hectares, of which Burley tobacco on 1060 hectares (17). Bearing in mind that the average number of stalks are 22 000 per hectare, the total number of Burley stalks was 23 510 520. The average weight of the dried stalks is 300-400 g, which means it could get 6000-10000 kg of dried stalks per hectare, or 7053-9404 tons that could be used to obtain different products. It can be said that every year remains about 76 000 tons of all types of tobacco stalks in Serbia, which have no economic value. This data illustrates the enormous potential of tobacco stalks as biomass.

The aim of this paper is the prediction of the potential use of tobacco stalks as biomass, based on the experimentally determined chemical composition. The literature findings showed that some previous authors have done the analysis of the chemical composition of leaves and stems of large leaf tobaccos (18). The fact that tobacco stalks were not the subject of serious research, especially in our region, and that tobacco is placed in the waste that is non-toxic, was the reason for our research. Burley, as large leaf tobacco, has been selected, because of its share of total production (about 17%), but above all because of the way of drying (drying on the stalk). This information is very important, because it does not require additional investment for raw materials drying.

MATERIALS AND METHODS

As material for this study we used Bulrley tobacco stalks, grown in Vojvodina production area (Banat – Čoka) in Republic of Serbia, which were collected from the field after harvesting tobacco. Samples are prepared by grinding and homogenization of the stalks. Preparation of the samples for the analysis of chemical composition was performed in the standard manner. After grinding, the stalks are milled and sieved to a series of vibrating sieves. The fractions of particle size of 0.5 - 1.0 mm were taken for the analysis of the chemical composition.

Within the analysis of the chemical composition of tobacco stalks following research was made: determination the moisture content of the samples (19), lignin and extractive substances soluble in a mixture of organic solvents (20, 21) and the determination of the ash content (22).

Nicotine level was determined using a UV spectrophotometer; total nitrogen was determined by the Kjeldalh method, while the reducing sugar was determined by the picric acid colorimetric method (23). All analyzes were performed in triplicates. Based on the moisture content, the results of the analysis of the chemical composition of the samples of tobacco stalks are expressed relative to the dry weight of the samples. Based on the results of the lignin and ash content, HHV values of test material were calculated by using two different formulas.

HHV_1=0.0889 [L] + 16.8218 (24)

HHV_2=19.914 – 0.2324 [Ash] (25)

RESULTS AND DISCUSSION

In the Table 1 are shown the results of the analysis of the chemical composition of Burley tobacco stalks. For clarity reasons the results in Table 1 represent average values.

Table 1. Chemical composition of Burley tobacco stalks

Compounds	Moisture	Protein	Nicotine	Reducing sugar	Cellulose	Lignin	Ash
%	4.55	8.85	0.14	below detection limit	46.47	18.50	4.21

On the basis of literature data (26), Burley tobacco leaves have the highest average content of proteins in an amount of 10-12%. It was expected the lower content of proteins in tobacco stalk, which is confirmed by experiment. The protein content of 8.85% provides the possibility of extracting from tobacco stalks, their purification and use in the food industry, or for therapeutic purposes.

The nicotine content in Burley tobacco leaves is around 2% (26). It was expected significantly lower content in tobacco stalks (18), as evidenced by the experiment (Table 1). The obtained result is still lower than expected, so the authors argue that the extraction of nicotine from the stalks will not be economically cost effective, for usage in the manufacture of pesticides or in pharmaceutical industry. If the stalks will be used for the production of briquettes, the nicotine level in the smoke after combustion would be below 200 ppm, which is far below of the European Union regulations (500 ppm).

The content of reducing sugar in Burley tobacco leaves is around 0, 01-1%, while the stalks have much less (26). Due to very low values, we were unable to determine the exact content of reducing sugar in our investigation, which was expected based on the literature data (18).

According to the literature data, tobacco stalk contains 35-40% celluloses, midrib 10-15% and lamina 10-12% (26). Higher cellulose content than expected, showing that Burley tobacco stalks have essential potential; they may become a material for industrial preparation of paper, paper packaging, newspaper, which leads to the waste utilization, and also improves the economic value of tobacco stalks. Based on the literature review about amounts of Burley tobacco stalks per hectare, and cellulose content in the stalk, it can be concluded that it may be obtained 4.500 kg of cellulose per hectare. This confirms the possibility of tobacco stalks utilization in the cellulose production.

According to the literature data lignin content in tobacco is 4-5%, while the tobacco stalks can contain about 20% (26). The results obtained in our experiment (18.50%) were slightly lower than it was given in the literature.

Mineral content varies considerably in fermented tobacco leaves, from 8.5 to 23% (mean value 17.2%). It was found that the lower classes of tobacco have higher ash content, and that the quality of tobacco is inversely proportional to the amount of ash (26). In the majority of plants, mineral matters make up about 3% of dry matter. Thus, tobacco contains a significant amount of ash as compared to the leaves of other plants. Furthermore, tobacco stalk contains less amount of ash in relation to the leaf. According to literature data, ash content in tobacco stalk is about 6%. Result of our research is somewhat lower than expected, which can be considered as a good result. In fact, during the combustion of biomass, it remains a very small or negligible amount of ash, which is a positive characteristic in comparison with fossil fuels.

On the basis of data on the quantity of lignin and ash content HHV values are calculated, using two different formulations. The results are shown in Figure 1.

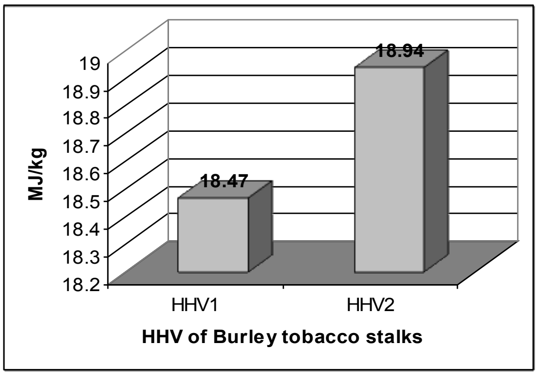

Figure 1. The calculated values of HHV (MJ/kg)

The calculated values for HHV from 18.47 to 18.94 MJ/kg have showed that the Burley tobacco stalks have a significant energy potential. According to Brkić et.al.(27), heating value of straw is about 15 MJ/kg, of wood 18.6 MJ/kg, of fuel oil 42 MJ/kg and of diesel fuel is about 41 MJ/kg. In general, the calorific value of biomass, which is formed from the remains of agricultural production ranges between 13 and 18 MJ/kg (28). If we compare the obtained data of tobacco stalks thermal power with the foregoing values, it can be concluded that the use of Burley tobacco stalks for production energy pellets and briquettes are profitable, because they have a high calorific value.

CONCLUSIONS

The research presented in this paper is relating to the determination of possibilities of Burley tobacco stalks utilization, on the basis of chemical composition. On the basis of these results it can be derived the following conclusions:

- protein content of 8.85% indicates that it is possible to isolate and it in a variety of purposes, while the part which lag behind it may be used as biomass;
- nicotine content of 0.14% is expected, so it would not be economically cost effective to carry out the extraction nicotine from the stalk;
- sugar content is below the detection;
- cellulose content (46.47%) is extremely high, which means that the Burley tobacco stalks represent a great potential for the production of cellulose;
- calorific value calculated based on the lignin content (18.47MJ/kg) and ash content (18.94MJ/kg) indicates that the Burley tobacco stalks represent a significant energy potential.

Exploiting of agricultural waste in terms of obtaining secondary products, which could be used in other industries, as well as in energy production, it is still at a low level, both in the Republic of Serbia as well as in the region. According to the results of this investigation, tobacco stalks can be used completely to get some of these products, or for energy purposes. In this way it can be achieved the appropriate economic effect and, more importantly, reduce environmental pollution.

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BIOGAS (BIOMASS)-USE, REGULATION AND STRATEGY ON THE USE OF RENEWABLE ENERGY IN THE EU AND IN THE REGION

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ABSTRACT

Biogas (Biomass) is a renewable energy source , with a low amount of carbon.If used correctly, biomass is a sustainable fuel that can significantly affect the reduction in net carbon emissions compared with fossil fuels.Aldo, combustion of biogas as a natural gas leads to the formation certain amounts of carbon dioxide (CO2) . Carbon in biogas derived from plant material , which is it self incorporated carbon from atmospheric carbon dioksida.Therefore the use of biogas regarded as CO2 neutral and does not increase the amount of greenhouse garden. Replacing fossil fuels biogas leads to emission reductions CO2 .[1].

Key words: Biogas (Biomass), renewable energy,low-carbon.

INTRODUCTION

Energy consumption is growing dramatically in developed countries. Has been constantly increasing, while in other countries the consumption growth of 50 % in each decade . Generally , it is expected that the 2030th the energy needs for a rise of more than 50 % . [2]Biofuel production is mainly related to the production of biodiesel , bioethanol and biogas. Biogas is produced in many countries , but few of them have developed a program of biogas production . Traditional small family biogas plants are increasingly being replaced by industrial plants for cogeneration of heat and power . As the biogas can be produced by treating the waste in this way can solve the problem of disposal of unwanted materials , with energy products and agricultural fertilizer with environmental protection.It is unlikely that biogas will play an important role in the transport of [3] due to the substantial investment that its application is granted, primarily in the storage tanks under pressure . On the economic level, biogas technology can save individual producers a lot of money in energy costs. For example, dairy farms using biogas technology can save thousands of dollars each year in electricity and heating [4] .

BIOMASS AS A RENEWABLE ENERGY SOURCE

As a renewable resource for getting fuel to produce electricity and thermal energy , biomass shall mean the biodegradable fraction of products, waste and residues from biological origin from agriculture (including vegetal and animal substances), forestry and related industries , as well as the biodegradable fraction of industrial and municipal waste [5] . Biomass can be divided into primary and secondary products [6] . The primary photosynthetic products generated by direct use of solar energy and include crops and wood , remains of vegetable by-products and waste from industry, primarily timber and agriculture . Secondary products indirectly using solar energy, decomposition or conversion of organic matter (eg, animals) and encompasses the entire plankton , manure and sewage . The processing of the most different types of biomass are produced of biofuels that are used for the transport , in some industrial processes , as well as heating . Depending on the raw materials used for production , the four different generation biofuels [7] :

- First generation biofuels are made from starch or sugar from corn , wheat , sugar cane , sugar beet , and herbs that contain a higher percentage of starch or sugar (lack of first -generation biofuel production has a negative impact on the price of basic foodstuffs and economy of the country) ,
- Second generation biofuels produced from lignocellulosic biomass (wood , used paper , reeds and grasses) and agricultural residues ; production of second generation biofuels is still inefficient for commercial use , but some countries are investing heavily in research and development ,
- Third generation biofuels produced from algae or rapeseed plants that do not threaten the food supply (productivity, third-generation biofuels is about 30 times higher per unit of surface area of the first or second generation biofuels) and
- The fourth generation biofuels are produced from raw materials that have been genetically modified to provide greater energy yields and / or their building macromolecules susceptible economical degradation , a characteristic of them and absorb large amounts of carbon dioxide from the atmosphere .

UTILIZATION OF BIOGAS

Using all of the biogas is increased more for the following reasons [8] :

- fuel prices are increasing more and more ,
- significant efforts to increase the use of renewable energy sources and
- production is possible in installations of small -scale and very simple construction .

Biogas can be used directly for cooking and the cogeneration of electricity and heat , which is particularly feasible when the biogas is used in , or in the vicinity of the generation.The use of biogas solve the problem of power supply in rural areas where they traditionally use wood as fuel . In addition to environmental reasons , the use of biogas insteadwood is preferred for health reasons because biogas burns without smoke [9] . One of the possible applications of biogas as a vehicle fuel for biogas is the cleanest fuel available . Biogas produces 95 % less carbon dioxide emissions compared to diesel , and a 80 % reduction in nitrogen oxide emissions . Also , the use of biogas does not result in the emission of particulate matter in the atmosphere [10] . One cubic meter of biogas released 23 MJ (5500 kcal) of energy, which corresponds to the thermal power of 0.6 l diesel fuel [11] . However , a major problem that arises is the possibility of gas leakage from the reservoir.[12] . In recent years, examines the possibility of using biogas with diesel fuel in internal combustion engines . This concept provides a lower emission of pollutants in relation to the use of diesel fuel and better engine performance over the use of clean biogas [13] .Biogas can be used for heating greenhouses , because , in addition to heating , and provides an increased concentration of carbon dioxide the plants which are used in the photosynthesis . Methane in the biogas is used to produce methanol , the organic solvent used for the preparation of formaldehyde, chloromethane...The atmosphere of methane and carbon dioxide inhibit the metabolism of plants , and reduces the formation of ethylene in the fruit , and cereals , and other than that , and killing harmful insects , molds and bacteria which can cause spoilage . Waste treatment in closed tanks, avoiding the emission of methane has 22 times the impact on global warming than carbon dioxide [9] . Each year around the world , as a result of uncontrolled microbial activity in the atmosphere released 590-880 million tons of methane . About 90% of the emitted methane derives from biogenic sources.[14] .

ANALYZE THE REGULATION AND STRATEGIES FOR USE OF RENEWABLE ENERGY

State and EU regulations on the use of renewable energy

The question of the use of renewable energy is current in all developed countries , especially in EU countries. Each EU country sets targets for the share of renewable energy in the total energy and the goals expressed in numbers and deposited time . Depending on the conditions in the country and facilities of large energy producers , set goals and deadlines are very different .In recent years , many regulations were adopted in the EU dealing with the challenges of establishing bioeconomics and initiate changes in the European economy. This stems from concerns about the potential impact of uncontrolled use of biomass for renewable energy in food production in Europe and the Third World. Solving this problem requires a multidisciplinary strategy and comprehensive approach including various regulations . Especially need more interaction and better alignment between research andinnovation in the EU and the priorities of extra incentive regulation in bioeconomics [15] . The adoption of Directive 2001/77/EC on the promotion of electricity from renewable energy sources in the international energy market and Directive 2003/30/EC on the promotion of the use of biofuels or other renewable fuels for transport , the European Union has defined different types of renewable energy sources [16] . According to these directives , it is essential that each Member State shall provide a minimum share of 10 % share of biofuels in transport. How to transport fuel can be easily traded , states that do not have sufficient available sources of biofuels can provide imported. In this way , in addition to the balance between domestic production and imports , and encourages the development of bilateral and multilateral trade agreements , association of social and economic aspects , as well as the stability of power supply. In contrast to the potential of Serbia , where the main potential of biomass for energy production . Biomass as an energy source in the EU participates in the total energy of about 20 % , which is placed in the third options.

EXAMPLES OF GOOD PRATICE IN THE EU

Total energy production from biogas in the EU in 2010. Was 30 331 GWh . Of these , more than 50 % of the energy produced in Germany [17] . Germany is a leader in the production of biogas, 2010. Had more than 7,000 biogas plants , of which about 84 % based on Co-digestion of animal and vegetable waste . One example is the use of biogas companies in the food processing Vogteier Erdenwerk GmbH and Niederorla farm GmbH . As a raw material for the production of biogas used waste corn (70 %) , silage (20-25 %) and manure . The process is carried out in the thermophilic digester volume of 2000 m3 , a gas is stored in a tank volume of 3500 m3 . Combined heat and power is 537 kW . Utilization of heat in the process is about 70 % , and wherein the water vapor is obtained by the temperature 160 ° C [18] . As an example of good practice can serve Lemvig biogas plant in Denmark. It was built in 1992 and renovated in 2008 . Machinery processing 615 tons per day of which 82 % is manure from 75 farms , while about 18% of organic waste . The 2011th biogas production was 8.5 million m3 per year , and 2012th 10.2 million . The plant consists of four digesters total volume of 14300 m3 . The process is carried out by digestion in the thermophilic temperature of 53 ° C and with a residence time of 26 days . Input manure is heated hot digestate pasteurization process . One part of the biogas formed is used to heat the center Lamviga [19] .

GOOD PRACTICES IN THE COUNTRIES IN THE REGION

In the Balkan region were built only a few plants for the production of biogas from agricultural raw materials , in Croatia, Hungary , and one plant in Serbia . In Croatia there are two plants in agricultural cooperatives Osatina in Ivankovo . Raw materials for the production of biogas as manure from the farm (about 2500 head of cattle) , corn silage and grain corn silage waste . The total capacity of the plant is about 4.6 MWh (electrical and thermal 2x1MWh 2x1 , 3mWh).[20]In addition , provided the means to build power plants in Gradec near Zagreb for the construction of a 2 MW (1 MWh of electricity and heat energy 1MWh) , with the planned construction of another plant of similar strength in the Lower Miholjcu . The largest number of different power plants exist in Hungary [21] . In Kecskemet there since 2008. Plant for the production of biogas owned company PilzeNagy Kft . The total capacity of the plant is about 0.7 MWh , while the electric power 330 kWh and 400 kWh heat . In Serbia there is only one large plant for the production of biogas , which is starting up in 2012.

It is located in the village of Gornja Draguša , Blace and private ownership within the dairies ' Lazarus ' Blace . Installed capacity of power plants , a total of about 2 MWh (1MWh electricity and 1.2 MW of heat energy) [22] , applied equipment and technology is GHD Co. , Technology , Chilston USA , where electricity is distributed through the power grid Serbia . The raw material for the production of biogas (about 50t/day) the manure from the farm of 400 cows, corn silage and whey from cheese production process . The investment is about 2.2 million, half of which are provided by USDA through the program USAIS .

CONCLUSION

Serbia has the ability to use, but there are no data on the cost-effectiveness of the use of renewable energy sources . In fact , all of the available estimates of the possible use of renewable energy sources in Serbia related to the physical , not the economic potential. As the cost of energy production from OI still higher than the cost of the energy produced in the traditional ways of fossil fuels , it is necessary to introduce a selective rates that encourage the construction of plants for the production of energy from alternative sources. Also , it stopped monitoring the impact of incentives and measures to adjust energy prices according to condition (new technologies , implementation of innovative solutions for new sources ...) in the field of renewable energy .The lowest net cost per kWh of energy can be obtained by burning the remains of the wood-processing industry, which is about 0.7 e / kWh . In contrast, the most expensive energy obtained by combustion of vegetable oil (6.1 E / kWh) but the raw material is approximately 2.5 times the heat power of the timber. In addition , storage of waste timber industry requires a large space that can further affect the price of fuel. Economically justifiable to build a plant in the area of sources of raw materials in order to reduce transport costs ,combustion plants in areas rich in food processing industry and equipment for the production of biogas as part of large farms . Price of plants depends on the technology used and the size and power of the device. The price of electricity produced from biomass as fuel are in the range 7 to 12 Ec / kWh , while the cost of electricity from biogas was 11 to 16 Ec / kWh . Lack of biogas production is limited by the ability of storage. according to somecalculations, 0.5 kWh of electricity can be provided from 6-8 m3 of biogas , which can be obtained from the manure of 5 dairy cows , sewage waste from 100 households or kitchen waste from 75 households .The amount of one hectare of maize to be sufficient to produce a biogas so that the 5 households with 2-3 members may supply electric energy for a year.. Economic experience of the U.S. shows that it is economically justified to invest in the construction of plants for the production of biogas from manure of ruminants , if the farm has more than 150 head of cattle . The price of energy has been calculated for the system to work 345 days a year with the degree of utilization of 85 % , the ratio of electrical / thermal energy is 0.57 and the energy value of gas h/m3 6.5 , for the period of the plant for 20 years. As can be seen from the data , the savings depend on the availability of raw materials , which means that in each case must predict the possible benefits of investing in the plant .

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20. Anonymous26:http://www.osatina.hr/hr/component/content/article/44izdvojeno/87-bio-plin
21. Anonymous 27: http://energy4farms.eu/biogas-plants-in-europe/biogas-plants-in-hungary/
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AN ASSESSMENT OF THE NEGATIVE IMPACTS AIR TEMPERATURE CHANGES ON FOREST ECOSYSTEMS IN SERBIA

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ABSTRACT

The concept of the spatial development of the Republic of Serbia, aimed at the alleviation of the effects of global warming and climate change on the forest ecosystems in Serbia, should include the determination of the effects of climate change on the availability of the natural resources, above all forest ecosystems and biodiversity aimed at planning sustainable development and ecologically acceptable activities in the domains susceptible to the climate change. This paper analyzes the trend changes in the mean annual air temperature and the air temperature in the growing season, in the period from 1949 to 2010 (a series of 62 years), on the network of 32 meteorological stations in Serbia, and problems and challenges in forestry in Serbia caused by climate change. Based on this analysis it can be concluded that the trend of increase of mean air temperature (by about 1.2°C in the twentieth century) is present in the greatest part of the territory, except in southeast Serbia, where the trend of the decrease of mean air temperature was reported. It is expected that these trends of climate change in Serbia will continue in the future, which will significantly alter the structure and function of forest ecosystems, thereby imposing the need for the implementation of adaptive forest management.

Key words: the impact of climate change, forest ecosystems, air temperature, trend changes, adaptive forest management, Serbia.

INTRODUCTION

Global climate, biological, chemical and geological processes and natural ecosystems are interconnected, and changes in any of these components of the environment may affect humans and other living beings. Since the effects of global warming can be so intense in some regions that they can cause the changes in the forest productivity in composition of the plant and animal species in them, the forest cover would become unsustainable. Some effects of climate change are already noticeable and there is a need and opportunity to be better prepared for future change. Individuals, societies and institutions should be aware of the impacts that climate change is likely to have and should have strategies to adapt to them. Forest, and the goods and services they provide, are essential for human well-being. An assessment of the likely impacts of climate change on forests and forest-dependent people, therefore, is important for effective climate change adaptation. This paper is aimed at pointing out to the possible conditions of the forest ecosystems in Serbia due to global warming and the type of actions which can be taken, based on the study of the trend of the changes of air temperatures in Serbia.

MATERIALS AND METHODS

The paper is based on the quantitative, mathematical-statistical methods, comparative analyses, evaluation method, synthesis method with elements of data generalization and systematization. For this research data from the Republic Hydrometeorological Service of Serbia were used. Due to the reduction of degree of error, it was performed the averaging by altitudes or height zones in which are the located meteorological stations (areas up to 200 m above sea level, areas of 200-500 m above sea level, areas of 500-1,000 m above sea level and the areas of more than 1,000 m above sea level). To check the statistical significance of the values of the linear trend of the mean annual air temperature and the air temperature in the growing season, it was used a test of independence of the two statistical features (t test) according to formula:

$$t = R\sqrt{\frac{n-2}{1-R^2}}$$

Based on the coefficient of determination (R2) and the degree of freedom was determined the actual value of the t test, and based on the degree of freedom (n-2) and an appropriate level of risk 0.05 and 0.01 are determined the critical values of t test. For degree of freedom 60 (n-2 elements), the critical values of t-test are: t (60; 0,05) = 2,00; t (60; 0,01) = 2,66. By comparing the actual and the critical value of t test it was determined the statistical significance of the linear trend of the mean annual air temperature and air temperature in the vegetation period in Serbia in the period 1949-2010. In order to study the variability of the temperatures, the standard deviation was used.

The proposed measures are based on the previous works and experiences that have proved effective.

RESULTS AND DISCUSSION

It is known that the occurrence and survival of vegetation in certain area, its distribution and altitudinal differentiation, along with the other ecological conditions, to a great extent also depends on the climate characteristics of the area. The numerous researches point out to this fact: Kolic [1], Jovanovic and Kolic [2], Krstic [3], Krstic et al. [4], Smailagic et al. [5], Krstic and Cirkovic [6].

The occurrence of desiccation to a great extent depends on the high temperatures and amount of precipitation. Along with the amount of precipitation and their distribution in the growing season, the lack of moisture in the soil has a great impact on the process of forest of desiccation. Fighting against the heavy drought, forest trees decelerate transpiration, which implies absorption of lower quantities of nutrients from the soil and deceleration of all other physiological processes. Under such conditions, if the period of drought is extended, the trees physiologically weaken and become less tolerant to the other anthropogenic, abiotic and biotic causes of forest desiccation.

According to Popovic, T. et al. [7] estimates based on climate modeling, using moderate scenarios, indicate that the annual temperature in Serbia until the end of the century will increase for 2.6°C. Warming will not be equal throughout the year, summer will be warmer for 3.5°C, fall for 2.2°C, winter for 3.2°C, and the spring for 2.5°C. It is expected the increase in frequency, intensity and duration of heat waves, while the projections for the number of frosty and icy days say that they will continue to decline.

Our paper analyzes the trend changes in the mean annual air temperature and the air temperature in the growing season, in the period from 1949 to 2010 (a series of 62 years), on the network of 32 meteorological stations in Serbia.

According to the obtained results, the trend of changes in mean annual air temperature in Serbia for the period 1949-2010 (62 years) at most meteorological stations is positive (exceptions are Kursumlija and Crni Vrh). The greatest increases in the values of the linear trend have the meteorological stations Rudnik, Loznica, Negotin and Belgrade, whereby the values of trend of changes are statistically significant at the 99% probability.

In Table 1 is shown trend of changes of the mean annual air temperature and air temperature in the vegetation period in Serbia for the period 1949-2010.

Negative or minimally expressed positive trend of changes of mean air temperature is characteristic for the south-east of Serbia, the areas along the valleys of the South and Great Morava, and Veliko Gradiste, but the values of the trend of changes at any meteorological station are not statistically significant.

When it comes to the trend of changes of air temperature during the growing season according to the obtained results, the trend of changes at the most meteorological stations is positive (exceptions are Kursumlija and Crni Vrh). Like in the trend of changes of the mean annual temperature, in the trend of changes in air temperature during the vegetation period is also noticeable the existence of territorial uniformity. In the area of Vojvodina (with the exception of Palic) the values of trend of changes of air temperature in the growing season ranges from 0.010°C annually (MS Sremska Mitrovica) to 0.016°C annually (MS Sombor), whereby the values of trend are statistically significant at the probability 95% for the area of Kikinda and Sombor, and for other meteorological stations values of trend of changes are not statistically significant.

The negative trend of changes of air temperature in the growing season have Kursumlija (-0.009°C/annually) and Crni Vrh (-0.11°C/annually), while the value of the trend of changes in the area of MS Crni Vrh is statistically significant at the 99% probability, and the value of the trend of changes in the area of Kursumlija is not statistically significant.

Minimum expressed positive trend of changes of air temperature during the vegetation period is characteristic for south-east of Serbia (Leskovac 0.001°C/ annually, Dimitrovgrad 0.001°C/annually), areas along the valleys of the South and Great Morava (Vranje 0.005°C/annually, Nis 0.009°C/annually, Cuprija 0.002°C/ annually) and Veliko Gradiste (0.007°C/annually), but the values of the trend of changes at any weather station were not statistically significant.

Table 1. The trend of the mean annual air temperature and the temperatue in the growing season in Serbia in the period 1949-2010 (°C / year)

Meteorological station	**Altitude (m)**	**The trend of the mean annual air temperature °C/per year**		**The trend of temperature in the growing season °C/per year**	
The area 0-200 m.a.s.l.					
Negotin	42	0,021	**	0,021	**
Zrenjanin	80	0,016	**	0,013	
Veliko Gradište	80	0,007		0,007	
Kikinda	81	0,015	**	0,015	*
Sremska Mitrovica	82	0,011	*	0,010	
Vršac	84	0,016	**	0,012	
Novi Sad	86	0,014	**	0,011	
Sombor	87	0,015	**	0,016	*
Banatski Karlovac	89	0,012	*	0,011	
Palić	102	0,018	**	0,021	**
Loznica	121	0,023	**	0,025	**
Smederevska Palanka	121	0,011	*	0,011	
Ćuprija	123	0,003		0,002	
Belgrade	132	0,020	**	0,020	**
Zaječar	144	0,015	**	0,014	*
Kruševac	166	0,012	*	0,011	
Valjevo	176	0,016	**	0,018	**
Kragujevac	185	0,013	*	0,013	*
The area 200-500 m.a.s.l.					
Niš	204	0,009		0,009	
Kraljevo	215	0,010	*	0,008	
Leskovac	230	0,000		0,001	
Požega	310	0,016	**	0,021	**
Kuršumlija	383	-0,003		-0,009	
Vranje	432	0,004		0,005	
Dimitrovgrad	450	0,000		0,001	
The area 500-1000 m.a.s.l.					
Novi Pazar	545	0,017	**	0,016	*
Trgovište	600	0,011	*	0,014	*
Rudnik	700	0,024	**	0,028	**
The area above 1000 m.a.s.l.					
Zlatibor	1.028	0,014	**	0,013	
Crni Vrh	1.037	-0,097	**	-0,11	**
Sjenica	1.038	0,014	**	0,013	*
Kopaonik	1.711	0,014	*	0,017	*

* statistically significant trend in the probability ***p = 95%***
** statistically significant trend in the probability ***p = 99%***

In order to study the variability of mean monthly temperature and analysis of dispersion from the average of the mean monthly temperature, the values ofstandard deviation of the mean monthly temperatures were also calculated (table 2).

Table 2. Standard deviation of the montly and annual air temperature in Serbia in the period 1949-2010

Meteorological station	Altitude (m)	I	II	III	IV	V	VI	VII	VIII	IX	X	XI	XII	Annual
Negotin	42	2,7	3,2	2,5	1,5	1,5	1,3	1,3	1,7	1,2	1,3	2,0	2,0	0,8
Zrenjanin	80	2,7	3,5	2,5	1,7	1,6	1,5	1,4	1,7	1,6	1,5	2,2	2,1	0,8
Veliko Gradište	80	2,3	2,9	2,2	1,7	1,5	1,4	1,3	1,6	1,6	1,5	2,1	2,0	0,7
Kikinda	81	2,7	3,4	2,3	1,7	1,6	1,4	1,4	1,6	1,5	1,5	2,2	2,1	0,8
Sremska Mitrovica	82	2,4	3,2	2,3	1,6	1,6	1,3	1,2	1,4	1,5	1,5	2,0	2,1	0,7
Vršac	84	2,7	3,3	2,4	1,8	1,6	1,4	1,3	1,7	1,6	1,7	2,3	2,2	0,7
Novi Sad	84	2,7	3,5	2,4	1,7	1,6	1,4	1,3	1,6	1,5	1,5	2,1	2,2	0,8
Sombor	87	2,6	3,4	2,3	1,6	1,6	1,5	1,4	1,5	1,4	1,5	2,1	2,1	0,8
Banatski Karlovac	89	2,4	3,1	2,3	1,6	1,6	1,3	1,2	1,6	1,5	1,5	2,1	2,1	0,7
Palić	102	2,6	3,2	2,2	1,6	1,6	1,4	1,4	1,6	1,4	1,5	2,0	2,1	0,8
Loznica	121	2,4	3,3	2,3	1,6	1,6	1,4	1,2	1,5	1,3	1,5	2,1	2,1	0,8
Smed. Palanka	121	2,5	3,2	2,3	1,7	1,6	1,4	1,4	1,7	1,5	1,6	2,2	2,2	0,7
Ćuprija	123	2,4	3,1	2,2	1,7	1,5	1,3	1,4	1,7	1,6	1,6	2,2	2,1	0,7
Belgrade	132	2,5	3,3	2,5	1,8	1,8	1,5	1,5	1,8	1,6	1,5	2,3	2,1	0,8
Zaječar	144	2,5	3,1	2,4	1,6	1,5	1,3	1,4	1,7	1,5	1,4	2,0	2,3	0,7
Kruševac	166	2,4	3,1	2,3	1,7	1,5	1,3	1,3	1,7	1,5	1,6	2,3	2,3	0,7
Valjevo	174	2,4	3,2	2,2	1,6	1,5	1,3	1,3	1,6	1,4	1,5	2,1	2,1	0,7
Kragujevac	185	2,4	3,2	2,3	1,7	1,6	1,4	1,4	1,7	1,5	1,6	2,2	2,2	0,7
The area 0-200 m.a.s.l.		**2,5**	**3,2**	**2,3**	**1,7**	**1,6**	**1,4**	**1,3**	**1,6**	**1,5**	**1,5**	**2,2**	**2,1**	**0,8**
Niš	204	2,3	3,0	2,3	1,8	1,6	1,4	1,5	1,8	1,6	1,6	2,3	2,2	0,7
Kraljevo	215	2,2	3,1	2,3	1,7	1,6	1,3	1,3	1,6	1,6	1,5	2,3	2,2	0,7
Leskovac	230	2,4	2,9	2,1	1,7	1,4	1,3	1,3	1,7	1,6	1,6	2,3	2,3	0,7
Požega	310	2,2	2,9	2,3	1,7	1,5	1,2	1,1	1,3	1,3	1,4	1,9	2,2	0,6
Kuršumlija	383	2,2	3,0	2,2	1,7	1,4	1,2	1,3	1,7	1,5	1,5	2,3	2,2	0,7
Vranje	433	2,1	2,7	2,2	1,7	1,5	1,3	1,3	1,8	1,6	1,5	2,2	2,1	0,6
Dimitrovgrad	450	2,2	2,7	2,1	1,6	1,4	1,2	1,3	1,6	1,5	1,5	2,2	2,0	0,6
The area 200-500 m.a.s.l.		**2,2**	**2,9**	**2,2**	**1,7**	**1,5**	**1,3**	**1,3**	**1,6**	**1,5**	**1,5**	**2,2**	**2,2**	**0,7**
Novi Pazar	545	2,3	2,6	2,1	1,8	1,6	2,6	2,8	1,7	1,5	1,6	2,0	2,1	0,9
Trgovište	600	2,0	2,7	2,1	1,6	3,2	1,1	1,2	1,6	1,5	1,4	2,2	2,1	0,6
Rudnik	700	2,4	3,5	2,7	2,0	2,8	1,8	1,4	2,1	2,3	2,0	2,7	2,3	0,9
The area 500-1000 m.a.s.l.		**2,3**	**2,9**	**2,3**	**1,8**	**2,5**	**1,8**	**1,8**	**1,8**	**1,8**	**1,7**	**2,3**	**2,2**	**0,8**
Zlatibor	1.028	2,3	3,0	2,5	2,0	1,8	1,4	1,4	1,8	1,7	1,7	2,4	2,1	0,7
Crni Vrh	1.037	2,6	3,7	3,2	3,0	2,6	2,7	2,4	2,5	2,7	2,4	3,1	2,8	2,1
Sjenica	1.038	2,6	3,1	2,5	1,6	1,4	1,2	1,2	1,5	1,4	1,6	2,3	2,5	0,7
Kopaonik	1.711	2,0	2,4	2,3	1,9	1,5	1,4	1,5	1,7	1,5	1,6	2,1	2,2	0,9
The area above 1000 m.a.s.l.		**2,4**	**3,0**	**2,6**	**2,1**	**1,9**	**1,7**	**1,6**	**1,9**	**1,8**	**1,8**	**2,5**	**2,4**	**1,1**

By analyzing data from Table 2 it can be concluded that the values of standard deviation range between 1.1 (Trgoviste - June; Pozega - July) to 3.7 (Crni Vrh - February) and that the temperatures in the warmer part of the year are more stable than in the colder part of the year. Understandably, the greater variability of temperature in the winter months in some years is the result of the penetration of cold and warm air masses. When the influences of western air masses are stronger, the winters are relatively warm, and when is dominant the influence of northern and northeastern polar masses, the winters are very cold. The greatest variability of mean monthly temperature is in February, and the lowest in June and July.

CONCLUSION

Based on the Spatial Development Strategy of Serbia 2009-2013-2020 [8], scenario A1B and A2, SRES/IPCC, during this century point out to the fact that in the next decades more adverse effects on the biological diversity in Serbia can be anticipated, which would be, among other, reflected in changes of vertical and horizontal zonal distribution of vegetation; increase of risk from diseases and pests; increased risk from disappearance of numerous species due to synergistic effects of climate change and site fragmentation; redistribution and migration or disappearance of some forest species due to high temperatures and decrease of ground waters; increase of the risk from wildfires, etc.

Climate changes and global warming leads to numerous ecological problems, creating negative impact on forest ecosystems: rapid deforestation and forest degradation, biodiversity loss, occupation of habitats by allochthonous species, change in pollination system, change in plant dispersion and regeneration, change in forest growth and ecosystem biomass, change in relation between species/habitat, change in ecosystem nitrogen cycle, increased mortality due to climatic stress and reduced forest ecosystem vitality and health due to cumulative impact of different stresses [9].

Given the possible irreversible processes in the climate system with the immeasurable consequences to the living world, it is necessary to take the preventive measures aimed at alleviation of the effects of the climate change and adaptation to the altered climate conditions [10].

There is a large number of potential methods, related to resolving issues that have arisen in forestry owing to global climate change and forest adaptation to new environmental conditions [11-15]. According to Lim and Spanger-Siegfried [11], the need for adaptation within forest management varies across ecosystems and tenure types and is related to the vulnerability of forests to climate change as well as to the vulnerability of forest-dependent people to changes in the provision of ecosystem goods and services. The United Nations Development Programme – Global Environment Facility has developed an Adaptation Policy Framework (APF) that provides an approach that permits users to clarify their own priority issues and to implement adaptation strategies, policies and measures.

The APF has four basic principles:

- Adaptation to short-term climate variability and extreme events is included as a basis for reducing vulnerability to longer-term climate change.
- Adaptation policy and measures are assessed in the context of development.
- Adaptation occurs at different levels in society, including the local level.
- Both the strategy and the process by which adaptation is implemented are equally important [11].

Roberts et al. [12] provide survey of current forest management trends which are promoting forest and forestry adaptation to new climate changes. The proposed management measures are mainly oriented to creation of stable, resistant to negative climate changes, forests. The management model which aims at preserving forests in their most natural form, avoiding mono-cultures and creating mixed forests, both in the structure of species and age, is supported. Furthermore, it aims at maintaining natural or nature appropriate regeneration, as methods of maintaining genetic diversity, and consequently, forest ecosystems sensitivity reduction.

The fact that the climate change occurs much more rapidly than it was anticipated has pointed out to the need to incorporate the problems regarding the adverse climate change on the natural resources in the priorities of the National Strategy of Scientific and Technological Development of Serbia. It is needed to conduct the continuous researches and monitor the influence of the climate change on the vertical and horizontal zoning of vegetation, alternations in the current forest ecosystems and effects of this change during the establishment of new forests.

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SPATIAL, ECOLOGICAL AND TECHNO-ECONOMICAL CRITERIA FOR LOCATION OF WIND POWER PLANTS IN SERBIA

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ABSTRACT

Wind power plants as facilities for electricity production, potentially could affect the natural and urban environments. In the process of selecting the optimal location and designing of WPP there are possibilities to avoid or minimize adverse impacts on the environment. Therefore, it is necessary to take into account the existing spatial and urban plans adopted at the national, regional and local levels in relation to natural and anthropogenic characteristics of the study area, especially if there are legally defined limits in terms of protection. In the process of selecting the optimal location of WPP the important role have stakeholders, having in mind the ratification of Aarhus convention of the UN on public participation in decision making. In the field of spatial planning important role in the decision-making in the field of environmental protection. With comprehensive planning and sustainable site selection as well as proper disposition of wind mills, potential adverse impacts on protected areas and other significant facilities and neighborly areas could be minimized.

Key words: wind power plants, eco-spatial criteria, planning, techno-economical criteria.

INTRODUCTION

Climate change, reduction of CO_2 emissions, reduction of fossil fuel reserves and high fuel prices have led to increased government support for by enacting legislation and regulations, promotion and commercialization of renewable energy sources. Wind energetics is globally developing and the installed capacities increase significantly each year, as the wind energy is competitive and economically viable energy source.

Due to the continuous need for additional energy sources in Serbia, wind energy is imposed as an ideal new energy sector. Serbia is among the areas with significant energy potential. Previous studies of the energy potentials are mainly based on data from meteorological stations. On the basis of tests and measurements carried out by the wind Hydrometeorological Service of Serbia, areas rich in wind, or suitable locations for development of WPP in Serbia are mountainous areas of Southern and Eastern Serbia, and especially the Pannonia plain. The Pannonia Plain, north of the Danube River, which covers approximately 2,000 km^2 is suitable for the construction of wind power plants, because of the constructed road infrastructure, utility networks, proximity to major centers of electricity consumption, etc..

Although there exist significant potentials for using of wind energy in Serbia and for building of wind power plants, there are also significant problems in implementing such projects as identified in the practice during the development of the spatial and urban planning documents as well as project designs.

Having in mind the fact that key participants in the processes of spatial and urban planning and project designing are not yet fully aware of the impact assessment as an instrument for the protection of the environment, often the role and importance of these processes is not fully understood.

POSSIBLE IMPACTS OF WIND POWER PLANTS ON THE ENVIRONMENT

Wind power plants as facilities for generation of electricity, potentially could affect the natural and urban environment. In the process of selecting the optimal site for siting the WPP and design development there are numerious possibilities to avoid or minimize adverse impacts on the environment. Therefore, it is necessary to take into account existing plans at national, regional and local levels in connection with the natural, anthropogenic characteristics and geological conditions of the area, especially if they are protected by law.

Two main groups of related criteria should be taken into account during construction processes of WPP. The first criteria group consists of energetically-economical and technically-technological criteria, so called Techno Economical criteria group, while the second group consists of spatial planning and environmental criteria i.e. of Eco-Spatial criteria group.

WPP are often constructed on unbuilt land (outside of settlments), mostly on agricultural land where it is necessary to find an optimal solution respecting the energy (the existing electricity network), spatial planning (defined by planning documents) and environmental requirements (protected areas and environmental protection).

Defining the optimal location is the most sensitive phase in WPP siting process and 12 key criteria, devided into two criteria groups: Eco-spatial criteria group and Techno economical criteria group were identified.

Spatial and ecological criteria group

Protected areas

In the Republic of Serbia there are clearly defined legal frameworks that emphasize the obligation of conservation and sustainable use integration of natural resources as an imperative. Natural heritage refers to protected areas and habitats of certain species of flora and fauna that may be located within the protected areas of national and international importance (National Parks, Special Nature Reserves, Ramsar sites, IBA, IPA, MAB, etc.). EU member states have been obliged to classify the IPA

(Special Protection Areas by the Birds Directive) and suggest areas of particular importance to the community by the Habitats Directive, until the date of their accession. As a result of this process emerged EU "Natura 2000" network of protected areas as habitats for the endangered and protected species. This document must be taken into account when assessing the impact of WPP on the environment.

Sensitivity of natural heritage refers to the impact of instalations and buildings on specific habitats, such as habitats of certain species, particularly birds and the integrity of sites designated for the purpose of their conservation. The building of WPP could affect the protected areas in the construction phase and the phase of exploitation period of wind mills. These effects may be of temporary or permanent nature. It is necessary to identify all aspects of each potential solution of proposed project that would, by themselves or in combination with other solutions could endanger the goals of preserving of values of the particular area.

Relevant national institutions in the field of energetics, environmental protection and spatial planning can give consent for WPP project design if it is determined that it will not nave adverse effects the integrity and preservation of protected areas and species that exist within them. If necessary, the competent authorities may require changes to designs and fulfillment of additional conditions for the project, which, after adjustment can be realized.

If it is certain that theWPP project could have a negative effect on the integrity of a protected area of national or international significance, the consent of the competent authority could be procured only when there is no alternative solution for the location areas where public interest is an imperative including reasons of social or economic nature. In that case, it is necessary to define strict protection measures that would contribute to the minimization of negative impacts.

Geological conditions

When selecting optimal locations for WPP is necessary to perform analysis and evaluation of geological and hydrogeological structure of candidate sites and perform zoning of the proposed sites in relation to the geological suitability for the construction of WPP. After the performed geotechnical stability analysis, it is necessary to identify specific geotechnical solutions and protection measures at sites if necessary.

Capturing of wind

The capture of wind is one of the most important criterion that has to be recognized in the process of WPP sites selection, during the early stages of planning, to ensure the development potential of adjacent sites for a similar facility. Generally, in order to ensure optimum performance and to take into account the effects of turbulence, the minimum distance between wind mills should be equal to triple rotor diameter (3d) in the direction perpendicular to the direction of wind and the sevenfold rotor diameter (7d) in the dominant wind direction (down the wind). Bearing in mind the requirements for optimal performance, acceptable wind turbine spacing adjacent to the borders of the estate is greater or equal to twice the length of blades, unless otherwise agreed with owners of adjacent properties or prescribed by the competent authorities. However, if the license for building WPP on the adjacent site is already issued, the recommended minimum distances of turbines perpendicular to wind and in the direction of wind should be respected.

Techno-economical criteria group

Cultural Heritage

In the process of locating WPP significant role plays the distance of the candidate site from the site of the existing cultural heritage, keeping in mind the direct impact of these facilities on the integrity, primarily of visual integrity. Also, during construction of WPP it is necessary in accordance with national legislation, to require conditions from competent authorities in the field of protection of cultural heritage. If during the WPP facilities construction process appears the archaeological heritage on the candidate site, it is necessary to suspend the work and to inform the competent institutions.

The noise

Significant impact on the environment have WPP in the context of noise production. Two major sources of noise are identified: aerodynamic noise caused by the propeller as it moves through the air and mechanical noise generated by operation of the mechanical elements of the case - the generator, gearbox and other parts of the drive. Aerodynamic noise is a function of several interdependent factors, including the design of blades, rotational speed, wind speed and turbulence of the incoming air, which can produce specific sounds. Mechanical noise from wind turbines is tonal in nature.
Advances in technology and design led to a reduction of noise emitted. Aerodynamic improvements are combined with each other, enabling the WPP to be quieter, including the transition from the lattice to tubular poles, working at varying velocities, the transition to three-way models, etc. Improvements in the design of multipliers and use vibration damping techniques over the past ten years as a result had a significant reduction in mechanical noise. The latest wind turbines with direct drive are without high speed mechanical components and therefore do not generate mechanical noise. Turbine noise increases with increasing wind speed, but slower than the increase of background noise generated by wind. The influence of noise due to wind turbines is likely to be larger at low wind speeds, when the difference between the noise WPP and the background noise is probably higher. Wind turbines do not work at a lower speed than the speed of wind, called a 'cut in' speed (minimum wind speed below which the WPP does not produce usable energy, that is the speed at which includes a system for energy production), which is typically about 5 m/s. Larger WPP and those with variable speed emit lower levels of noise on the 'cut in' speed than smaller WPP with fixed speed. Noise is spread in some directions more than in others, where the zone in the direction of dominant winds blow (down wind) usually have the highest predicted noise levels. At higher wind speeds, wind noise usually has the effect of masking noise of the WPP.

Good acoustic design and carefully considered locating the turbine will prevent a significant increase in ambient noise levels at sensitive locations in the immediate

environment. Generating sound from modern WPP can be regulated, thus alleviating the problems of noise, even though it loses some energy from the production. Must be achieved an appropriate balance between energy production and the impact of noise.
Noise impact should be evaluated in accordance with the nature and character of the noise sensitive locations and in accordance with the legal acts that regulate this area. Prescribed noise limits should apply to areas used for vacation and recreation or activities for which a quiet environment is highly desirable. The prescribed level of noise is necessary to apply to localities in the wider surroundings of WPP while taking into account the noise of the turbine and background noise.

Maximum permissible limits of environmental noise is 35 dB (A) at night and 40 dB (A) during the day outside public buildings and 30 dB (A) - at night and 35 dB (A) – during the day within the public facilities. In areas near the WPP where the existing noise level is less than allowed, the maximum increase of 5 dB (A) above the existing noise level is considered acceptable in providing protection of the surrounding population. Recommendations of the Irish guidelines for planning of WPP (Irish Planning Guidelines for Wind Farms) indicate that noise is unlikely to pose a significant problem when the distance between the nearest WPP and a building is greater than 500 m. The competent institutions may require evidence that the proposed type of turbine will use best engineering practices related to the creation and prevention of noise.

Distance from traffic infrastructure

The existence of access roads or navigable watercourses is a very important phase in setting up facilities or during construction period of WPP because it can significantly reduce total investment costs, specially handling costs. During the exploitation period of the wind power plan complex, although they are being built in accordance with engineering standards compliant with legislation, best practices suggest that it is advisable to achieve a safe distance from the road infrastructure, and this distance should be equal to the sum of column height and length of blades. Generally, during the construction period of WPP as well as during the exploitation period, these objects can draw attention of users of transport infrastructure to a certain extent in the positive but also in negative sense. Over time, the turbines become part of the landscape and not cause a significant drawing of attention of drivers.

Distance from the electric power network

When selecting the optimal location of the WPP it is necessary to ensure availability of adequate electric power infrastructure due to the need of takeover of power generated into the energy system. Therefore, proximity to existing transmission system is a significant technical and economic criterion in choosing the location of WPP. On the other hand, it is necessary to take into account the need to ensure adequate free space between the poles and cable lines laid down by the relevant electricity distribution company. For example, in Ireland there is legal obligation to inform the distributor of electric power on the proposed facilities that are within 23 meters of any line for transfer or distribution.

Distance from the electronic communication systems

Like any electrical equipment, WPP produces electromagnetic radiation, which can interfere broadcasting radio communications. Interference with communication systems could be overcome by installing deflectors or repeaters. Relevant institutions will require the investor of project to obtain requirements from national and local broadcasters. This also applies to mobile phones operators. WPP may not produce electromagnetic interference in the work of telecommunication networks and they need to comply with the measures for the suppression of electromagnetic interference in the operation of telecommunication networks and signal reception. It is therefore necessary to locate WPP at certain distances of at least 300-500 meters from the existing telecommunication facilities.

Air traffic safety

WPP site selection may have implications for the operation of systems for communication, navigation and surveillance used in air traffic control with respect to the safety of aircrafts and the flight corridors.

In order to achieve safety and efficiency of managing aircrafts near the airport, the International Civil Aviation Organization (ICAO) has defined the airspace above which is not allowed to set up new facilities. Not any part of the WPP should penetrate into this space.

Shadowing effect

WPP as well as other high structures, can cast long shadows when the sun is low in the sky. The effect known as shadow flickering (shadowing effect) is created when the propeller cast a shadow on the window located nearby and propeller rotation leads to alternating formation and disappearance of shadows. That effect is of short duration and occurs only in certain combined circumstances, such as, for example, when the sun shines and the angle is low (at dawn and before dusk), and the WPP is located exactly between the sun and the object that casts a shadow and at the same time there is enough wind to ensure the propeller running.

With careful choice of location, planning and design, and using the relevant software for the calculation of the shadow effect, this effect can be completely avoided. It is recommended that the duration of the effect of shadows on the nearby commercial and residential buildings within 500 meters does not exceed 30 hours per year of or 30 minutes per day. At distances from the WPP that are greater than ten diameters of rotor, the potential for the shadow effect is very low. In conditions where shadowing effect can be a problem, designers should ensure calculations that will quantify it and, where appropriate, take measures to prevent or mitigate the potential effect, such as the exclusion of certain WPP at a certain time.

CONCLUSION

Electrical energy generated from wind energy comes from renewable source, and the production of such electricity has no harmful emissions and is generally considered a technology that has positive effects on the environment. Through attentive and comprahensive planning, sustainable site selection and optimal disposition of wind mills potential adverse impacts on fragile ecosystems and habitats of animal species, especially birds, bats and others, could be reduced to a minimum.

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EXAMPLES OF ENERGY EFFICIENCY: CONSTRUCTION OF LEPENSKI VIR, GAUDI'S PROJECTS AND NYBERG VILLA

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ABSTRACT

Irrational consumption of resources for construction, inadequate approach to design and avoiding natural laws and cycles, as well as inhuman and short-termed ideas during the construction and design, create the habitats that reflect a negative energy, whose impact we are not aware of. The times when human survival, and not profit, has brought up the ideas about design of facilities, carry the sign of energy efficient construction.

Key words: Lepenski Vir, Gaudi, Nyberg.

INTRODUCTION

During its life, men created glorious buildings that overshadowed civilizations with their appearance and technical solutions. These monumental buildings were often in the complete disbalance with nature. Sudden industrialization in the XX century (which continued in the XXI century) caused an increased emission of CO_2, and all this led to the current situation, which even stopped giving us a warning, but had a direct impact on our lives. The only culprit and the only savior is the man i.e. all of us.

Current (lack of) culture of construction planning has brought us to destruction of living conditions. Rapid technological development isolated us from nature and directed architectural design to the wrong direction. Bioclimatic changes, natural disasters, high mortality rate, polluted food and water are just some results of human negligence that put our lives in jeopardy today.Architecture has carved the world in such a way that unsustainable and energy inefficient buildings are a part of our lives and create the "sick city" system, where most of human population lives. Most of the population do not live in pleasant environment, and all this is reflected on all segments of life of an individual. Space in which we live in is staged, insufficiently illuminated and aggressive, and in time, we become like that.

Pseudo-urbanization turned our current habitats i.e. cities into generators of negative impulses that had a significant impact on psychological and physical health of people. Irrational consumption of resources for construction, inadequate approach to design and avoiding natural laws and cycles, as well as inhuman and short-termed ideas during the construction and design, have created the habitats that reflect a negative energy, whose impact we are not aware of. A person spends most of the time in enclosed areas, and it is necessary to have an emission of positive sources of energy in order to make closed areas conceived like that healthy.In a "race" for profits, construction parameters necessary for creation of healthy environment are mostly forgotten.

Return to the nature in form of analysis of its fenomena, messages and principles is just a beginning of creation of the new future. Such future must be sustainable and this would be the only way to make a positive impact on the planet and its population.

Architecture is an utilitarian science, with the concepts of sustainable development and an architect's task is to create a quality space for the user i.e. person.

Besides the functionality within the building, the designed form of the building in space has an impact on the way in which the building and the space are experienced. The form of the building plays a great role in formation of harmonic, healthy and aesthetically pleasant feeling. The right solution is in the forms that we encounter in nature and their usage during the design process, all in function of higher quality of life and survival on planet Earth.

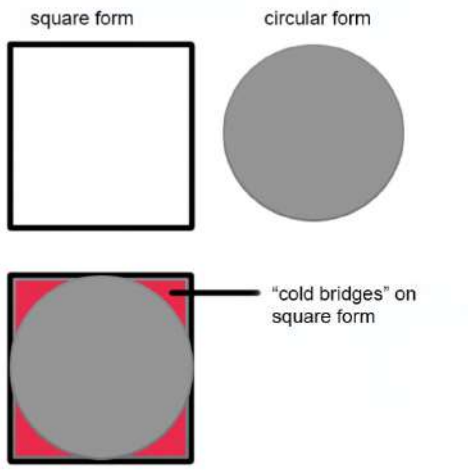

Figure1. Square and circular forms

The most prominent are examples of a natural circular form and a squared anthropogenic form. The circular form is the more acceptable form in terms of energy efficiency. Creation of "temperature or cold bridge" is an occurrence that appears with the squared form and creates a significant decrease in temperature and the loss of energy. "Cold bridges" have a negative impact on the health of people that use the area because they cause the appearance of condensation that has a negative consequences on certain chronical diseases. Figure 1 shows how the use of circular form in architecture decreases the appearance of temperature bridges i.e. the energy is preserved.

EXAMPLES OF ENERGY EFFICIENT CONSTRUCTION

The times when human survival, and not profit, has brought up the ideas about design of facilities, carry the sign of energy efficient construction. These facilities are in not monumental in most cases, but they enabled some civilizations a long-term survival. Selection of construction material was most often *in situ* or in the vicinity, with or without any processing (physical or mechanical) and this is, of course, in accordance with the energy efficient construction. The place where the buildings were raised was carefully selected based on the wise perception of the terrain morfology and climate change frequency.

The oldest architecture in Europe done by the principles of sustainable architecture is Lepenski Vir architecture. It was created in the early Mesolithic period (9500- 7200. godine p.n.e),and in the early and middle Neolithic (6250-5500) in the areas of lowest Danube terrace. It represents one of the most curious and most brillian cultures of prehistoric period with highly developed social and economic relations.

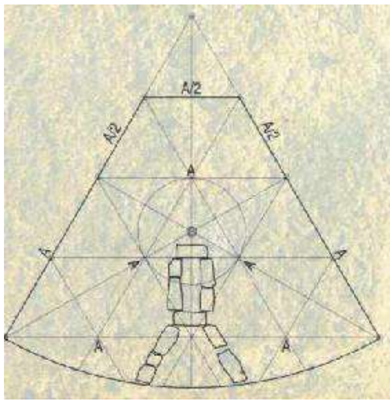

Figure 2. Schematic of mathematical division of space by triangular model

In all stages of construction, Lepenski Vir represents a high quality and energy efficient solution because the foundations of the habitat derived from circular form (truncated circle area) with narrow "walls" i.e. a roof that leaned directly to the basis.

Figure 3. Reconstructed house

In order to increase the utilization of the area, equilateral triangle is cut for one-fourth in the rear and expanded at the front with the arc. This form also enabled optimal illumination during the daily and annual insolation. Wide faces of the houses were turned towards Danube and the narrow rear side are almost dug into the hilly terrain. The buildings were set in the form of fan and they were maximally open towards sun and light and thus represent an example of efficient use of thermal energy.An example of Lepenski Vir could be a foundation for design in modern architecture.

Antonio Gaudiis a part of Art Nouveau, but he also managed to build his own style that "brought back" buildings to the nature and gave them "living" dimension. Such style of modern architecture, "organic architecture" sees the building as the living organism.Antonio Gaudi and his architecture are examples of designing forms in accordance with the laws of the nature.

"There are no straight lines or sharp corners in nature. Therefore, buildings must have no straight lines or sharp corners."

Figure 4. Gaudi, Casa Mila

NYBERG Villa is an example of how form can have a direct impact on energy efficiency of the building. It represents the best designed house in Sweden in terms of energy efficiency. The rounded form of the house eliminates cold bridges and decreases the total surface area of façade walls. The form becomes one with the nature and impacts the more functional use of space and equal approach of light in different daily and annual periods.

Figure 5.Vila Nyberg

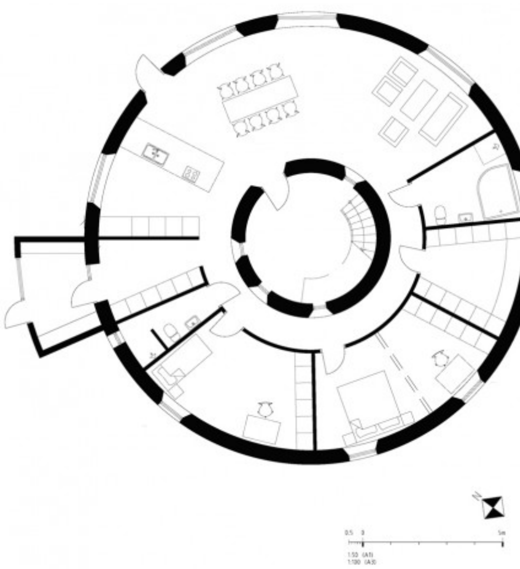

Figure 6. Nyberg Villa foundation

CONCLUSIONS

The future of construction is to achieve a harmonic space, and the only way is to return to the nature, or in accordance with the current technological potentials, the solution could be in the rational synthesis between nature and technology.

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THE ENVIRONMENTAL PERFORMANCE OF BIOENERGY – CASE OF *Miscanthus giganteus*

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ABSTRACT

A thesis that the chain of production and use of the second generation bioenergy crops can be established in the Republic of Serbia is presented in this paper. For functioning of such a chain it is necessary to achieve the highest possible yield per unit of land areausing the least extent of establishing and maintaining the plantation which emphasizes the 'Resource efficiency'. High productivity of miscanthus with minimal irrigation and fertilization and opportunities for development on marginal lands were confirmed by field experiments on marshy land (Zasavica) and the tailing damp of the MB KolubaraFurther studies designed to examine the impact on the environment, soil, water and climate are in progress as well as the assistance to the decision makers in determining of suitable locations for the production of agroenergetic crops in Serbia.

Key words: bioenergy crops, perennial grasses, biomass, reclamation.

INTRODUCTION

Although bioenergy plays a central role in the national action plans for the development of energy in the EU, there are some pending issues concerning the real impact on the enviroment and the welfare of the population[1]. Renewable energy resources also consume natural resources in different proportions, so it is necessary to calculate precisely the significance of their contribution to the environment.Plantations of energy crops that occupy agricultural land, may contribute to the reduction of biodiversity and affect the structure and function of ecosystems in various ways.On the other hand biomass from forest, agricultural, municipal or industrial waste is more efficient in terms of resource requirements from the "energy plantations" but its quantity is limited.Due to the complexity of mutual influences three bioenergy resources development scenarios have been made: (1) bioenergy: A) ‘Market first’(B); ‘Climate focus’i C) ‘Resource efficiency’. Comparison of bioenergy potentials according these three scenarios with earlier EEA reports indicates the importance of inclusion of land use change in the analysis.Deduction of these parameter decreases the amount of energy that can be produced but more than that it influences on changes in the composition of different types of biofuels. This means that most (or almost all) of the first-generation biofuels are excluded becausethe inclusion of changes in land use in the calculation makes their balance of the production of greenhouse gases negative. The production ofbiofuels also significantly varies according to the efficiency of water use, the influence on erosion and biodiversity, and in accordance with the scenariosUnlike the previous reports from 2006, when annual production of industrial crops for human/animal nutrition was dominant, a sharp turn towards perennial grasses production is anticipated for a period up to 2020th.

Serbian Ministry of Energy, Development and Environmental Protection passed a simplified National Renewable Energy Action Plan, drafted in accordance with a form prescribed by the Directive 2008/29/ES (Decision 2009/548/EC) in December 2012.

In the section 4.6. Concrete measures to promote the use of biomass energy it is stated that biomass has an important role of primary energy in all three sectors: heating and cooling, electricity and transport.National biomass strategy is crucial for planning of the role and interaction among the final of energy use patterns and interaction with other non-energy sectors (food and food processing industry, pulp and paper industry, construction, furniture industry, etc.) It is noted that currently, in 2009 agricultural land used for growing of certain energy crops does not exist. Measures for increasing the biomass availability are proposed, taking into account other biomass users (agriculture and forestry), which are indirect through the measures envisaged for agriculture that pertain arable land. [2].The total area of unused arable land is 250,000 ha, representing 4.9% of total arable land. It is estimated that the area of degraded land is around 35,000 ha, including surface mining pits and tailings [3].

Started from the mentioned strategic documents we are elaborating a thesis that it is possible to establish the chain of production and use of the second generation bioenergy crops in the Republic of Serbia.For the functioning of such a chain in a sustainable manner it is necessary to achieve the highest possible energy yield per unit area of land with minimal use of measures that include establishing and maintaining the plantation with a focus on marginal land.

MATERIAL AND METHODS

By using the method of field experiment, we monitored development of the biomass of Miscanthus giganteus on arable, marginal (wetland) and degraded (dumps of lignite mine tailings) lands. Experimental results have been incorporated in the context from the above-mentioned documents.

RESULTS AND DISCUSSION

The possible impact of bioenergy cropping on different environmental media is influenced by a variety of factors:

- **Climate:** Both land-use conversions and intensification can lead to additional GHG emissions. Land contains carbon which is stored in vegetation and soil. The amount of carbon depends on the type of soils and vegetation. In general, agricultural land contains less carbon than land with natural vegetation cover, even if compared to natural grassland areas. According to the Global Carbon Project (2012) about 10 % of global greenhouse gas emissions in the period 2002–2011 were related to land use change - principally associated with deforestation and expanding agricultural land use. Intensification is often cited as a means of avoiding the expansion of agricultural land use but it can work against efforts to mitigate climate change. Intensifying output by applying more fertilizers increases emissions of nitrous oxide, which is a GHG. Generally, such increases are less (in CO_2-equivalent terms) than agricultural land expansion. Agricultural intensification can also lead to additional environmental impacts. These are often linked toreduced crop variety (as only very productive crops are grown) and the increased use of external inputs(fertilizer, pesticides, water etc.) [1].

Our experimental fields occupy a very small areas so it is not possible to monitor these effects, but certainly the production of biomass from perennial grasses (Miscanthus) helps to reduce pressure on forests in are traditionally the most frequent type of biofuel.

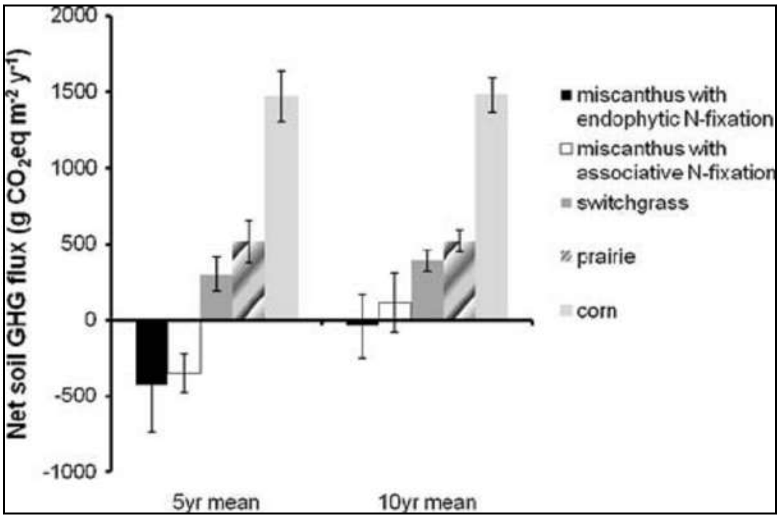

Figure 1. Projected net annual soil GHG flux in CO2 equivalents (g CO2eq m-2 y-1) for biofuel crops grown for 5- and 10-year periods: GHG flux included net CO2, direct, and indirect N2O, and CH4 fluxes from the crop ecosystem. GHG fluxes represent means (±SE) [4].

Estimates for miscanthus GHG fluxes were calculated in two ways: with endophytic N-fixation and with associative N-fixation [4]. Positive fluxes indicate a net source of GHG that would accumulate in the atmosphere and negative fluxes indicate a net sink of GHG that would be sequestered in the agro-ecosystem. Not included in the GHG fluxes were C in aboveground plant biomass that would be harvested or GHG emissions incurred throughout the production chain (farm machinery, conversion processesand so on).

- **Water**: Agriculture is the major source of nitrogen pollution of European water bodies, including lakes, rivers, ground water and the European seas The agricultural sector alsoaccounts for a large proportion of water use across Europe, particularly in southern countrieswhere the importance of irrigation means that agriculture can account for as much as 80 % of total water use in some regions [1].

Our results indicate that in agroecological conditions of Serbia irrigation of miscanthus is necessary and sufficient for the first year of development [5]

- **Soil**: Farming exposes soils to water and wind erosion, and can lead to soil compaction and salinisation if inappropriate farming practices are used contributing soil loss, declines in soil organic carbon content and productivity as well as other environmental impacts.

It worth noting that bioenergy-induced land use change can have positive effects, for example ifan area converted to energy crops was previously degraded land. If these lands are managedappropriately then it could lead to improved soil quality and vegetation structure, and thereforeenhanced habitat quality. Increased cropping of perennial biomass, such asmiscanthus, fast-growing poplar or reed canary grass, offers benefits as input requirements are generallylower than those of annual crops and perennial crops can be grown on low quality soils that are notsuited for rotational arable crops. In addition, many perennials are also shown to improve soil quality,increase the amount of carbon sequestered in the soil, and reduce soil erosion. Because of these factorsperennial crops are projected to play a strong role in the environmentally oriented storylines in thisanalysis.

In terms of soil erosion, the highest risks occur during winter, before growth starts, when there is a lack of soil cover and when the rainfall is usually more severe, but due to the perennial character of this crop this risk is minimum compared with other crops. On the other hand, the danger of reducing the biodiversity might exist due to the fact that *Miscanthus* is cultivated in monoculture [6].

- **Biodiversity**: Numerous studies have recognized that the changes to water tables, soil structure and the destruction of habitats that occur where land is converted to agricultural uses can have negative impacts on biodiversity.New energy crops are often selected because of their fast and productive growth but can have their origin in other continents. This means that some (e.g. miscanthus) are classified as invasive alien species. If such species escape from their confined cultivated environment they can dominate or push out native species and thus alter European ecosystems. For this reason, the likelihood of a species becoming invasive in Europe needs to be assessed before itis cultivated in new areas. That issue was not addressed specifically in this study but academic and fieldresearch is available on evaluating and mitigating the invasion risk posed by some biofuel crops [1]. This information can be utilized by national bodies responsible for the development of energy cropping.

At the experimental field Zasavica located right next to the protected natural resource of the same name, the five-year experiments with miscantus experimental fields have shown that the bioproduction of energy crops with the use of irrigation and basic fertilization in the first year (mis I) is higher than bioproduction of native commonreed and becomes very close without application of agro-technical measures (mis II) (Fig.2), and it is approaching the production of native willow [7]. The location is partially drained wetland where maize was previously cultivated and it is classified as land of category VII.During the 5 years of cultivation it is not noticed that miscanthus left the location where was planted in.

Miscanthus is also a crop with a low susceptibility to diseases, so there is a minimum need to use pesticides, and thus there is little risk of pesticide contamination of the soil and groundwater.

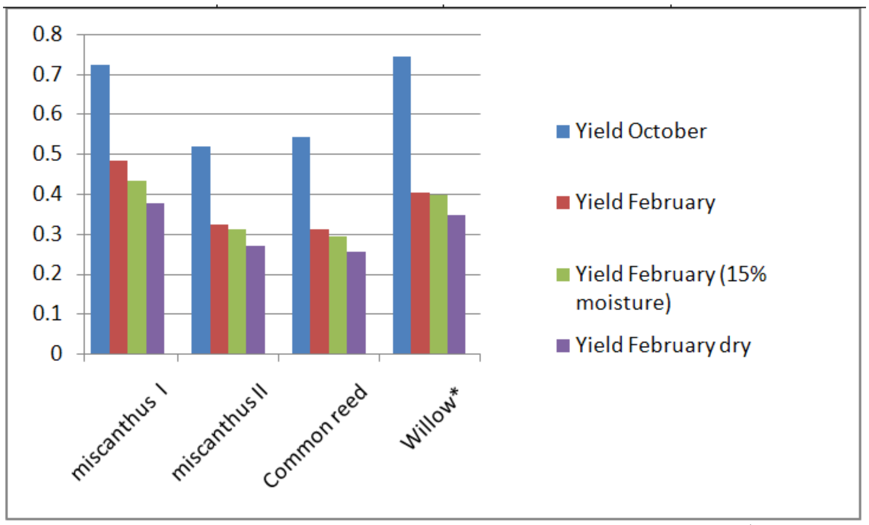

Figure 2. Comparative review of 1st vegetation yield (T ha $^{-1}$) at field experiment on Zasavica.

The second experimental field was established on the dumps of lignite mine tailings of the MB Kolubara. Variants of the experiment were two doses of NPK fertilizer, two terms of fertilization and two planting densities [8]. The yields (Fig. 3) were not in the function of these variants but in the function of competition with the native vegetation. The experimental parcel was formed just before establishment of the experiment so that a spontaneous development of pioneering vegetation occurred there.In this case, the plantings of miscantus not only that did not havenegative effect on the spontaneous vegetation but they are in a strong competition so that he even their future development is challenged.

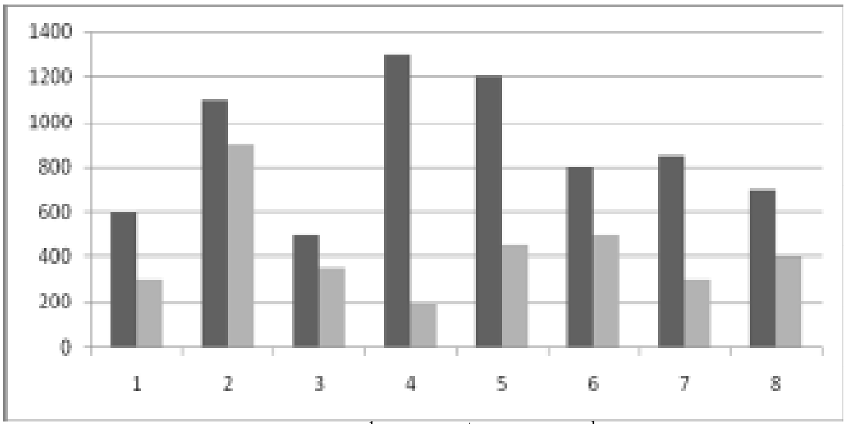

Figure 3. Miscantus yield (T ha $^{-1}$) after 1st (□) and 2nd (■) vegetative period. 1-8 variants of field experiment

CONCLUSIONS

Based on these findings the central message points out that bioenergy crops (miscantus) can play an important role in meeting the energy needs as long as they are contributing to the preservation of natural capital, but only if it is based on a resource-efficient use of biomass through the entire production chain from biomass to energy.

Further analytical work is necessary in order to help to decision makers from the aspect which includes modeling and monitoring of energy, economic and environment preservation efficiency.Miscantusa production in Serbia is possible on degraded lands too, with wisely chosen set of agro-technical measures.

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FINANCIAL REPORTING AND APPLICATION OF INTERNATIONAL ACCOUNTING STANDARDS IN AGRICULTURAL ENTERPRISES

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ABSTRACT

Social processes, particularly in the last decade, has been influenced by all legal entities, the enterprises and individuals, requiring them to quickly react and adapt to the new conditions of life and work. Financial reporting enterprise management is carried out continuously, and it is also done for the purposes of reporting the state authorities.The process of evaluation in agricultural companies takes place in continuity with the application of international accounting standards and international financial reporting standards. Proper introduction of the valuation of certain parts of the enterprise in the books is the basis for fair financial reporting.

Key words: financial reporting, company, estimate, value.

INTRODUCTION

Agricultural businesses in recent years consistently recorded negative operating results. Negative results of operations are the result of very adverse economic conditions over a long period of time. Results of ownership transformation are far from expected and potentially possible (Vukoje et al., 2013, p. 64). Modern economy is a complex mechanism where there are numerous and diverse activities, as well as the multiple relationships that constitute "economic phenomenon". Mass and diversity of these phenomena and the need for organizing economic life and solving business problems require the abstract formula of scientific treatment of economic phenomena and they are replaced with concrete, empirical, synthetic measures of content, scope, the tendency of these phenomena, and economic indicators (Pejanović, R., 2013, page 25).

Financial reporting that the company creates and discloses, must be in accordance with the adopted accounting policy of the same, with full respect of international accounting standards and international financial reporting standards.

For proper evaluation of the survey was to irrefutably proven market value of property. On the basis of the value determined by management with the ability to issue preferred business decisions. International Accounting Standards provide a recommendation to the valuation of assets of enterprises every three years or a shorter period, in order to more realistically reflect the value of the Company's books.

Rationally defined financial targets enterprise leading to the strengthening of the financial strength of the company, and the overall objective of each company, and that is to preserve and increase its assets (Ivaniš, 2012, p. 471). Therefore, valuation of property companies is an important activity and responsibility in every modern organized economic system.

In addition to the above, a large agricultural enterprise should take into account the value of important currencies and their movement in its financial statements to reporting it as realistic as possible in their reports (Danieis, D. J, et al. 2011, p. 416).

Until a few decades decision standards prescribe the form and content of the external financial statements , without addressing key issues such as the objectives of the report, the primary users, information needs, as well as to which type of report will best meet the needs identified. It should be noted that the assumption of the financial statements, the going concern basis, that is the goal that the company will continue operating for the foreseeable future (Greuning, H., 2006, p.4). Finally, it should be noted that the work of standardization associated with the audit, which is process-based and is recognized as a control mechanism that enables users of financial statements to the audit report can call and rely (Soltani, 2010, p. 10).

MATERIALS AND METHODS

The research presented in this paper was reported of assets and equipment for a company that operates as a public utility company with a predominant activity in the field of agriculture. By its size it has been the second largest in the Republic of Serbia in the aforementioned areas and exists on the Serbian market for over fifty years. The survey was conducted in 2012. The paper specifically analyzes the evaluation of fixed assets in the accounting records of the company, and the total valuation of fixed assets and the assessment of possible differences in parts of the property that is not introduced in the books of the company.

The main objective of the research is that, to show the value of fixed assets that are in the company as a presentation given in the table, which may serve primarily to management in order to make valid decisions about the management of the company. In addition to the prominent resulting views can be useful to other stakeholders, in order to highlight the importance of timely and high quality financial reporting.

The research was based on actual data of the said company, whose name is not given in the paper because it was not obtained approval to disclose the full name of the company. Data was collected by type of account in company, and is grouped and presented in order to be used as a basis for further analysis and as a basis for the adoption of specific management decisions. In addition to the above, tabulation may be the basis for decisions on re-assessing the value of a particular group within the fixed assets and with respect to the valuation of fixed assets used in accordance with IAS 16.

By analysis andcomparison ofthe presentedgroupof fixed assets, management has the ability to make the decision to carry out and complete valuation of fixed assets in use, in order to subsequently be able to incorporate the results into its books. This approach is in line with EU recommendations of evaluation and recommended that the evaluation is done every three years for part or all of the assets of a company.

If you increase the value of fixed assets after valuation under IAS 16, and the resulting values are brought into the books of the company has the ability to more easily accomplish, or obtain loans from banking institutions, or may have easier access to financial markets open. There is also an aggravating circumstance, and it is manifested in the increase of the property tax business. This last event is often decisive for companies, regardless of the benefits that may be, are not included in the methods of assessing the value of assets, and the main reason is the illiquidity of such treatment, which is characterized particularly by agricultural enterprises in our country.

RESULTS AND CONCEPTUAL FRAMEWORK FOR FINANCIAL REPORTING

At the beginning of the eighties of the last century began with the introduction of a conceptual framework for financial reporting, and the role of decision standards becomes active, they create external financial reports with the vital needs and requirements of users of these reports. To be actively applicable, this framework must include the judgmental and with a view to resolving accounting issues.

During the presentation of the financial statements or in the process of determining the amount of net profit, reveals problems related to the accounting period, and the difficulties of assigning revenues and expenses in the short term. Other big problem is the problem of continuing operations or continuity problem, or how long a company will operate in the future (at least for a period of one year from the balance sheet).

In addition to the two notes presented to the third problem, which is the problem of income and expenses, and income tax can be calculated as the difference between the payment on behalf of revenues and payments of expenses. Accordingly, the income must be allocated to that accounting period in which the goods were sold or the services rendered, and expenses must be allocated to that accounting period in which they arise, in order to generate profits.

The creation of the Great Depression 2008th year were the most affected financial markets and capital, that she has brought to the surface a number of accounting issues related to financial instruments, determining the fair value disclosure and recognition of losses due to the reduced value of off-balance sheet exposures, assessing their credit risks and other issues.

The International Accounting Standards Board (IASB) saw the need for reprocessing requirements relating to financial reporting. The aim of these activities was for users of financial statements to become easier to understand. Thus, for example, IFRS 9 issued in November 2009. Replaced classification criteria and measurement of financial assets in IAS 39 means the first phase of a complete replacement of IAS 39 with a view to reporting principles for financial assets easier and more transparent. IAS 39 establishes principles for recognizing and measuring the information about financial instruments in the financial statements of the company, and therefore is in agricultural enterprises. A financial instrument is in contract which creates a financial asset of the company (cash, or contractual right) Majstorović (et al., 2011, p. 71-73). The assessment depends largely on the skill, knowledge and skills which govern appraisers (Ilić D., et al., 2013, p. 5-8). Agricultural businesses in assessing the value of the property using the MRS should provide and display explanations, because display using MRS and "fair reporting" requires explanation (Fleming, C., 2011, p. 68).

In some situations the company makes strategic decisions, perform the valuation of real estate and other fixed assets. In the event where the owner and management are in a dilemma, whether to keep the existing company with an unchanged activity, or to sell the company, and secondly, you make the decision to assess the value of the company and this estimate is the basis for making strategic decisions about the future of the company (and RodićFilipović, 2010, p. 3).

The ultimate goal of the action taken is not only the use of international accounting standards, international financial reporting standards, international standards of assessment, but the objective presentation of reliable data in the financial statements. An objective presentation of an imperative presents strategic decision-making (Radulović B., 2012, p. 35).

Finally it should be noted that the audit business is a special type of audit that deals with the systematic examination of the business enterprise or part thereof in order to identify and present as many opportunities to increase efficiency, effectiveness and economy enterprises (Porter B., et al., 2002, p. 11). Should endeavor to always use objective standards because they provide an authoritative basis of audit findings (White, G., et al. 2003., P. 11-12).

The study was done in a public utility company, which has existed since 24.11.1962. Decision on the organization was published in the Official Gazette. List of Novi Sad number 29/2005 and 53/2008this where company was organized as a public utility company. It has an extremely heterogeneous facilities and infrastructure, and construction projects. The age structure is different. Regularly maintained by a professional service company, in exceptional cases, maintenance is entrusted to external contractors and in cases of specialist and non-standard repairs.

The data collected by accounts of fixed assets in which the water in the same company are grouped in Table 1:

Table1. Summary account of fixed assets and accounts of the differences

Total fixed assets(CSD)	**The total fixed assets of the business records (RSD)**	**The difference in value of fixed assets of the business records (RSD)**
954.124.657,97	431.163.689,00	522.996.968,97

Source: Authors, 2014.

Grouping in terms of substance is made in three categories:a total fixed assets of agricultural enterprises in the amount of 954,124,657.97dinars, then as total assets carried in the books of the company in the amount of 431,163,689.00dinar sand third category that represents the value of fixed assets thatare not in the business records of the amount of 522,996,968.97dinars.

The largest part of the differences in the amount of 522,494,936.79 dinars comes from agricultural land that was not introduced in the books of the company to the general ledger, and compared to total fixed assets that represent 55 % of the value of all fixed assets of agricultural enterprises. In addition to an unusually large percentage differences may be noted that from the perspective of the real display in the books of the company there is a high level of reserves in the financial statements of the company. The mentioned companies are no differences in the conduct of the value of the accounts of buildings, computers and IT equipment, buildings operational, plant and equipment to be used, poultry, and there is a deviation on account of artwork that has company in the amount of 466,032.12 dinars which is a little deviation less than 1 % of all of the differences in the accounts.

Evaluation of legal persons, and especially active companies, it is essential for them for two main reasons. The first reason relates to the real measurement of the actual situation, and the values that the company has on the date the estimate is done, you would then bein the financial statements contain possible adjustments to the accounts. in the form of posting surpluses or deficits. In essence this means displaying the actual value of the company, which the company gives a realistic picture of themselves (banks, foreign investors, and other interested parties). The second reason relates to the fair presentation of values and possible changes in the tax return of companies, after sorting of books, with the tax authorities of the state. On the basis of a realistic assessment and introduction of new assessed value of property, one can determine the increase or decrease in the tax basis of legal entities.

The results of research can be used to enhance the management of activities in addressing the introduction of agricultural land in the books. After that management can make a decision to do the revaluation of agricultural land per IAS 16, and subsequently, to arranging business books of account. This would allow for a fair presentation of the Company's books, and could be used and the benefits such as for example the possibility of obtaining loans from commercial banks and others. After making business decisions about the new assessment value of fixed assets in use in IAS 16 is to be expected that the value of property has increased by over 30 % and it would be closer to the real market value as of the valuation date. As a result of this new evaluation of agricultural enterprises would increase spending and businesses in the form of increased costs, such as cost of property taxes. Apart from legal restrictions, cost, and their increase after each new valuation of the assets at fair value, are an important reason why companies are not included in the evaluation process of new fixed assets in use.

CONCLUSION

Adjustment in agricultural enterprises should follow the legislative changes and regulations in the field of the chart of accounts as the basis of the introduction of books, thus allowing fair coverage of all interested stakeholders. The whole business requires the maintenance of effective financial statements, as well as the implementation of new guidelines of international accounting standards and international financial reporting standards. Process of Serbia's EU, increasingly, in practical terms, is taking root principle of unification of financial reporting.

The main goal of every company is to provide a permanent and desired development. The above-mentioned objectives the company aims to realize the current conditions and the present time, and bearing in mind the immediate and distant future. In this way, in addition to survival, the company has a need to invest in their development.

Proper and timely financial reporting may allow management to effectively achieve the set financial objectives of agricultural enterprises. This affects the strengthening of the financial strength of the company, and contributes to the achievement of the general objectives of the company. This conservation is reflected in preserving and enhancing the assets of the company. Management companies should take into account the assets used by, and therefore need to take into account the valuation of assets under management, should take into account the recommendations of international accounting standards and international financial reporting standards, and in particular to respect the IAS 16 view properties by fair value is the basis for the optimum operation and evaluation of agribusiness. Each new property valuation should be done within three years.

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ASSESSMENT OF THE VALUE OF BUILDINGS AGRICULTURAL COMPANY

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ABSTRACT

Adequate estimate can be committed only by a group of experts in a particular field, at the request of the customer which is usually the management. It is important that the group are represented by experts who know the theory of the balance sheet, accounting rules, financial analysis, market experts, experts in technology assessment companies. The goal of proper valuation is arriving at incontestably proven market value of the assets of the company. After completion of assessment, results management can be introduced in the books. This makes real image of value properly at the date of assessment, which is important for owners of companies, the management, and the state, which can collect revenue for example property taxes in real terms.

Key words: evaluation, value, buildings.

INTRODUCTION

In accounting continuously collect and arrange data in relation to business events company. All changes are recorded in chronological order, based on original documents. Accordingly, the accounting documents and data have the character evidence rule (Rodic, Vukelic and Andric, 2011, p.3). Prescribing mandatory application of fair value for the evaluation of companies, means abandoning previously used historical values . Time to change the contents of the financial statements of the financial position at the reporting date (Škarić Jovanovic, K., 2012, p.42).

Agriculture as a manufacturing industry has many similar features as well as other manufacturing sectors. Many factors make it even more complex. The specifics of this branch should be noted, in order to establish a system of accounting of the business activities of the company. This allows the company to draw up a true and fair financial statements (Petkovic, Đ., 2011, p. 314). Market value is defined as the amount for which an asset could be exchanged on the open market and specific, under normal circumstances, and through the voluntary transaction between the parties, who are well informed on the relevant facts. Appraisal is an expert opinion on the value of, and the procedure for determining the value on the basis of a systematic approach (Djuric, Z., 2009, p. 5).

The use of different methodologies for valuation of capital of the company, but it should be noted that nowhere is defined as the procedure performed , and what all certified appraiser to use in their work to come up with the results of the assessment, which will be expressed in the opinion, delivered by the Purchaser in accordance with contractual obligations. Assessors independently define the procedure to be applied (Leko et al., 1997, p. 15-18).

METHODOLOGY AND RESULTS

The aim of the study is to present initial results on the accounts of plant and equipment company with a predominantly agricultural activity. Showing evaluation is made on 30.06.2012., the comparison with the newly obtained data and concluding observations, with possible applications in the future at the level of assessed companies, as well as in similar enterprises. The results after one year, or on the date 30.06.2013. were used and introduced into the books of the said company. Data were statistically analyzed and presented in this paper.

The research was carried at fair value in accordance with IAS -16s. The basis of assessment is the expression of the real value of assets and capital in accounting and business records, with the goal of fair reporting in the financial statements of the company, with practical application. Valuation date is 30.06.2012. year, and a year later, on 30.06.2013. The assessment has been used for the introduction of the Company's books.

The company has a very heterogeneous facilities and infrastructure, and construction projects. After examining the technical and technological documentation, as well as insight into the real situation, it can be concluded that the greenhouse age 6 years is in a satisfactory and appropriate condition, regularly maintained in all weather conditions, but due to the effects of UV radiation, can be expected to be in a relatively short period of time will have to be replaced with protective film, which is in accordance with the technical requirements for such facilities. The company was introduced by the gas company for gas distribution equipment is in excellent condition, regularly maintained in accordance with the Energy Law in Article 130, from which comes the obligation of maintenance of such equipment.

The facilities are in working order and appraisers stand obsolete object, but you can still practice in them. The age structure is different, but the company has a lot of old equipment, noting that all equipment is operating and that the same is regularly maintained by a professional services company, that all equipment is in working order mining. In the last seven years, one piece of equipment is re-purchased. It is a small-scale agricultural mechanization, machinery, transport vehicles, special purpose vehicles, cranes, multi-function machines. The Company is in accordance with the financial capabilities to continuously procure new equipment, which can be seen from the large number of inventory numbers that accompany this equipment. The company has a special division of IT technology, which performs regular maintenance of such specialized equipment; the level of the whole company.

The company owns a carpenter department, building sector, which performs maintenance of all office equipment, buildings, and other objects that they canconfide in, making new furniture, and infrastructure. The equipment is old, but is also regularly maintained by the company, and only in exceptional cases, maintenance is entrusted to foreign houses. It can be concluded, that the equipment is appropriate and in working order.

MACROECONOMIC ANALYSIS AND ASSET STRUCTURE

Since the establishment until today, the predominant part of their activities, it is realized by performing tasks for the founders and the City of Novi Sad. Physically located in several locations in the city. Administration and management in one location, production and sales on the other, near the production is and machinery, and in the sunny quay to perform the functions of hospitality and tourism. At several locations in the city are located workstations.

The company also has several shops, where are soldown production and good spurchased for resale. Appraiser expires opinion, the problem is the lack of commercial buildings, which would be housed administration, as well as non-regulated property relations in the district, where the manufacture and repair of machinery companies.

Company to achieve significant cost savings, if unify in one place. This would reduce the costof rent, transportation and other costs. However the primary goal should be to resolve property rights.If the company won the right to be the soleowner of the land where he now performs the process of production, it would be a potential owner of the land at extremely valuable location in the city, which would increase the total value. This would affect all the Company's financial statements in the future.

The second bit location of the company's decades-long lease and has a monopoly over the objects on the sunny quay. There are opportunities to continue to develop activities in the field of hospitality and tourism. Total non-current assets Property, plant and equipment held by the company at the date of the assessment. It should be noted that there is no registered encumbrances of real property in the land register, or mortgage, or pledge of movable property. The assessment is done and it is proposed company, to perform clustering in groups and subgroups.

Certified appraiser used different methodological approaches, in order to more realistically reflect the value on the date of the assessment. Acknowledges the potential revenue, which is especially true in the first and a first group of buildings.
When making assessments authorized assess or has determined fair value of the property based on the elements that determine the value of the property. The basis for estimating the market value and the six category estimates.

When collecting relevant data to produce the estimated present value, particularly to take account of market value, or the value that can be monetarily expressed in nominal terms, which would be subject to assessment could exchange in the open and competitive market, under normal circumstances, either voluntarily, in the transaction between the parties who are well informed on the relevant facts. Used the following methods: Cost method (method of determining the actual value), the comparative method (method of comparing sales, direct price comparison) and the income capitalization method (method of evaluation of revenues).

The estimate is given by the projection of price and value, based on current market condition sand the information available at the time of assessment. It should be noted that the conditions in the market vulnerable to the impact of large uncertainty, and very frequent changes. The assessment was performed in accordance with the so-called possible values, the combination of different approaches and methods presented, taking into account the available data. At the end of the appraiser points out, the study can be used for the purposes of accounting reporting for management, but not as a substitute for athorough analysis of the investment in the company. Display the results of the assessmentis given in Table 1.

Table1. (I-Group-buildings, KTO-022001)

Serial number	Inventory number	Name	Estimatedpresent valueas at 30.06.2012. the RSD
1	1092	Water and Sewerage	3.676.965,05
2	6905	Public lightingStrand	7.127.692,11
3	7964	Wells forwater supply	393.333,34
4	7965	Wells	393.333,34
5	7990	Irrigation system	15.500.314,01
			27.091.637,85

Tabulation first a group of buildings, after the assessment is given in Table 2.

Table 2. (I-Group-buildings, KTO-022000)

Serial number	Inventory number	Name	Estimated present valueas at 30.06.2012. the RSD
1.	1802	Roads185 meters	45.000,00
2.	1081	Shunt	2.800,00
3.	7755	Terrace5x6m	242.492,00
4.	4801	Cab612pcs	36.720.000,00
5.	7818	Locker Room12 pcs	6.000.000,00
7.	58211	Small-sizedcabin68 pcs	4.080.000,00
8.	7753	Cabins30 pcs	1.800.000,00
9.	7736	Cabins110pcs	8.140.000,00
10.	5753	Otherbuildings	153.593.817,90
			210.624.109,90

By analyzing the state of a group of buildings on the account 022000 and the account 022001, pre and post assessment evaluation can be concluded: the state of the account 022000 pre assessment was nominally expressed 143,271,535.87 dinars, after the evaluation of the state of the account is 022000 210 624 .109,90 dinars, or differences in account 022000 before and after the assessment is 67,352,574.10 dinars in accounts 022001 pre assessment was nominally expressed 40,055,513.81 dinars, after a review of the status of account 022001 is 27,091,637, dinars, or differences in account

02200 before and after the assessment is 12.963.876.81 dinars. The company's prior assessment of the accounts 022000 and 022001 had a value of buildings 183,327,049.60 dinars. After assessing the accounts 022000 and 022001 can be brought into the books of the total value of 237,715,747.80 dinars, or after the assessment of buildings increase the value of 54,388,698.15 dinars, or the percentage increase in the value of all the buildings in the company is 29,66 %.

Assumptions financial statements are the accounting basis and the concept of going concern and the company will continue in operation for the foreseeable future (Greuning, H., 2006, p.4). The assessment is done in situations where enterprise makes strategic decisions. In the event that the owner and management in a dilemma, whether to keep the existing company with an unchanged activity,whether to sell the company, and secondly,you make the decision to company value estimate, and that estimate is the basis for making strategic decisions about the future. In addition to the above, there is also the possibility of negligent performance of such works, andbased on that can arise certain consequences (Slovic, D., Knezevic, B., 2010,p.27). In quantitative terms, the financial strength of the company means the amount of funds, and inqualitative terms, financial strength include:continuingability to pay, permanent financing capability, the preservation of property and assets increase (Ivaniš, 2012,p.81).

The ultimate goal of the action taken is not only the use of international accounting standards, international financial reporting standards, international standards of assessment, but the objective presentation of reliable data in the financial statements. An objective presentation is an imperative strategic decision-making (Radulovic, 2012,p.35).

CONCLUSION

After submitting estimates of management of the company may take further action to introduce new value of the property from which it operates in the books, stating that after a year, or on the date 30.06.2013. that has not yet been introduced into the appraised value of the books. This realistic view of the work may indicate that there are a number of concerns about the introduction of the appraised value of the books. The reasons may be the desire of management to avoid higher property taxes due to the fact that the value after the evaluation increases. Maybe other reasons, such as for example is bad an dunprofessional management and others.

Financial Statements, International Accounting Standards and International Financial Reporting Standards are necessary for the conductof fiscal policy in the company. Financial policy is aimed atachieving and maintaining financial strength of the company, with established principles to ad here to in the performance of their duties. Customizing the companies should monitor and legislative changes and regulations in the field of the chart of accounts. The whole business requires the maintenance of effective financial statements, as well as the implementation of new guidelines of international accounting standards and international financial reporting standards.

Management companies should take into account the assetsused by, and therefore need to take into account the valuation of assets under management, should take into account the recommendations of international accounting standards and international financial reporting standards, and in particular to respect the IAS16 and its fair valued is close the assets managed by and introduced changes to the property in the books. Each new property valuation should be done within three years.

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BUSINESS PLAN IN AGRICULTURAL ENTERPRISES

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ABSTRACT

In conditions of globalization and comprehensive changes in the environment, planning as an essential feature of modern business increasingly depends on good managers. Creation of business plans is becoming a key management function for which, so far, has not been paid enough attention, especially in companies in the fields of agriculture and agribusiness. For these reasons, in the period ahead of us all managers should pay more attention to business planning, because not a few companies in the last period due to the failure of the business plan fell into big problems. The aim of this paper is to present the problems of business planning in terms of management, and the activities that can be used in the operation of an agricultural enterprise.

Key words: business planning, business and financial plan, management.

INTRODUCTION

Planning represents the primary stage of the management process in which planning decisions are made about the objectives, strategies, policies and plans of the individual (Williams, 2010, p. 76). Planning a business decision takes place under conditions of a large and growing competition and increasingly sophisticated consumers. In this context , a business plan could be understood as a conceptual framework in which to specify the direction of the business shares of the company for a certain period of time, first of all, in order to prevent adverse effects on its business activity (Lojaničić, 2007, p . 62). As a planning document, a business plan contains a specific set of management decisions that direct the operations of the company. It provides harmonization, training and motivation of managers and employees in the company, as well as quick adaptation to market conditions (Hisrich, Peters, Shepherd, 2011, p. 199).

There are many perceptions of the business plan of completely generalized and more precise understanding of which is closer to determine important characteristics of the elements of the business plan. Taken in its broadest sense, every document on the planned business activity is the business plan. Therefore, the only requirement to be a specific business document could be said that the business plan is that it contained the future business activities of the company. In addition, it is logical that every business plan is followed by financial effects.

Detailed business plans investments are known by the following names: investment studies, feasibility studies, feasibility studies, study opportunities, investment feasibility study, business plan, etc.. Investment project regularly means new investment, whether initial or additional.

BUSINESS PLANNING AGROBUSINESS

Business plan and investment studies in agribusiness, include documents that detail the structure and flow of activities to be carried out. The above-mentioned documents require the collection and processing of identical data sets, as well as the application of an identical methodological framework. In addition, the business plan often includes a portion that relates to investing. Therefore, it is unnecessary for this part of the plan to separate investment study. Consequently the above, it follows that in practical work should attach more importance to content, rather than form.

It is of great importance to know how to prepare and make such documents that are the basis of practical economic activity, and less important to be nominally called. For small and medium enterprise business plan often and investment plan, which is an entrepreneurial venture structured, analytical and practical elaborate de facto as an investment project. In the agricultural sector, which has its specific production cycle, specific commitment of capital from sowing to harvest is collection of managers in all phases of activity compared with planned results. Business plans are not produced only small and medium-sized enterprises, but also large economic entities, corporations and business conglomerates, and in all economic sectors, indicating that agribusiness does have its own peculiarities, especially in terms of commitment of capital.One of the key specifics of the turnover of capital in agriculture, it is low compared to other activities, and is approximately one per year.

Once the business plan is developed for the internal needs of enterprises, it can choose its form and content. However, this is not the case with business plans that are designed for external users, because this practice has resulted in a number of vast and incomparable data. Therefore, there is a need for standardization of business plans. This need arises from the detail business plans, as well as the number of business plans submitted to the lending institutions. That is why business plans are made according to certain standards, and each more or less uniform which primarily depends on the type of projects to which they relate. Despite minor differences, the form of business plans for external users is all the more pronounced standardize (Ivaniš, 2013, p. 46).

A business plan can be defined as follows: A business plan is a methodological process business ideas proving feasibility of its implementation, with the notion of methodological treatment implies that the checks carry out by the idea of a recognized guide, which defines the form and content of the business plan (Ivaniš, 2013, p. 47).

In addition to respecting the implementation of the adopted strategy of the business plan, companies should undertake activities to develop sales of its products and services at the cheap and widely available method (Kotler, Ph., Wong, V., Saunders, J., Armstrong, G., 2006, pp. 135). Part of the business plan marketing activities, which include a combination of different measures are caused by the application of information technology (Fletcher, K., 2003, p. 490).

Most representative connection between the establishment of new businesses and business plan that accompanies this process, since the establishment of new enterprises often require larger amounts of capital, and investors to invest capital in a newly established company requires a lot of information about various aspects of business operations that can best provide them with business plan. Except noted in the last decade in the Serbian economy, business plans were used for enterprise transformation in privatization deals between the new owners and the state that sells social capital based on the law on privatization, mainly with the aim of proving that the new owner obligations are based on the approved business and other plans.

PROBLEMS IN THE IMPLEMENTATION OF BUSINESS PLANS IN AGRICULTURAL ENTERPRISES

Problems in the management of agricultural enterprises and small businesses differ from those inherent in large companies, some differences can be noted, however, when it comes to drafting a business plan (Ožegović, Seifert, 2009, p. 71-72). Business plan of agricultural enterprises is made for a period covering a longer period of time (3-5 years) and not just one year. Business plans start ups can be made for a period which may be longer than 5 years. The existence of an adequate business plan is an essential prerequisite for the successful conduct of business (Djordjevic, Ćoćkalo, 2012, p. 13). However, the real and the primary reason for interest in the management of a business plan is that it represents the most appropriate tool for communication with company financiers (investors and creditors). Using a business plan is the best of the future operations of the company, stating the benefits that financiers can expect from the investment of funds in the particular companies. Therefore, as the main interested parties to read the business plan are investors and creditors. In addition to the above, it should be noted that they have to take into account the specificities of agriculture as an economic sector, as well as the characteristics of the same rule for a longer period of time.

In countries in transition, business plans are beginning to emphasize the parallel with the process of political and economic democratization in these countries. The interest of foreign capital for investment in the economies of countries in transition is manifested, and the imposition of the standard language of business communication by his representatives. In addition, the basic features of the elements of the business plan of agricultural enterprises, whether in terms of existing or start-up companies, are the following:

- emphasis on certain elements of the plan that are primarily interested financiers (investors and creditors),
- usage of appropriate methodology in developing a business plan that provides mutual comparability of the relevant planning parameters and
- the inclusion of the strategic plan (longer period).

All financiers companies can be divided into two major groups, namely: investors and creditors. Generally, investors and lenders in the business plan calls for many of the same types of information, and the difference is only in the way the different elements evaluated the business plan. Similarities and differences in their ways of reasoning and the qualification of certain elements of the business plan can be best understood if we take into account the most important elements of a business plan (Ivaniš et al 2013, p. 38-40).

FINANCIAL ASPECTS OF BUSINESS PLAN AGRICULTURAL ENTERPRISES

The business plan has several parts that represent parts of a single whole. The informational basis of the business plan is the basis of agricultural enterprise physically and financially part (Lojančić, 2007, p. 131). Analysis of physical units of agricultural enterprises can serve as the basis of the business plan and also the development of the company.

Parts of a business plan must be consistent and verifiable, in order to plan a whole had a high degree of reliability. Due to the existence of errors in the business plan, you should make sure that they are not transferred to the financial aspect of the business plan. The importance of the financial aspect of the plan is to be based on quantitative indicators examine the profitability or unprofitability of the investment, and whether the company will go into some business venture or not.

Finally, it should be noted that a large number of agricultural enterprises, especially small farms use their own funds to finance new business ventures. They invest in a new business owns savings or some forms of personal property. Internal sources of financing often include funding from immediate or extended family of small agricultural enterprises and farms.

In such cases, an agricultural entrepreneur has its business plan to convince his family and to the realization of his business enterprise is real and absolutely certain, and that the investment of his family fully profitable (Marković, 2008, p. 200-201). This approach is perhaps the most difficult, for reasons of personal investment funds relative to activities in the field of agribusiness, which are the lower capital turnover ratio compared to some other industries (such as shopping), and there is a strong dependence on natural conditions, especially in plant production , as well as strong competition in the market for agricultural products.

In addition there is a relatively higher risk for certain agricultural products demand. In this sense, a business plan is a kind of guide that allows you to successfully cross the road from the initial stage in which to create a business idea to its final realization (Penezić, 2010, p. 219).

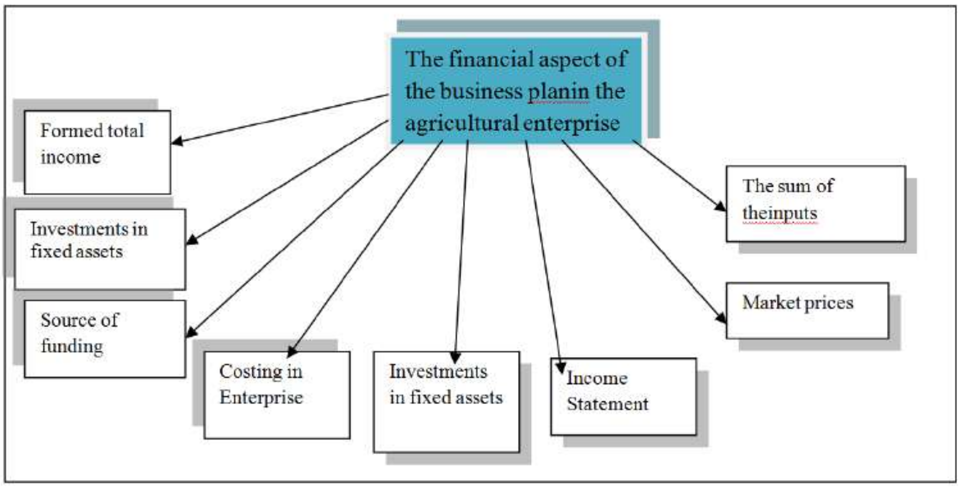

Figure1. The financial aspect of the business plan(authorsin 2014).

CONCLUSION

Business plans are the basic tools of each manager. They make a mirror of economic ambition, business philosophy and business management skills. The primary purpose is to help managers to define goals of the business, a reality with as little earthquake, are surprises and unplanned activities. Planning a business decision takes place under conditions of a large and growing competition and increasingly sophisticated needs of consumers. Business plan could be understood as a conceptual framework in which to specify the direction of commercial stocks of agricultural enterprises for a certain period of time.

In addition to respecting the implementation of the adopted strategy of the business plan, actions should be taken to develop the sales of their products and services on the cheap and widely available manner, as soon as possible to collect manufactured products, because the turnover of capital in agricultural enterprises is low.

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UNCONVENTIONAL MARKETING IN AGRICULTURAL ENTERPRISES

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ABSTRACT

Unconventional marketing of agricultural enterprises is introduced by managers in order to increase the impact of the company on a wide range of potential customers and consumers. In the case of the introduction of the mentioned marketing and distribution channels that support it, it creates a direct relationship between producers and consumers in a well placed sales, created and consumer habits again come to the dealer and buy back the same or other goods. In addition to the primary goal, creates impact and broad dispersion influence producers to consumers, and thus increases thesecurity ofthe manufacturer because they are forced to sell their products only to retailers but sold a large number of consumers.

Key words: event marketing, agricultural enterprise, profit.

INTRODUCTION

Managers as a responsible professional people to create the overall policy of agricultural enterprises have the ability to introduce new forms of marketing to make the results of their activities were more successful. Improving the performance of companies in the domestic and international market needs to follow the process to minimize costs, since these results in an increase in the effects of management companies.

This paper presents two non-standard approaches to marketing. First, recognition of events as a function of better performing companies in a number of events, in which the company agribusiness has a chance to perform with their products. The second part offers the possibility to marketing functions through IT technology and new channels of distribution of goods. No matter what kind of approach to word marketing in agriculture should take into account the increasing attractiveness of the company in order to increase the efficiency, quality control and building and improving the loyalty of a wide range of potential customers.

MARKETING EVENT AS A CHANCE FOR THE DEVELOPMENT OF AGRIBUSINESS

Marketing of agricultural enterprises, should respect the great events that may be important for the marketing activities of the company such as trade shows, sporting events, and other global events. Professionally created work groups planning events in order to improve the performance results of the company (Kotler & Keller, 2006, p.8).

In the literature (Hall, 1977) under the marketing event includes the observation function event management, which involves communication with the stakeholders and other events. Organizers of the event are essential to modern marketing communication should take into account the factor of competitive advantage (Ljubojević & Andrejevic, 2002). In addition to the presented positions can be noted that the authors introduce the observation and specific offer service economy, events that are consequences of socio-economic development, raising living standards, increasing leisure time, etc. (Andrijević & Grubor, 2007, p. 4). The experience can be seen through the joint implementation of certain activities of employees and the public (Getz, 1977).

Experience is primarily concerned with satisfying the senses of consumers. Thus the views of the author, the agricultural enterprises are implemented, primarily due to the fact that a large number of primary agricultural products produced sensually perceived by customers of the same.

Implementation of significant events is performed continuously throughout the year, ranging from green markets to large shopping market; marketing or promotion of agricultural enterprises is used to improve the performance of the enterprise and may include the following activities shown in Figure 1:

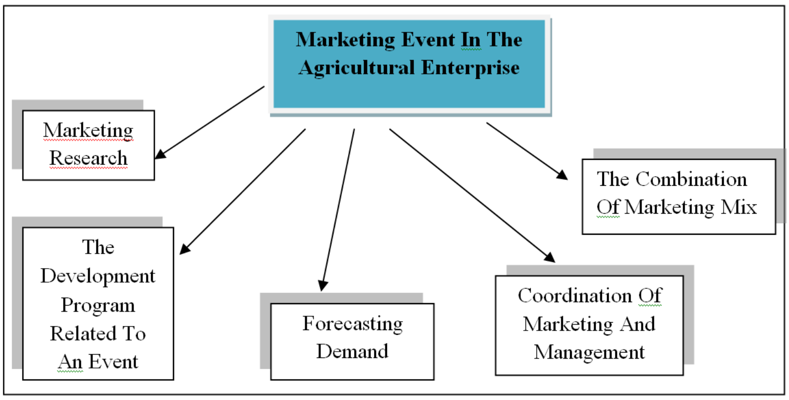

Figure 1. Overview of marketing events in the agricultural enterprise.
The authors (2014).

Managers should recognize in their performance and business market orientation to minimize all costs, but with a certain level of quality in the bidding to prospective clients.

Authors such as (Shnitt, 1999) distinguish between traditional marketing concept and an important event for marketing. The traditional event marketing emphasis is placed on observation:

- directing activities for the benefit of the program of events,
- closely watching the competition,
- Understanding of visitors, and consumers as rational participants and
- the application of the analysis in the implementation of marketing companies.

Marketing experience (experiential marketing) beyond watching and observing such deflection in four main directions:

- experience of consumers,
- Research Procurement
- observing users as rational participants and
- the application of modern and new methods in the implementation of marketing.

Based on an active approach to marketing managers is given the option to have different approaches to combining the marketing mix. Thus said the author distinguishes the following types of marketing:

- designed marketing
- emotional marketing (basically the emotions of potential users)
- marketing thought, based on the intellectual characteristics of potential users,
- Action marketing and
- conjunctive marketing which essentially combines the aforementioned into a whole that any company can adopt and implement, in accordance with the circumstances in the market.

It is important that professionals who are responsible for implementing the marketing companies in most cases use a variety of marketing activities and interact with a large number of potential users and customers in domestic and foreign markets. Therefore, the marketing mix is a combination of methods created to achieve the set goals. Decisions related to the marketing mix, especially decisions on pricing and promotion decisions are in the short term, because they are subject to change. Combination of marketing mix show greater stability, as there are many possibilities of combination.

MARKETING AT THE TURN OF NEW MILLENNIUM

Modern marketing that company should apply respects: a product, a service, an experience, an event, person, place, property, organization, information, and ideas. Revenue growth, improved quality of life, changes in the lifestyles of urban life leads to such important events may become more interesting in terms of supply of professionals who offer such services in the market. Different methods of attracting increase the chances of project profitability that is offered on the market (Grubor, A., 2013, p. 47).

Modern marketing is subject to a large extent the changes that are caused by the application of information technology (Fletcher, K., 2003, p. 490). The main objective of these activities is to increase exchanges with consumers in the long run; it creates a loyalty between companies and consumers. This is a common benefit from this relationship can be seen through four principles:

- Create a database of customers,
- The concept of Internet access companies,
- set up a company banner to related pages and
- Provide easy access and efficient response to calls of customers (Kotler , 2007, pp. 254-257).

The aim of these activities is to improve profitability by attracting and retaining customers. Electronic marketing refers to the application of marketing principles and techniques via electronic media and the Internet. This allows companies to inform, advertise and develop the sales of its products and services at the cheap and widely available method (Kotler, Ph., Wong, V., Saunders, J., Armstrong, G., 2006, p. 135).

It's just an opportunity for digital marketing with respect to the concept of sustainable consumer society at the global, regional and local level. The goal of economic activity is the application of modern a marketing depending on various market and technological conditions , in order to increase the efficiency of operations through the use of modern marketing (Grgar, D., Radanović, B., 2013, p.75).

The information age has imposed a new era and changed the traditional distribution channels. The introduction of computer technology with the manufacturer and the customer has led to falling costs in many industries (Granados, FN, Kauffman, JR, Lai H., Lin. H., 2001, Vol. 28, No. 2, p. 39-45). The afore mentioned technologies have enabled manufacturers to bypass dealers and other intermediaries.

CONCLUSION

Managers should recognize in their performance and business market orientation of agricultural enterprises run, all while minimizing costs. Marketing approach involves the provision of services with a certain degree of quality, which is bidding to prospective clients unconventional marketing. This approach includes consideration of the electronic performance of agricultural enterprises use IT technology and appreciation of events at all events where agribusiness has the conditions for participation.

Companies respond to market conditions, practical and effective solutions to ensure commercially viable business. This means among other things the establishment of modern marketing and the introduction of so-called. Some companies may put the whole business in the concept of e-business, which provides a proactive approach to increasing the impact of market performance on the domestic and international markets. The main objective of the above mentioned activities is to increase exchanges with consumers in the long run.

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RESEARCHING EFFICASY OF THE ORGANIC PROCEDURE IN SUPPRESSING CHIGOES *(Varroa destructor)* SHOWN ON THE HONEY BEE (*Apis mellifera* L.)

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ABSTRACT

The research is conducted on the apiary of the author of this work, in 2013 in Vrazogrnac (municipality Zajecar) with the aim of examining the efficacy of the organic procedure in the suppression of chigoes (*Varroa destructor*) on the Carniolan honey bee. The experiment consisted of systematic selection of colonies, taken from the L.R. hives. Statistically, experimental groups were not significantly different in terms of bee number, honey production, bees'health, and the age of the queen bee in the year observed. The products used are marked as "ecological" and they are included in organic procedures for the reduction of contamination of colonies with varroosis. The products have the certificates and they were placed in the fertile bodies of the hive. Bee products were produced without the presence of harmful chemical material and residues. This justifies the application of organic protection in the treatments on the honey bee since it has the aim of producing healthy bee products. Organic apiculture can have no alternatives.

Key words: Honey bee, chigoes (Varroa destructor), organic protection.

INTRODUCTION

In the years ahead of us, economy will be especially important. Namely, great population increase and the growing need for food, as well as the global climate changes, which are expected as a consequence of the increasingeconomic and technical and technological growth of the most developed countries in the world,imposed the urge for humanity to think about the sustainable development all the time. When it comes to agriculture and its development which is based on the concept of sustainability, one usually has in mind a specific idea. This idea is supposed to provide the production of quality food which will be stable enough, preserve basic natural resources and protect the environment while being economically efficient, that is profitable. Global musings regarding this topic brought the first results connected to apiculture as a branch of economy. The spread of the organic production in our region will contribute to contemporary understanding of ecology and its importance for our lives. The production of honey and other bee products will provide necessary healthy food only if apiarists are educated and introduced to new principles of ecological apiculture. This does not mean returning to its roots; it includes progress and abiding by the rules of such apiculture. In the organic production of honey and other bee products an important role needs to be attributed to the organic protection of bees. Respecting these rules enables the products to be of organic origin, completely healthy and safe, and to be made of plants which are not genetically modified. Moreover, this is a chance for Serbia to develop production in its rural areas.

MATERIALS AND METHODS

The research was conducted in the period of July-September 2013, on the apiary of family Stamenkovic in Vrazogrnac, municipality Zajecar. The Apiary is registeredand the colonies are regularly marked and monitored by the authorized veterinary service.

This research was conducted in several phases:

1. Chosen colonies were of the same strength (the number of bees), similar genetic potential of the queen bee, similar productivity and resistance to certain illnesses (created through monitoring and combining which lasted for many years);
2. In the experiment, the procedure of the process itself was respected (time and manner of the treatment) for certain products;
3. Assessing efficacy of the procedure for suppressing chigoes was achieved through counting fallen varroa on the controlled pads (KONI-pads);
4. The research was carried out on 20 controlled colonies with the aim of examining effects of organic procedures.

The examination was organized in the field on the given apiary. We chose the colonies which, following feeding on the Locust tree had a similar number of worker bees and the number of frames with a young brood. The selected colonies produced the same quantities of honey and had no instinct to swarm. The queen bees were Carniolan. In the previous years they were treated with the same products during the period of August-September, after removing fixed-frames. The queen bees were developed in 2012. Under the same circumstances the colonies were prepared for winter and the same amount of honey was obtained. During the spring examination, performed by the veterinary service, been the presence of Nozeme Apiss and Nozeme Cerana has not been noticed in the controlled colonies. For every check-up of the efficacy of research we used ten bee colonies with the aim of acquiring data which are statistically significantly different. With this procedure it is possible to determine how efficient organic procedure is in suppressing varroa.

With a view to examining the efficacy of the organic procedure in suppression of chigoes *(Varroa destructor*) on the honey bee (*Apiss melifera* L.) we used:

-On 18 July 2013, a product (with the declaration 100% ecological) was placed in ten controlled bee colonies. The product was made by soaking wooden slatsin the extract made of plants: It containsflavonoid, terpenoid, tannins and bitter substances. It is labeled ***"A".*** One of these slats is placed in fruitful body of the hive. Two of the slats are placed hanging in each controlled bee colony in the centre of the bee brood. The slats remained in the hives until they were completely used and turned into dust, following which bees threw them out of the hive.

-On 18 July 2013, a product (with the declaration 100% ecological) was placed in ten controlled bee colonies. The product was made by soaking wooden slats in herbal oils and extracts: thyme, wormwood. It is marked ***"B".***

It works through evaporation and as a consequence the female chigoes lay less eggs, chigoes cannot bear to be in the area where slats are placed, they do not take food and finally they die. In addition, two slats are installed in each colony.

RESULTS AND DISCUSSION

In July, bee colonies had 10-12 frames, which is a challenging factor for the process of destroying the varroa. All the products were prepared in such a way so that their effect includes the whole cycle of bee development, starting from an egg to an adult bee. In July, varroa actively enters the drones'brood, and the period of drone hatching is 24 days long, while a bee needs only 21 day. The results of this research obtained through these treatments depict a real picture and efficacy of the products used. Ecological treatment with the product ***"A"*** (Figure 2) showed good results and statistically, there is no significant difference in the efficacy of the treatments used in conventional treatments. With 127 fallen varroa from each colony, this can be considered a reliable product for suppression of chigoes**. Jovan Kulincevic et al., 2012**, reached similar results in their experimental apiaries. For greater reliability and credibility of the efficacy, more years of treatment and monitoring are needed.

Figure 1. Control pad with a fallen varroae after the treatment of the ecological product **"B"** (photo:Jovana Stamenković)

Application of the ecological product ***"B"*** exhibited the average number of 82 fallen varroa (figure 1). As an ecological product it deserves additional testing, however compared to the product ***"B"*** it has three times less fallen varroa. The advantage of this product is that it is used during honey-collecting and it has no residues.

Figure 2. Control pad with a fallen varroae after the treatment of the ecological product **"A"** (photo:Jovana Stamenković)

Due to their drawbacks, previously mentioned methods do not provide us with a universal and permanent approach in solving the varroa problem with the honey bee. Biological methods are not efficient enough (table 1), chemical methods lead to dangerous creation of residues and the development of the resistant individuals, and queen bees of the resistant lines *A. Mellifera* transfer the resistence to varroa on a small percentage of the progeny. Logical conclusion from the current data is that methods in the system of integral protection need to be combined in an optimal and rational way. This means applying knowledge from the area of bilogy, bees and varroa and knowledge concerning features and toxicology of the active substances of acaricide, as well as concerning apitechnic. The aim of this would be obtaining healthy and productive colonies and bee products which are healthy and in good condition. **(Slobodan Milenkovic, 2000)**

Table 1. Control Test of the fallen varroa treated with the ecological products

Control Test of the fallen varroa treated with the ecological products			
Controlled Day	**Redni broj košnice**	**PRODUCT "A"**	**PRODUCT "B"**
		Number of fallen varroa	**Number of fallen varroa**
18.07.-22.07.2013.	1 1A	61	38
	2 2A	54	34
	3 3A	60	29
	4 4A	58	25
	5 5A	58	26
	6 6A	62	36
	7 7A	46	29
	8 8A	57	30
	9 9A	61	24
	10 10A	59	21
Average		58	29
22.07.-28.07.2013.	1 1A	42	37
	2 2A	33	31
	3 3A	40	31
	4 4A	35	24
	5 5A	31	24
	6 6A	42	36
	7 7A	30	30
	8 8A	32	27
	9 9A	40	23
	10 10A	38	22
Average		36	28
28.07.-15.08.2013.	1 1A	42	32
	2 2A	31	28
	3 3A	35	26
	4 4A	31	20
	5 5A	30	21
	6 6A	39	33
	7 7A	29	28
	8 8A	29	21
	9 9A	34	22
	10 10A	36	20
Average		33	25
No. of varroa in each treatment		127	82

CONCLUSION

Based on the results of the research on the experimental apiary which had the goal of examining the efficacy of the organic procedure in the suppression of chigoes, we can draw following conclusions:

- It does not have a negative effect on the bees or the brood,
- The primary work organization of the members of the bee colony is not disturbed,
- The suppression rate of the varroosis is around 20-80%,
- It excludes the danger of contaminating the bee products with residues,
- Besides the increased work they do not demand additional investment,
- Products in organic protection show good results;nevertheless they are not enough for a complete combat against varroa, it is important to combine them with the existing physical methods in the organic apiculture, such as cutting the drone's honeycomb, forming swarms, replacement of the old honeycomb with the new one.
- All the measures in the organic procedure for suppressing varroa should be applied regularly in apitechnique.

Apiarists often do not notice the chigoes (*Varroadestructor)*until it reaches a high level of contamination, and then is usually too late for the bee colony and it is not possible to save it from inevitable death. That is why the size of the population of the *Varroa destructor*in hives needs to be controlled regularly. Furthermore, one should never believe that their hives are free from *Varroa.* Once the presence of chigoes is confirmed (and there is no hives without them) the level of contamination ought to be assessed regularly throughout the whole year. Due to significant fluctuations in the contamination level among hives in one apiary it is necessary to control the representative sample of the bee colonies, while it is recommended to control all the colonies in the apiary. Taking everything aforementioned into consideration and having in mind its exponential increase, it can be deduced that in the combat against varroa, various methods need to be combined, that is, one form or one type would not be enough.

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URBANIZED HABITAT OF MAN IN NATURAL DISASTER CONDITIONS

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ABSTRACT

Natural disasters, the most drastic ones, such as earthquakes, floods, volcanoes and strong winds (cyclones, hurricanes, typhoons, storms and tornadoes), cause large number of human casualties and huge property damage. Only during the period between 1900 and 1976, number of people died is over 60 thousands, and number of wounded or remained homeless is over 3 million per year. Hence, preventive measures should be taken as protection from natural disasters, with adherence to certain regulations. Natural disasters risk level is high because they happen suddenly and have high intensity.

Key words: natural disaster, protection, risk, prevention, regulations.

INTRODUCTION

Various natural disasters are permanent stimulus of human kind development. Level of effectiveness of certain region is proportional to level of social, economic, political and technical concentration of people and material goods. The most drastic consequences of natural disasters according to International Red Cross were in the period 1900-1976. Number of earthquake casualties only reached 2.662.165, and number of wounded or people who remained homeless is 28.894.657 (Table 1).

Table 1. Consequences of natural disasters according to the International Red Cross during the period 1900-1976

Type of disaster	Number of dead	Number of wounded or remained homeless
Earthquakes	2662165	28894657
Floods	1287645	175220220
Volcanoes	128058	337931
Strong winds	495795	4573663
Total:	**4573663**	**209026471**

Defense and protection is permanent characteristic of every society and it is in fact man's necessity. For protection of human lives and material goods from danger of natural disasters, based on achieved experience, various organizations are created, but which are not and cannot be efficient in all cases because disasters appear spontaneously and suddenly. Majorly, for that reason is necessity of protection from previously mentioned disasters is most important.

One of main tasks of ecology is scientific and professional research of environments stability conditions, which people live in, in normal as well as in natural disasters' conditions. However, there are attempts to minimize their influence, which will not drastically change natural flow of people's lives and environment. That should be our everyday care, and of our future generations too. This problem led to setting new principles in designing space and reconstruction of ruined cities. Urban ecology task is city as life's habitat of man as a unity and social groups, i.e. it is a science of life functions of towns. It also reveals and determines rules for functioning of towns, which manifests in area of synthetic action of physical, chemical, economical, social, biological and inevitable natural conditions, which are most often accidental with catastrophic consequences. Urban ecology, as specific scientific discipline, tries to establish clear relation between factors, according to which the quality of life takes place. Each human individual in community is basis of modern urban society. Society develops and must respect human necessity for better life quality in all conditions, including natural disasters. Consequence of economic development is increasing involvement of natural disasters. Technological environment of man itself, being very complex and unfavorably influencing individual as initiator of these processes, especially when natural disasters occur. Individuals, as well as society are most often not prepared and are decapitated in the first moments of disaster occurrence, when much can be done to decrease consequences and irrecoverable damage. For that reason, protection, preparing and training for this kind of situation is best way of preventing damage.

SPATIAL PLANNING AND EARTHQUAKE PROTECTION

Earthquake is natural occurrence, which is unpredictable neither by place nor time of happening, according to nowadays scientific knowledge. Also, it is impossible to predict how big damage will occur under such circumstances. Earthquake is natural occurrence which occurs in bigger or smaller time intervals, followed by bigger or smaller ruining of human creations, buildings of all kinds and certain number of human casualties. Cities and towns exposed to earthquakes are categorized as ones of the most beautiful human creations. That is not a coincidence, because that are the regions where various natural phenomena overlap and even confront which have always been attractive and important places for human activities, so people constructed them, not rarely in spite of difficulties and natural barriers.

Complexity of earthquake generation mechanism and heterogeneity of surface layers of ground provide big difficulties to determining local movements of ground during the earthquake. However, forces that generate in a building during the earthquake do not depend only on ground movement but on mechanical characteristics of whole structure. As essential characteristics of ground movements upcoming in the future cannot be precisely determined, seismic actions on structure could also not be determined with certainty. Even if, at some point in the near future, predicting short time interval in which an earthquake (of certain intensity) will most probably occur, become possible, still remains the fact that for the moment, and in the long future, this phenomenon will not be possible to prevent. That is the reason why experience in previously damaged objects in past earthquakes, experimental and field research of soil and structures, provide us possibility to, with necessary level of engineering precisement, define economically acceptable criteria of designing and constructing. Constructive solutions which are optimal when seismic actions are not considered don't have to remain unacceptable when structures are designed to withstand intensive soil displacement. It is important to mention that earthquakes occur in not so big, same regions (most often in Japan and Pacific zone).

Composing of unique integral governing of seismic risk comprises: determining of appropriate seismic risk on acceptable level of seismic actions, aseismic design and building of infrastructural objects, spatial urban planning in seismic conditions, preparedness for earthquakes. Governing of seismic hazard and seismic risk can be achieved in several ways. It can also be reduced through spatial and urban planning. Concentration and population density are two crucial developing elements, which are defined on all levels of urban planning. They refer to planning concept of spatial distribution of residents, buildings and social goods and activities and as such, they directly influence level of seismic risk. On local level of planning, purpose of areas is determined through functional zoning (habitation, education, trade, industry, health care etc.) Special difficulties in earthquake protection are for completed objects when regulations for aseismic construction are not obeyed, especially for old cultural and historical city cores in old towns.

Empirical relation between magnitude and earthquake intensity is:

1) Earthquake of low intensity – light earthquake (Kraljevo the 3rd of November 2010.)
   - magnitude M=5.4° on Richter scale
   - h – depth of seismic focus,
   - d – distance of object
   - I – intensity on Mercali scale

$$I = 1.5M - 3.5\log\sqrt{h^2 - d^2} + 3 = 1.5 \cdot 5.4 - 3.5\log\sqrt{10^2 - 10^2} + 3 = 7.07^\circ$$

Region of Kraljevo after relevant seismic map, with returning period of 500 years, is located in the 8th seismic zone, and thus it should withstand, with no big damage or human losses, earthquakes of intensity of 8th degrees on Mercali scale. Nevertheless, in Kraljevo some people died, and 16000 thousands buildings were damaged, from earthquake which, as calculation showed, was less than 8° (7.6° in epicenter). Buildings designed according to aseismic building regulations, were also damaged.

2) earthquake of light to moderate intensity (M=6°, h=12km, d=15km)

$$I = 1.5M - 3.5\log\sqrt{h^2 - d^2} + 3 = 1.5 \cdot 5.4 - 3.5\log\sqrt{10^2 - 15^2} + 3 = 7.6^\circ$$

Mercali scale

PROTECTION OF TOWNS FROM FLOODS

By increasing number of towns by the rivers, unfavorable effects of rivers also increase. At the same time, damage from big river waters, floods and river erosion also manifest. For that reason, works on protection from harmful effects of water, local and primitive as well as more complex measures. Floods appear with big waters, due to failure of protection buildings (levee, dam, floodgate,…) caused by mistakes in the design process, construction process, up keeping or maintaining of protection buildings. Flood damage usually can't be totally and permanently avoided, but only can be decreased. High water level of some watercourse, in terms of flood protection, is considered water flows which flow out of basic riverbed and flood protected or non-protected surrounding areas. For planning, designing and maintaining system for flood protection, it is important that all the parameters of big waters are maintained along the river flow. Also it is important to determine possibility of appearance of big waters, under so-called ''return period'' of appearance. It is necessary to determine ''appearance risk'' of some big waters. This risk is can be calculated using next expression:

$$R = 1 - \left(1 - \frac{1}{T}\right)^n [\%]$$

where:

- R is risk of appearance of big waters,
- n is number of years in long period after appearance of big waters, for which this risk is calculated
- T is return period of big waters appearance.

Example: If at some waterflow appear big water in 1980, whose returning period is 50 years, than risk from appearance of such or bigger waters for period until 2012, is:

T=50 years, n=2012-1980=32 years

$$R = 1 - \left(1 - \frac{1}{T}\right)^n = 1 - \left(1 - \frac{1}{50}\right)^{32} = 1 - 0.5239 = 47.76[\%]$$

T=65 years, n=35 years

$$R = 1 - \left(1 - \frac{1}{T}\right)^n = 1 - \left(1 - \frac{1}{65}\right)^{35} = 1 - 0.5812 = 41.88[\%]$$

Expressions for appearance of big waters, as well as characteristics of big waters can be: natural, anthropogenic and combined. Natural causes are: intensive rains, sudden melting of snow and ice, sudden melting of snow followed by rains, barriers in riverbeds, stockpiling of snow or river deposits, waves generated from winds followed by increasing level of water, as well as big waters waves on main flow and tributaries. Anthropogenic causes are: demolition of dams, watergates and waterpits on rivers, intensive onflow of water from basin due to forest clearing, compared to normal state in basin, construction of dams, watergates and waterpits, bridges etc. which contribute to creating additional backwater in waterbeds.

Combined causes of forming and changing river regime of big waters appear on almost all watercourses in the world, and in our country also. Big floods in Serbia happened during the period from 1996 to 2009 from January to November 2009. 365 buildings were flooded by Western Morava, Đetinja, B. Rzav, Moravica. In 2010 and 2011 spring large number of rivers flowed out of the riverbed and flooded hundreds of houses, and thousands of hectares of cultivable land, making huge material damage to many regions.

VOLCANOES

Volcano represents opening in earth crust, through which melted rock mass, ash and gasses are being extruded on surface, where they get cold and sediment. Volcano is geological form (usually mountain, however there are underwater volcanoes also) where melted rock mass comes out on the surface of earth crust. Volcanoe can be active or inactive, depending on its eruptions and tectonic activities nearby. On top of volcano's dome is crater, and link between crater (temperature in range of 600 to 1200 ˚C) and hearth is volcano channel. Magma on the surface of earth is called lava.

Appearance shape of volcano depends on many factors. One of them is acidity of magma. If magma contains more than 63% of silicium it is considered as sour magma and consequences of eruptions like this can be catastrophic. Magma containing 52-63% of silicium is intermedial. If it contains 45-52% than it is basic lava. Lava with content of silicium lower than 45% are called ultrabasic.

Significant eruptions of volcanoes are: Vesuvius, 24.08.79. eruption destroyed Pompeii, killing 20000 people. Eruption of volcano on Sumatra 1815. overwhelmed town of Sumbava with 14000 residents, and from side effects another 44000 people died. Volcano Krakatau on island with same name in Indonesia 1883. created depression 300m deep, sound of explosion was heard 5000km away (the loudest sound ever produced). Volcano caused huge shock wave, making number of human casualties 40000. Volcano Mount Pele destroyed town of St.Pierre on which occasion 26000 people died. Volcano on the mountain of St. Hellena in Washington state in 1980. had the force of 500 atomic bombs, because all trees on area of 600km2 were burned to the ground.

WINDS (CYCLONES, HURRICANES, TYPHOONS, STORMS, TORNADOES)

Tropical storms, such as tropical cyclones, hurricanes, i.e. typhoons behave differently from extra tropical cyclones of moderate regions. Wind speed is obtained from relation:

$$V_{\max} = ay + b, \; y = -\log\left(-\log P\right)$$

where a,b are constants which are unique for every location, y is auxiliary variable, and P is probability which is later transformed into lifetime of structure:

$$T = 1 - \frac{1}{T}$$

Expression for maximum speed is now transformed into:

$$\ln V_{\max} = a_{II} y - b_{II}$$

where a and b are previously given values (a_{II} i b_{II}) and are related to distribution of extreme values Frechet. For some locations with tropical storms starting values of ''fastest mile of winds'' are determined at height of 10m, and for Miami and Florida amounts: a_{II}=0.26 i b_{II}=3.81. For practical needs, wind force or wind pressure is proportional to squared value of speed, i.e. wind force ≈$C \cdot V^2$, where C represents factor of proportionality, named as shape factor, and is experimentally determined in aerotunels on models of real buildings. Airflow, moving with speed V, causes force q at unit of surface, where q (dynamic or stopping pressure) is defined with

$$q = \frac{1}{2} \rho \cdot V^2$$

where ρ is air density.

Phenomenon related to wind actions are functions of: structure characteristic, mass, shape, stiffness and damping, depending on which are determined response of structure, i.e. displacement of structure is a function of arousing force and response of structure.

Term ''speed'' represents direction and intensity of speed, although not all the instruments can measure these values. Using expression for adequate wind speed wind forces perpendicular to 1m2 of surface, will be calculated.

CONCLUSION

Based on everything previously mentioned, it can be concluded that natural disasters cause large number of human casualties and huge material damage. As mentioned in introduction, most drastic natural disasters are: earthquakes, floods, volcanoes and very strong winds which annually take over sixty thousand victims and over three million are wounded or remained homeless. All these disasters happen suddenly, without warning, and even when we are warned of their upcoming presence, either there is very little time for evacuation or we are unable to save anything. For that reason, prevention is the best and most secure way of protection, and also most efficient because measures not taken on time cause huge material damage and human casualties which are unique and irrecoverable. Defense and protection are permanent characteristic of all communities and they are universal necessity of man when experience is gained based on scientific knowledge. Presented numerical examples contain most important characteristics of each type of disaster, so there is no need for special analysis.

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INVESTIGATION OF THE GREEN BARIER INFLUENCES ON THE TRAFFIC NOISE LEVEL

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ABSTRACT

The results of the noise level measurements in one of the streets with most frequent traffic in town Niš, are presented in this paper. The measurements are performed on the six measuring point in the morning and midday hours. Three of these measuring points are near green barier (i.e. with several deciduous trees near the street) and three without nearly green barrier. The results of measurements of the noise level at the measuring points are compared. According to our results the green barrier significantly reduce noise levels.

Key words: Noise level measurements, green barrier.

INTRODUCTION

Traffic noise in cities is a consequence of the progressive urbanization, and the rapid tempo of life. It is a growing public health problem in the cities. About 24 million residents in the European Union reported being highly annoyed by road traffic noise [1]. Noise annoyance and sleeping disturbance have been proposed as important mediators of the impact of noise on health [2]. The relation between road traffic noise of the order 67±2 dB and cardiovascular risk in the exposed group of young healthy individuals was proved. The constant exposure to noise of level 65 dB can cause the high blood pressure, while constant exposure to noise level higher than 75 dB can lead to increased levels of stress, increased heart rate and potential hearing loss[3].

Noise mapping has been used as an instrument for assessment of environmental noise which helps to manage proper urban planning [4]. Noise level mapping in urban areas allows the characterization of environmental variables, such as noise pollution and sound propagation. Strategic mapping [5] is very important for noise level assessment on the European level every five years. These maps are based on common methods and procedures. They are useful for evaluation of human exposure to the noise in European

Union. So that noise maps could be adapted for the assessment of noise pollution in natural parks [6]. Implementation of law programs under the European Directive on the assessment and management of environmental noise [5], can lead to increased use of noise barriers as a means of reducing road traffic noise.

The investigation of road traffic noise levels at the crossroads in the city of Niš shows that the level of exposure to noise is much higher than upper limit for residential areas and the upper limits of the zone around schools and medical centers [7].

Results of a pilot survey conducted at a residential area affected by the construction of a barrier are showed that although most residents felt that sleeping conditions were improved after the barrier was built, they sensed negative effects due to loss of sunlight and visual impact [8]. Green areas present good ecological solution in attempt to reduction the noise problems in urban areas. Wetland parks and garden parks are shown to be able to reduce noise annoyance to a greater degree than grassy hills [9]. Because of that green areas in urban zones and cities have and very strong cooling effect [10], [11].

The aim of this paper is assessment the noise reduction by green barrier in urban city areas. The results of noise measures in the frequent street, with and without green barrier are presented.

MATERIAL AND METHODS

Measurements were performed with digital sound meter PeakTech 8005. This sound meter can measure sound frequency interval from 31.5 Hz to 8 kHz. The noise measuring range is in the interval from 30 to 130 dB, with a resolution of 0.1 dB. This device meets the IEC 61672-1 standard, class 2. Calibration was performed by the manufacturer.

Measurement points are selected in accordance with the Regulations on methods of measuring noise content [12]. The measurements were performed on 6 measuring places (MP) in "dr Zoran Đinđić" street. This street was select as the street with the high frequency of traffic. The three of selected measuring places are without green barrier near the street T1, T2 and T3, and other three measuring places with the green barier near the street T4,T5,T6 (i.e. with alley of deciduous trees right next to the street). The measurements were performed in morning and in midday hours.

During measurements the temperature of air was ranged from 20°C to 35°C. Maximal wind speed did not exceed the value of 10 m/s. Also, due to the presence of houses and other buildings on MP microphone was placed at least 3 far m from the object, in order to avoid resonance. Measurements are performed at a distance of 6-10 m from the crossroads at the height of the instrument of 1.5 m from the ground. At the one measuring places, the measuring time was 10 minutes, and the interval between two successive measurements was 1 s.

RESULTS

In the Fig. 1, the results of noise level, in one street in Niš, are presented. On the left side of figure the noise level in the morning hours, and on the right side the results obtained in the midday. At the all measuring places (T1, T2, T2, as well as, T4, T5 and T6) noise level are presented using the box diagrams. On these diagrams boxes presents areas $\bar{x} \pm \sigma$, around the mean values of noise level $\bar{x}$ (σ presents standard deviations). In all boxes the median values (the central values of one measuring series) are presented. Around the boxes the minimal and maximal values, as well as, the 1% and 99% percentile of noise level values distributions are presented. The areas 1%-99% percentile and $\bar{x} \pm \sigma$ represents the significant values 98% and around 68%. On the figure the values of noise level limits for residential zone 55 dB is indicated with dashed lines.

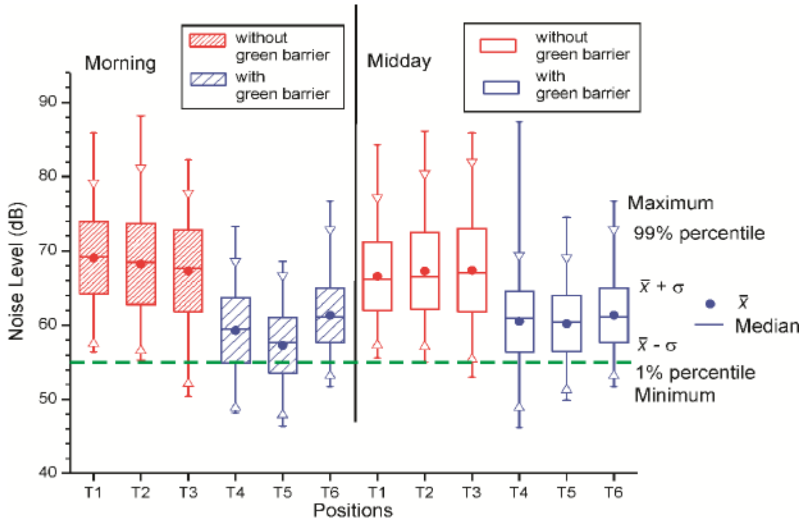

Figure 1. Noise level on the six differene positions, three with green barrier and without them.

DISCUSSION

Ministry of Energy, Development and Environmental Protection of Republic of Serbia is prescribed a decree about noise indicators, limits, methods for assessing indicators of noise, disturbance and adverse effects of environmental noise [12]. The limits of noise at open area, defined in the mentioned decree are:

1. Areas for recreation, hospital zones and rehabilitation, cultural and historical sites, large parks, 50 dB (in the night 40 dB)
2. Tourist zone, camps and school zone 50 (at night 45 dB)
3. Residential zone 55 dB (at night 45 dB)
4. Business and residential zones, commercial and residential zone and playgrounds 60 dB (at night 50 dB)
5. City center, craft, trade, administrative and administrative area with apartments, the area along the highway, 65 dB (at night 55 dB).

Fig 1. clearly showed that noise levels in all cases are higher than the limit values for residential zones (55 dB). For the measuring points without green barriers the noise levels exceeded the limit values of 65 dB (on the city center, craft, administrative and administrative area with apartments). However, for the measuring points with green barriers, noise levels are lower than limit values of 65 dB. These facts indicate that green barriers are very effective in noise reductions, in order from 5 to 10 dB, that is very significant for human health.

CONCLUSION

The noise level reduction from 5 to 10 dB, in the presence of green barriers, points to necessity of placing green barriers along the streets with frequent traffics, wherever it is possible. Because of that, it is necessary to increase the existing green barrier. For example the new trees and low-growing plants could be planted between the existing lines of trees. All of here proposed measures lead to noise level reductions, and improvement of the quality of life.

Acknowledgements

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MUNICIPAL SOLID WASTE TREATMENT IN THE WORLD

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ABSTRACT

This review study deals with an overview of municipal solid waste and the contribution that plastics of various types make to it. Recycling of plastics is discussed, with a concentration on postconsumer plastics-those that have served their intended use. It is discussed if it is more effective to manufacture new plastic material or recycle used, which is more economical.

Key words: municipal solid waste, energy recovery, recycling of plastics.

INTRODUCTION

Concerns about municipal solid waste (MSW), defined by the U.S. Environmental Protection Agency as including residential, institutional, office, and commercial waste, but not including construction and demolition debris, wastewater treatment sludge, and industrial waste, [1] stem from three main considerations. One is the amount of space occupied by the waste-space that therefore is not available for other uses. Another is the resources that are “wasted” when materials are sent to disposal. The third concern is the health and environmental impacts associated with emissions from the waste, either during or after disposal.

In the United States are generated 250 million tons of MSW in 2011-six million tons less than generated in 2007, which was a peak year for waste generation. Excluding composting, 66.2 million tons of MSW were recycled, an increase of 3 million tons from 2007. This is a 5 percent increase in recycling of MSW. The tons of food waste and yard trimmings recovered for composting were 20.7 million tons in 2011 compared to 21.7 million tons in 2007. This is a 5 percent decrease in food waste and yard trimmings recovered for composting. The recovery rate for recycling (including composting) was 34.7 percent in 2011, up from 33.1 percent in 2007. [1]

MSW generation in 2011 declined to 2.20 kg per person per day. This is a decrease of 6 percent from 2007 to 2011. The recycling rate in 2011 was 3 kg per person per day compared to 1.6 kg per person per day in 2007. Discards sent for combustion with energy recovery decreased about 12 percent from 0.3 kg per person per day in 2007 to 0.12 kg per person per day in 2011. Discards sent to landfills after recycling and combustion with energy recovery declined to 1.2 kg per person per day in 2011. This is a decrease of 7 percent from 2007 to 2011. [1]

Fig.1 shows a decrease in MSW generation in recent years. Fig.2 shows an increase in recycling over time. The state of the economy has a strong impact on consumption and waste generation. Waste generation increases during times of strong economic growth and decreases during times of economic decline.

Figure1. Generation of municipal solid waste in the United States [1]

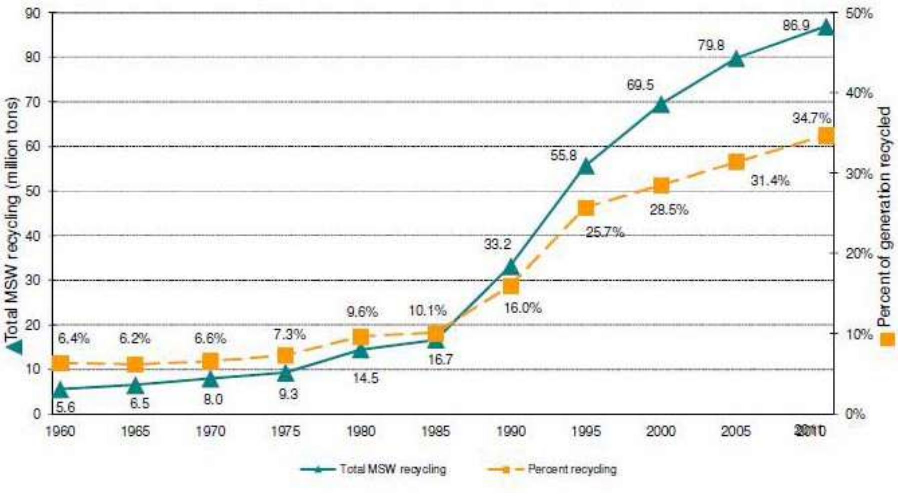

Figure 2. Recycling of municipal solid waste in the United States [1]

RESULTS AND DISCUSSION

Plastics account for only about 11.3 percent of materials in the U.S. MSW stream by weight (Fig. 3) but this proportion continues to increase. [1,2]

A breakdown, by weight, of the MSW materials generated in 2011 is provided in Figure 3. Paper and paperboard made up the largest component of MSW generated, while other miscellaneous wastes made up 3.3 percent of the MSW generated in 2011. As can be seen in Fig. 4-5. where each material as a percent of total recovery and total discards, respectively. As a percent of total recovery, paper and paperboard make up over half of the materials recovered. Yard trimmings comprise the next largest portion of total materials recovery. All other materials account for less than 10 percent each of total recovery. Food waste is the largest material in discards as it can be seen in Fig.5.

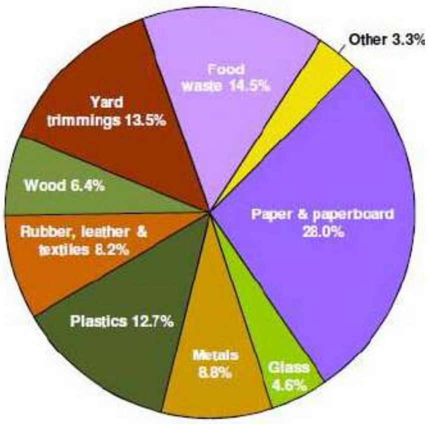

Figure 3. Materials in U.S. MSW 2011. [1,2]

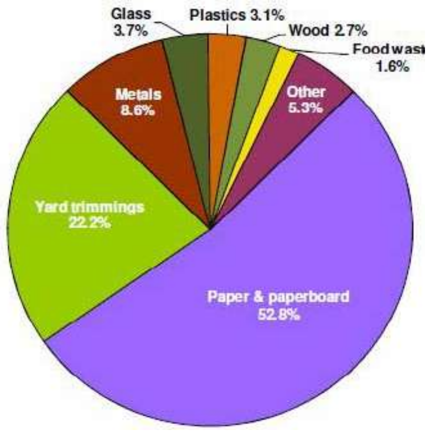

Figure 4. Materials Recovery in MSW, 2011 87 Million Tons [1,2]

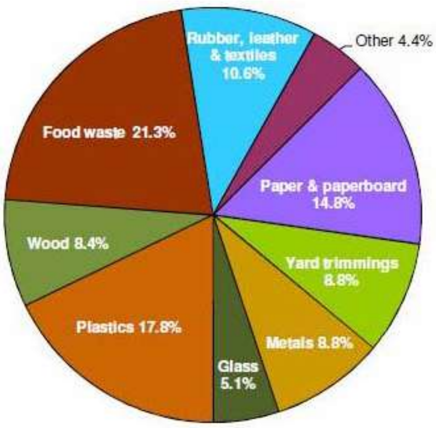

Figure 5. Material Discards in MSW, 2011, 164 Million Tons (after recycling and composting) [1,2]

As the MSW recycling pays itself off rather effectively, if it comes to the shortage of it, the MSW would have to be imported from the other continents, and that would increase the price of recycled product, due to the raw materials transport costs.

Historical trends in plastics recycling, in other words generation and recovery, amounts and rates in the United States are shown in Fig. 6. These values include feedstock recycling, but do not include energy recovery.

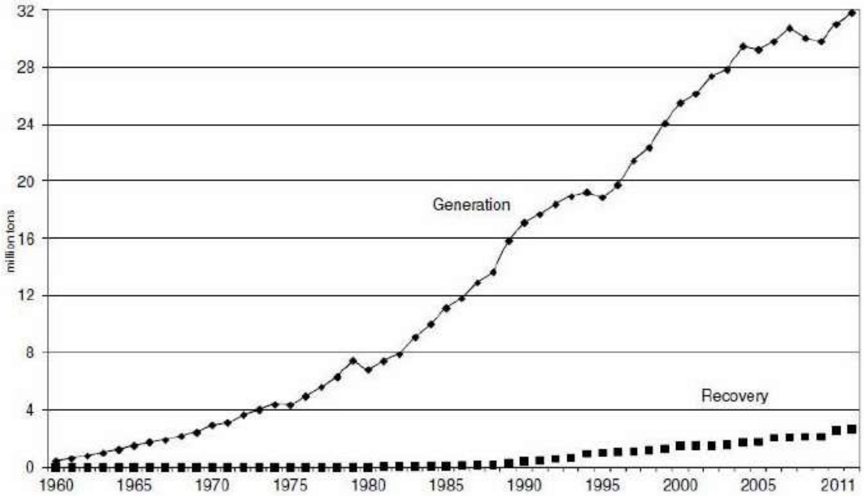

Figure 6. Plastics generation and recovery, 1960 to 2011 [1,2]

Plastics made up an estimated 390,000 tons of MSW generation in 1960. The quantity has increased relatively steadily to 31.8 million tons in 2011. As a percentage of MSW generation, plastics were less than one percent in 1960, increasing to 12.7 percent in 2011. While overall recovery of plastics for recycling is relatively small – 2.7 million tons, or 8.3 percent of plastics generation in 2011– recovery of some plastic containers is more significant. Polyethylene terephthalate(PET) bottles and jars were recovered at a rate of 29 percent in 2011. Recovery of high-density polyethylene (HDPE) natural bottles was estimated at 28 percent in 2011. Discards of plastics in MSW after recovery were 29 million tons, or 18 percent of total MSW discards in 2011. [1,2]

On the other hand, The European plastics industry has registered export growth (+6% and +5% on average per year between 2005 and 2011 for production and converting respectively), with a constant trade surplus (€20 billion in 2011, 61% attributable to the production of plastics). [3]

The plastics supply chain is significantly developed in Italy, "worth" about 11,000 companies (18% of the EU total), nearly 160,000 employees (11%) and a turnover of approximately € 34 billion. Exports of plastics and machinery manufacturing have returned to growth since 2009, and the balance of trade has remained positive. The only exception is the production of plastics (- € 3.5 billion in 2012), in as much as our country, the consumption of plastic raw materials (6.8 million tons) peculiarly exceeds production (4.3 million tons). [3-5]

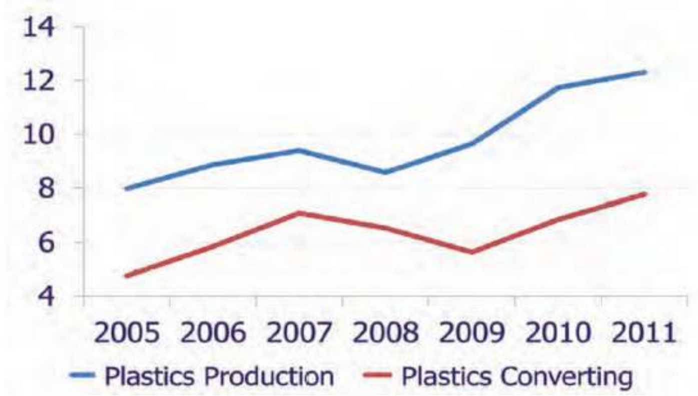

Figure 7. Details of the trade balance of plastics production and plastics converting in the EU (in billion euros), 2005-2011 [3]

CONCLUSIONS

Plastics are one of the primary entirely man-made materials not found in nature, although they are comprised of organic substances. Plastics are made, in fact, of raw materials that include petroleum (by-products of its refining process), natural gas, carbon, common salt and other natural products. Starting in the 1950s, worldwide production of plastics showed an average annual growth rate of 8.7%, increasing nearly nine-fold since the 1970s, Fig.8. [3]

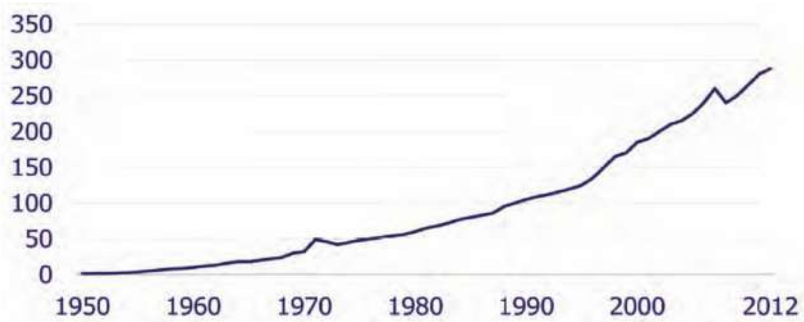

Figure 8. World production of plastics (million tons), 1950-2012 [3]

The demand and production of plastics are uniformly divided between the main macrogeographic areas, with a growing role of the emerging economies, Fig. 9.

However, straightforward comparisons between amounts of plastic recycled from municipal solid wast cannot be made, either, since definitions differ. Some, but not all, of the material identified in Europe as belonging to the distribution and industry, agriculture and electrical and electronics sectors, for example, would be classified as part of municipal solid waste in the United States.

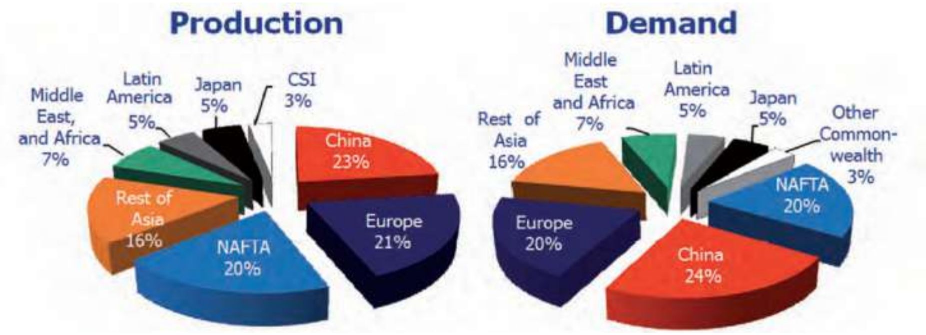

Figure 9. Global production and demand of plastics by geographical area (percentage of total), 2012 [3-5]

In the future, the increase in worldwide demand for plastics will continue at a high rate as the economy and population also grow. According to our simulation, by 2025. global production of plastics will exceed the threshold of 300 million tons to meet growing demand. Furthermore, demand in Africa, Latin America, the Middle East and China will grow by 54% (from 101 to 156 million tons), exceeding that in Europe and the United States (110 million tons) [3]. Plastics could provide a substantial contribution to the sustainability of major global challenges connected with an increase in population, climatic-environmental changes and growing scarcity of natural resources.

Acknowledgments

Authors are grateful to the Ministry of Education and Science of The Republic of Serbia for financial support (Project 172013).

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CENTER FOR SEPARATION OF MUNICIPAL WASTE IN SOUTH BANAT

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ABSTRACT

Waste generation is a result of the economic activities of each family and person. With the rise of social standards of the population and industrial development of a country, there is an increase in the amount of waste. In order to improve the quality of the environment, the local self-government in the Republic of Serbia is faced with the necessity of finding sustainable methods of waste management. The aim of this paper is to present the project activities center for waste separation for municipalities of South Banat: Vršac, Bela Crkva, Alibunar and Plandište. The project was developed by a professional team of the company for engineering services and mediation "ENVI TECH" and in accordance with the National Waste Management Strategy, the Waste Management Law, other laws and regulations of the Republic of Serbia and the EU Directives relating to waste management.

Key words: waste management, center for waste separation, recycling.

INTRODUCTION

Laws and implementing regulations issued by the Government of the Republic of Serbia in 2009., in accordance with the EU, defined a new relationships in waste management. Waste management is an activity of public interest. To improve the situation and brought into line with the statutory provisions, it is necessary to analyze the situation on the ground and to propose appropriate technical solutions. Solutions must help to local governments in Serbia to agree with the basic strategic orientation, organized and well managed waste management processes and operations that make up the system and allow the progress that this job brings with it, especially in regard to the protection and improvement of environmental quality[1,2].

The paper shows the project activities center for waste separation for municipalities of South Banat: Vršac, Bela Crkva, Alibunar and Plandište. In order to improve the current situation, a professional team of the company for engineering services and mediation "ENVI TECH" was hired for development planning and programming document called "WASTE MANAGEMENT PLAN" to assist in establishing an efficient waste management system. Management of waste generated as a result of the activities of the population in each of the municipalities in the area entrusted to the utility company DP "2. October".

This project provides an overview of the current situation, analyzed the practice and made the interpretation of the important documents and regulations. It proposes reasonable and feasible solutions that include a wide range of measures to improve waste management, starting with the reduction of waste at source, separate collection, recycling and other methods of recovering materials from waste, to secure and environmentally sustainable final disposal. The necessary accompanying measures are recommended, educational and promotional activities, as well as monitoring of the system. All of analysis and the suggested solutions are based on the National Waste Management Strategy, the Waste Management Law, laws and regulations of the Republic of Serbia relating to this waste management, as well as the EU Directives[1,3].

REGION LOCATION AND ANALYSIS OF THE CURRENT SITUATION

The area of southern Banat extends north - northeast from Belgrade. Besides the municipality of Vršac, Bela Crkva, Alibunar and Plandište, it includes Pančevo, Opovo, Kovin and Kovačica. National Waste Management Strategy (waste management region defined by the first four municipalities) estimated total production of about 70 tons of waste per day. Administrative, industrial and regional center of this part of the region is Vršac. In four municipalities in southern Banat limited to the state border with Romania to the east, the river Danube to the south, the western border makes the sandstone Deliblato, and northern side boundary is channel Brzava (Fig.1) [4]

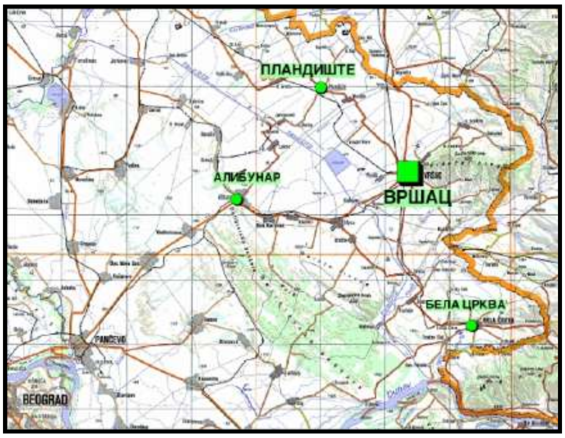

Figure 1. South Banat area

On the territory of the South Banat live 110 217 inhabitants, of which 60,104 live in the urban area and 50 113 in the village. Municipality of Vršac, or "2. October", has in recent years undertaken a number of measures to improve the operation of waste management, mainly of a technical nature, and the city dump to some extent repaired, leading to a state of reduced environmental impact in the immediate environment. The waste is compacted with bulldozers and covered with earth material, and the technological measures are introduced to extract certain types of waste. Part of the repaired area of the landfill is fenced and equipped with facilities for minimization - pressing and baling of certain types of waste (paper, plastic). In this area begins the separation of metal waste and separate the separate storage of old batteries (Fig.2). At the dump is done and the occasional shredding waste of green space and larger pieces of wood.

Figure 2. Stations to collect recyclables

These measures have not been sufficient to prevent the negative impact of decades of waste disposal, and access to engineering design and technical measures, in accordance with the National Waste Management Strategy and the regulations that apply to this area. "2.October" initiated the preparation of technical documentation for the rehabilitation of the landfill, based on modern principles and protection measures, as well as for construction and landfill equipment for regional level waste management, what is provided by the city's landfill site in Vršac. At the same time the access and the creation of conditions for the minimization of waste prior to its final disposition.

Technological project for sorting-recycling center aims to define the technological requirements and concepts of operation before proceeding to the design and selection of the technical elements of the machinery, equipment, facilities, installations and infrastructure.

Most of the waste transported to the municipal landfill makes heterogeneous wastes of different composition: household waste, organic waste, packaging waste, plastic scrap, metal scrap. At the landfill is bringing the remains of hazardous waste. Waste in landfills is in chaotic embankment, mixed with soil and rubble, with no possibility for any subsequent sorting. [1,4,5]

Morphological composition of municipal waste in the municipalities of South Banat region is shown in Fig.3.

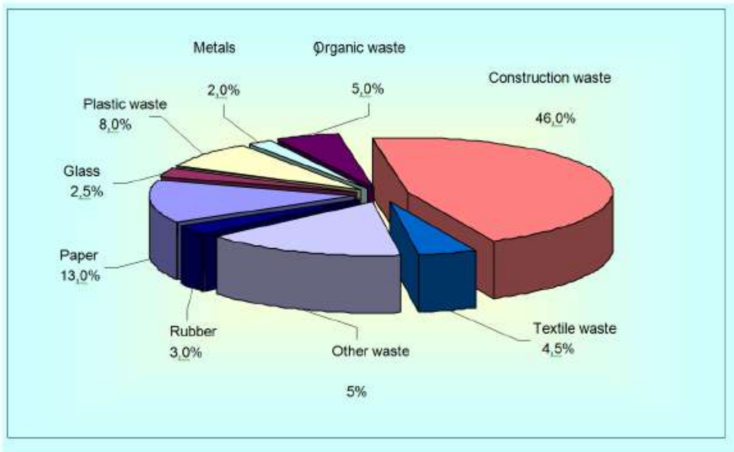

Figure 3. Cumulative morphological composition of waste for municipalities Vršac, Plandište, the White Church and Alibunar

REGIONAL RECYCLING CENTER

Regional Recycling Center is a complex technological establishment, located within the complex of the landfill and consists of several organizational units:

1. Plato for making waste,
2. Place for separation of larger pieces,
3. Place for mechanical and manual separation,
4. Space for harvesting and storage,
5. Handling space with scales and sanitation facilities and
6. Administrative space.

The complex is paved, fenced and equipped with all necessary supporting installations (water, sewer, fire protection, sanitary protection, lighting, power supply, telecommunications). Hale was built as a standard structure to concrete foundations.

Equipment for the separation of the waste consists of an entrance area where the transported waste, conveying the power grids equipped with a magnet to extract some metals, power grids, where the waste is separated by fractions of different size, conveyor belts for manual separation of certain materials, boxes for the collection of separated waste of space for baling and temporary storage.

Technological scheme of the recycling center is shown in Figure 4. The system consists of the subsystems of the primary and secondary separation plant for baling and wrapping, works for composting (suspended operations), storage, handling and operational facilities, internal transport and landfill. Transport of separated waste to the recycling center is the charge of the recycling center. The transport is carried out mostly by trucks or special vehicles, and it depends on the material that is collected and the amount that is collected in a given time.

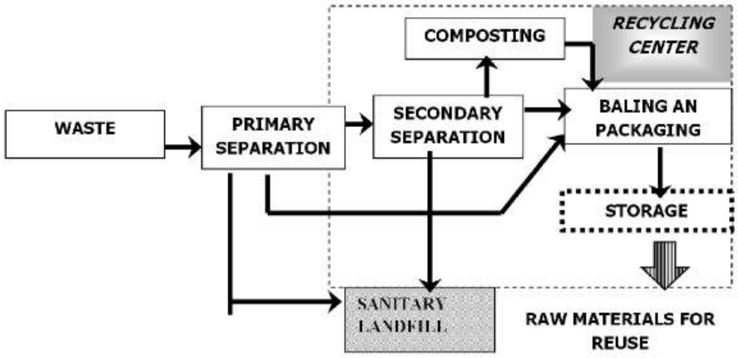

Figure 4. Technological scheme of regional recycling center

Wastes which are not previously undergone a process of separation of recyclable materials need to be further processed upon the reception in a circle recycling center. This operation is performed within the plant. Featured items by type of material from which they were made are brought to the pressing and baling, and the rest of the sanitary landfill.

The composting operation is planned for later development phase center. It is related to the treatment of organic waste.

Featured secondary raw materials are transported for further processing in the form of pressed bales, bound special ribbon or wire and packed on pallets. The exception is glass that is transported to the processing of special open containers. The remaining waste that is disposed of in a permanent disposal in a landfill is compressed before leaving the facility for separation.

Separated and baled secondary materials are stored in the open or closed storage, depending on the type of waste. At the exit of waste storage is measured and recorded.

In addition to technological equipment for secondary separation, the standard equipment of the recycling center are: buckets and garbage containers of various sizes, checkweigher, special vehicles and trucks to transport waste containers for automatic operation of machines and equipment, handling industrial trucks (forklifts) and other maintenance equipment.

TECHNOLOGICAL PROCESS IN RECYCLING CENTER

Regional Recycling Center treats all waste generated in the area of Vršac, Bela Crkva, Alibunar and Plandište. All other waste each municipality is treated separately or at the contract to a higher level, regardless of this. It is therefore important that each municipality develop their own waste management plan.

Waste sorting and treatment of waste municipalities in southern Banat - Vršac, Bela Crkva, Alibunar and Plandište consists of the next elements: transporter - accept municipal waste; grids - sorting waste by size; transporter - receiving the sorted waste under the drum; transporters - transport waste through the sorting cabins; cabins for manually selecting of waste; transporter - accept waste from sorting cabin; transporter - transport of waste to the ballistic separator; ballistic separator; air separator; transporter - transport waste to the plant for harvesting and baling plant.

The process of sorting and treatment of waste consists of several functional areas: Zone 1 - the delivery of waste to the receiving hopper; Zone 2 - Sorting of waste; Zone 3 - storage of waste (secondary raw materials); Zone 4 - disposal of other waste; Zone 5 - manipulative plateau. Manipulative plateau represents administrative and communication zone and make it a porter's lodge, local roads, workshops, parking and green space. [4,5]

CONCLUSION

In the Republic of Serbia until recently was not mindful of the importance of controlled and organized disposal of municipal waste collection, transport and final disposition of garbage. Dumps are formed in places that are inconveniently close to the village and on such areas that and represent an initial polluters of the enviroment because any kind of technological measures for waste disposal was not performed. Today, the fully prevalent idea is that waste should not be destroyed, but it should be used. In accordance with European legislation, a modern approach to the problem of waste disposal involves management system, which consists in reducing (avoiding, minimizing), utilization (recycling), reuse, treatment and disposal of waste in an environmentally way.

Concept of Project document "WASTE MANAGEMENT PLAN FOR THE REGION SOUTH BANAT" is made in accordance with the National Waste Management Strategy. This paper, based on the principles of mutual interests, sets new standards in this area: the long-term development concept, the application of new knowledge and technologies; solid profitability in many aspects; market orientation; good adaptability and ability to hire more people, educational nature; improving environmental practices.

Although the inter-municipal agreement concluded in 2008 when the SO VRŠAC adopted regional and municipal waste management plan and have all the necessary documentation, implementation of the project began on March 15, 2014. The company "Hyundai Energy" from South Korea will invest 14 million euros in the construction of modern sorting - recycling center at the landfill in Vršac. The Korean company will implement the project with a social utility company "2. October" The first phase of the project envisages the construction of a building in which, initially, will be housed equipment for sorting and recycling 24 t of waste collected only from the municipality of Vršac, while the subsequent investments and on the other three municipalities to expand the processing capacity of 100 t/day. The facility will be an area of about 2000 square meters and will be divided into two parts. In the first area will work sorting line, and the second will be installed recycling equipment. The implementation of the project and of the Regional Centre, the Republic of Serbia will get better the environment, and will make another step towards the achievement of objectives in the field of waste management [4,6,7] .

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ALLERGENIC TREE SPECIES IN THE GREEN AREAS OF SCHOOLS IN SOME SUBURBS OF BELGRADE

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ABSTRACT

Pollen allergies represent seasonal diseases that are related to the blooming time of allergenic plants. Pollen of various grasses, trees and weeds causes allergic reactions in sensitive individuals. School-aged children are particularly sensitive and there is a growing number of those who suffer from allergies caused by pollen from various plants. Due to that reason, the presence of tree species whose pollen has allergenic characteristics in the green spaces of schools in some of the suburbs of Belgrade has been analysed in this paper. It was spotted that the allergenic tree species are present in significant number in the researched areas. It has also been recorded that the majority of species that are present in all of the researched areas are *Cedrus atlantica* (Endl) Man. ex Carr.*, Thuja sp., Acer platanoides* L.*, Tilia sp., Betula pendula* Roth.

Key words: Pollen, schools, suburbs, tree species, green areas.

INTRODUCTION

The composition of air, besides the inorganic components such as nitrogen, oxygen, carbon dioxide and other gases, includes the organic components, such as pollen of various plant species. The number and composition of the pollen grains in the air are affected by climate, qualitative and quantitative composition of the vegetation cover, weather conditions and some chemical factors (D'amato et al, 2007, Ilić, 2008, Nestorović et al, 2011). Pollen of some plant species possesses allergenic properties. This implies that there are allergenic compounds in the structure of pollen grain which can cause an allergic reaction in the human body. This fact is one of the three main preconditions that plant species must have in order to be considered as an allergen. The other two preconditions are plant's adaptation to wind pollination and production of huge amounts of pollen (D'amato et al, 2007, Nestorović et al, 2011). All allergenic species are divided into three groups: trees, grasses and weeds. In Serbia there are three maximum concentrations of pollen in the air: an early spring – anemophilic trees and shrubs, summer – grasses, and summer-autumn – herbaceous biennial weeds (www.nspolen.rs). Besides the individual pace of plant's pollination, it is considered that the meteorological conditions are the main factor that determines the content and dissemination of pollen in the air (Puc & Wolski, 2002).

An allergy is an inappropriate response of the immune system to the usual substances of the environment that otherwise do not harm health. Pollen allergies of pollinosis represent seasonal diseases that are related to the blooming time of allergenic plants. Pollen of various grasses, trees and weeds causes allergic reactions in sensitive individuals. The most common allergic diseases are rhinitis, allergic bronchial asthma, allergic conjunctivitis, eczema, urticaria-hives (www.who.int, www.astma.rs).

School-aged children are particularly sensitive and there is a growing number of those who suffer from allergies caused by pollen from plants. The most common allergic disease in the world is allergic rhinitis which affects 10-25% of world population, with a high prevalence of school-aged children and adolescents. According to Živković (2002), the incidence of asthma in children in Serbia is 6%, allergic rhinitis 11,46% and eczema 14,27%. Air pollution also has a significant influence on both the airways of affected person and the mere allergens (Bogić et al, 2000).

Green areas of schools have multiple functions such as environmental, sanitary, aesthetic, educational and recreational (Gačić i Stavretović, 2008). Given that the main beneficiaries of these areas are children, it is necessary to pay special attention to this category of green areas of cities and suburbs. School-aged children are particularly vulnerable users of green spaces. Since children spend most of their time in schools and schoolyards, the research of the presence of allergenic species in these areas is very important. Very often children use the school yards for sports and playing and after class activities, so they are more exposed to the negative effects of allergenic species that are found there.

The aim of this paper is to determine the presence of allergenic tree species in the green areas of schools in some suburbs of Belgrade. Thus the condition of green areas of school yards will be determined regarding the prevalence of allergenic species, in order to be able to monitor future tendencies of change in the state. Also, conducted research should draw attention towards the issue, so that the future planning, design and maintenance are organised to implement using of species that do not have allergenic properties of pollen.

MATERIALS AND METHODS

This paper has analysed the presence of tree species in green areas of six school in some suburbs of Belgrade: Borča, Zemun polje, Surčin, Obrenovac, Železnik and Sremčica. Residential areas have been selected to form the semicircle around the city of Belgrade. The number of tree species and specimens in the yard of each researched school has been recorded, and then the number and percentage of species and specimens that have allergenic properties of pollen have been determined. The percentage of allergenic tree species has been determined in each researched area in particular, in regard to the total number of recorded tree species. Determination of the tree species has been conducted according to Vukićević (1996). Allergenic tree species have been determined according to Igić et al, (2005) and Nestorović et al, (2011). Recorded allergenic tree species have been divided to species whose pollen alergenic properties are: 1. very weakly expressed, 2. weakly expressed, 3. moderate, 4 moderate to very expressed, 5. very strongly expressed (D'amato et al, 2007, Nestorović et al, 2011).

The results of research provide conclusions about the presence of allergenic tree species, the most prevalent families in the studied area, and the percentage of allergenic tree species with regard to the total number of recorded tree species has been determined. By comparing the results obtained from the researched areas, it helped to identify the most prevalent allergenic tree species found in the green areas of school, as well as which of the researched areas has the highest number of allergenic tree species.

RESULTS

The researches have been conducted on the green areas of these schools:

1. Elementary School „Rade Drainac" Borča;
2. Elementary School „Ilija Birčanin", Zemun polje;
3. Elementary School „22. oktobar", Surčin;
4. Elementary School „Jefimija", Obrenovac;
5. Elementary School „Braća Jerković", Železnik;
6. Elementary School „Duško Radović", Sremčica.

In all six researched green areas, a total number of 39 tree species with a total of 540 individuals has been recorded. Out of this number there are 14 species from a subsection of *Pinophyta*, and 25 species from a subsection of *Magnoliophyta*. The total number of tree species, which possess allergenic properties of pollen to some extent, recorded in all six studied localities is 18 with a total of 396 specimens amounting to 73,3% from the total number of recorded specimens. If we observe the percentage of allergenic tree species (18) compared to the total number of recorded tree species (39), in all localities this percentage is 46,1%. Recorded allergenic tree species and allergenic properties of their pollen are shown in chart 1 (fig. 1) and table 1.

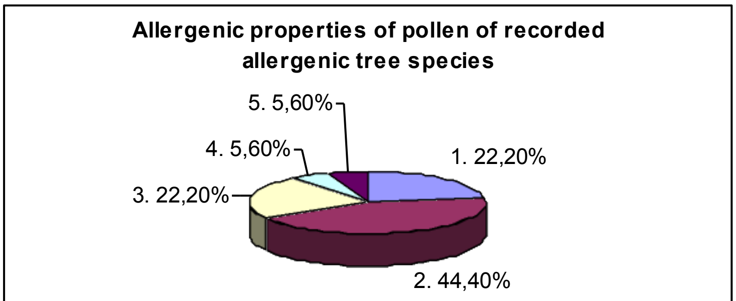

Figure 1. Allergenic properties of pollen of recorded allergenic tree species

1. Very weakly expressed allergenic properties of pollen, 22,20% (*Juglans regia* L., *Platanus x acerifolia* (Ait.) Willd., *Fraxinus ornus* L., *Fraxinus angustifolia* Vahl.),
2. Weakly expressed allergenic properties of pollen, 44,40% (*Acer negundo* L., *Pinus nigra* Arn., *Cedrus atlantica* (Endl) Man. Ex Carr, *Populus nigra 'Italica'* L. var. Du Roi, *Ulmus minor* Mill., *Acer pseudoplatanus* L., *Pinus silvestris* L., *Abies concolor* Lindl.et Gord.),
3. Moderate expressed allergenic properties of pollen, 22,20% (*Thuja orientalis* L., *Thuja occidentalis* L., *Acer platanoides* L., *Taxus baccata* L.),
4. Moderate to very expressed allergenic properties of pollen, 5,60% (*Tilia sp.*),
5. Very strongly expressed allergenic properties of pollen (*Betula pendula* Roth.).

Table 1. Allergenic tree species recorded in researched green areas

	Number of allergenic tree species in a locality						Total number of allergenic tree species in all localities
Locality	„Rade Drainac"	„Ilija Birčanin"	„22. Oktobar"	„Jefimija"	„Braća Jerković"	„Duško Radović"	
Total number of specimens in each locality	89	64	70	120	135	62	
Allergenic species							
1. *Cedrus atlantica* (Endl) Man. Ex Carr	2	6	2	9	38	10	67
2. *Acer platanoides* L.	13	2	15	16	3	7	56
3. *Tilia sp.*	13	17	5	7	10	1	53
4. *Thuja orientalis* L.	3	4	29		5	7	48
5. *Betula pendula* Roth.	9	6	3	18	4	6	46
6. *Pinus nigra* Arn.	1	2	2		15	16	36
7. *Platanus x acerifolia* (Aid.) Willd.	15	10			3		28
8. *Abies concolor* Lindl.et Gord.	1	1		7		3	12
9. *Thuja occidentalis* L.			2	6		3	11
10. *Populus nigra 'Italica'* L. var. Du Roi		10					10
11. *Fraxinus angustifolia* Vahl.				4		3	7
12.*Ulmus minor* Mill.			5	1			6
13. *Fraxinus ornus* L.	5						5
14. *Juglans regia* L.		2			1		3
15. *Acer pseudoplatanus* L.	3						3
16. *Acer negundo* L.			1		2		3
17. *Taxus baccata* L.					1		1
18. *Pinus silvestris* L.						1	1
Σ=	65	60	64	68	82	57	396

From the total number of 18 recorded species with allergenic properties of pollen, 4 species (22,2%) have very weakly expressed allergenic properties (*Juglans regia* L.,(family *Juglandaceae*); *Platanus x acerifolia* (Ait.) Willd., (fam. *Platanaceae*); *Fraxinus angustifolia* Vahl., *Fraxinus ornus* L., (fam. *Oleaceae*)) (chart 1). 8 species (44,4%) have weakly expressed allergenic properties of pollen, (*Acer negundo* L., (fam. *Aceraceae*); *Pinus nigra* Arn., (fam. *Pinaceae*); *Cedrus atlantica* (Endl) Man. ex Carr, (fam. *Pinaceae*); *Populus nigra 'Italica'*L. var. Du Roi, (fam. *Salicaceae*); *Ulmus minor* Mill., (fam. *Ulmaceae*); *Acer pseudoplatanus* L., (fam. *Aceraceae*); *Pinus silvestris* L., (fam. *Pinaceae*); *Abies concolor* Lindl.et Gord.(fam. *Pinaceae*)), while 4 species (22,2%) have moderately expressed allergenic properties of pollen (*Thuja orientalis* L., *Thuja occidentalis* L., (fam. *Pinaceae*); *Acer platanoides* L., (fam. *Aceraceae*); *Taxus baccata* L. (fam. *Pinaceae*)). Moderate to very expressed allergenic properties have been recorded at species (*Tilia sp.*, (fam. *Tiliaceae*)) (5,6%). Also, 1 allergenic species (5,6%)

have very strongly expressed allergenic properties of pollen (*Betula pendula* Roth.(fam. *Betulaceae*)).

In the yard of the elementary school „Rade Drainac" in Borča, there is a total of 19 tree species of which 10 species (52,6%) have the characteristics of allergens to a certain extent. It was recorded a total number of 89 specimens, of which 65 tree trunks with allergenic properties of pollen, which amounts to 73,03% (table 1). According to the number of trees, the most common is the species *Platanus x acerifolia* (Ait.) Willd.(15 trunks), while the species *Pinus nigra* Arn. and *Abies concolor* Lindl.et Gord. are present with one specimen each. Species *Betula pendula* Roth. whose pollen is a major inducer of allergic reactions, is present with 9 tree trunks in this area. There has also been spoted 13 specimens of *Tilia sp.* which can cause moderate to strong allergic reaction.

In the green area of the elementary school „Ilija Birčanin" in Zemun, 13 tree species have been recorded, of which 11 species (84,6%) is allergenic. There have been spotted 60 specimens with allergenic properties of pollen (93,7%) from the total number of 64 specimens. The most common allergenic tree species are *Tilia sp.* with 17 trunks, while the species *Abies concolor* Lindl.et Gord. is present with one specimen. There have also been spotted 6 trunks of the species *Betula pendula* Roth.

In the yard of the elementary school „22. Oktobar" in Surčin 12 tree species have been spotted, from which 9 species (75%) have allergenic properties to some extent. 70 tree trunks have been noted of which 64 species (91,4%) have more or less allergenic properties of pollen. Some trees that have been recently planted and belong to the allergenic species (*Cedrus atlantica* (Endl) Man. ex Carr., *Thuja sp.,Acer sp.*), only in the years to come will reach their peak in tearms of allergenic potential. There has been recorded the presence of the 29 tree trunks of the species of *Thuja orientalis* L., which is the most numerous allergenic species in this area while the allergenic species of *Acer negundo* L. is the least prevalent (1 trunk) (table 1). There have also been recorded 3 specimens of the species *Betula pendula* Roth. and 5 specimens of the family *Tilia sp.*

Elementary school „Jefimija" in Obrenovac exists and works from 2004. and so accordingly, the trees in the school yard are very young. On the green area of the school there are 18 tree species recorded, of which 9 species (50%) have allergenic potential. The total number of recorded tree trunks is 120, of which 68 trunks (57,5%) have more or less expressed allergenic properties of pollen. Species *Betula pendula* Roth. is the most numerous allergenic species in this area (18 specimens) while the species *Ulmus minor* Mill. is present with one specimen. Species *Tilia sp.* is present in this area with 7 tree trunks (table 1).

On the green area of the elementary school „Braća Jerković" in Železnik, 18 tree species have been recorded, of which 10 species (55,5%) have allergenic properties. The existence of 135 tree trunks have been recorded, of which 82 trunks (60,7%) have allergenic properties. According to the majority of specimens (31), *Cedrus atlantica* (Endl) Man. ex Carr stands out among allergenic species. The least prevailed allergenic species in this area are *Taxus baccata* L. and *Juglans regia* L. (one specimen each). The main species that cause allergic reactions, *Betula pendula* Roth., is present in this area with four specimens, while the species of the genus *Tilia sp.* are present with 10 specimens (table 1).

On the green surface of the elementary school „Duško Radović“ in Sremčica, there are 14 tree species, of which 10 species (71,4%) have pronounced allergenic characteristic to some extent. 57 (91,9%) allergenic tree trunks have been recorded from the total number of 62 trees (table 1). There have been recorded 16 specimens of the species *Pinus nigra* Arn. which makes it the most numerous allergenic species in this area. There has also been recorded one specimen of the species *Pinus silvestris* L. and *Tilia sp.* while *Pinus silvestris* L. и *Tilia sp*. is present with 6 specimens.

DISCUSSION

Modern way of life of people in the environment that is contaminated to a large degree, leads to an increase in the number of patients suffering from some kind of allergies, including allergies from pollen. By fat the greater percentage of population in the city area suffers from pollinosis than it is the case with population outside the city (Puc, 2003).

School yards are the places where children spend most of their time during the day, thus constant monitoring of green surfaces and areas and tracking the presence of allergenic species and tendencies are of great importance. Besides trees, grasses and weeds are also allergenic species. Stavretović et al, (2006) recorded the presence of highly allergenic species of *Ambrosia artemisiifolia* L. in different types of green areas of Belgrade. This species is present in some sports and recreational surfaces, the surfaces of residential areas and park areas. Besides the species of *Ambrosia artemisiifolia* L. in all specified areas which are frequently used by children apart from their school yards, there are other species of grasses and weeds which are strong allergens as well (Stavretović et al, 2010, Stevanović et al, 2010, Stavretović et al, 2011, Petrović et al, 2013).

In Serbia, 24 species, whose pollen has allergy causing effects, are monitored: hazel, alder, yew, cypress, elm, poplar, maple, willow, ash, birch, hornbean, sycamore, walnut, oak, pine, hemp, grasses, lime, plantain, sorrel, nettles, pigweeds, wormwood and ragweed (Nestorović et al, 2011, www.sepa.gow.rs). Pollen of the species of *Betula pendula* Roth. can occur in very high concentrations in the air – up to 5000 pollen grains/ m^3 of air (Puc, 2003). Over 90% of people who suffer from pollinosis are allergic to the pollen *Betula pendula* Roth. Milkovska et al (2006) allege that 19% of people with allergic respiratory manifestations in Skoplje are allergic to the pollen of *Betula pendula* Roth. The length of pollination of *Betula pendula* Roth. in Belgrade was 71 days during 2012., and for *Tilia sp.* it was 67 days in the same year (www.sepa.gov.rs).

In all researched areas, the total number of 39 tree species have been recorded with the total of 540 specimens. 14 species from this number are from the subsection of *Pinophyta*a, and 25 species are from the subsection of *Magnoliophyta*. From the total number of 39 recorded tree species, 18 species are allergenic tree species. The largest number of recorded allergenic tree species belong to the family of *Pinaceae (*8 species), family of *Aceraceae (*3 species), family of *Oleaceae* (2 species), while the rest of the 6 families (*Juglandaceae*, *Platanaceae*, *Ulmaceae*, *Tiliaceae*, *Betulaceae, Salicaceae*) is present with 1 species each.

8 out of 18 recorded allergenic tree species had weakly expressed allergenic properties of pollen.

The largest number of recorded allergenic species (8 out of total 18) had weakly expressed allergenic properties of pollen. In researched areas there are 176 conifer trees with allergenic properties, while the number of deciduous trees is 212. In all researched localities, the majority of tree trunks are in a good health condition, without the major damage caused by pests and diseases.

The largest number of specimens (93,7%) which has allergenic properties to a certain extent, has been spotted in the yard of elementary school „Ilija Birčanin" in Zemun polje, while the lowest percentage (57,5%) of specimens whith allergenic properties has been recorded in the yard of elementary school „Jefimija" in Obrenovac. It has been noticed that the species *Cedrus atlantica* (Endl) Man. ex Carr*., Thuja sp., Acer platanoides* L*., Tilia sp., Betula pendul a*Roth. exist in all researched areas. The most common is the species *Cedrus atlantica* (Endl) Man. ex Carr. with the total number of 67 specimens (table 1). The total number of recorded tree trunks of *Betula pendula* Roth. is 46, while the species *Tilia sp.* is present with 53 trunks. Both species have expressive allergenic properties, and they are the main inducers of allergic reactions. The largest number of trunks of *Betula pendula* Roth. (18) has been spotted in the yard of the elementary school „Jefimija" in Obrenovac, while the largest number of trunks of *Tilia sp.* has been recorded in the yard of the elementary school „Ilija Birčanin" in Zemun polje.

CONCLUSION

Given that very often there is no green area located near the place of residence in the suburbs of the city, so in that case children usually use yards of their schools for socializing, sports and recreational activities. This fact indicates that children often spend their time in the school yard even after class activities, and are thus more exposed to the allergenic tendencies of species found in the school yard.

Allergenic tree species are present in a significant number in all researched green areas of schools. The total number of 39 tree species with the total of 540 specimens have been recorded in all six researched green areas of schools in the suburbs of Belgrade. The total number of tree species which possess allergenic properties to a certain extent is 18, which is the total of 396 specimens of trees. The largest number of specimens which possess allergenic properties to a certain extent is recorded in the yard of elementary school „Ilija Birčanin" in Zemun polje, while the lowest percentage of allergenic specimens has been recorded in the yard of the elementary school „Jefimija" in Obrenovac. The most numerous species is *Cedrus atlantica* (Endl) Man. ex Carr. with the total number of 68 specimens. The largest number of *Betula pendula* Roth. tree trucks (18) has been spotted in the yard of school „Jefimija" in Obrenovac, while the largest number of *Tilia sp.* trucks was recorded in the yard of elementary school „Ilija Birčanin" in Zemun polje.

The most frequent families to which recorded tree species belong are *Pinaceae* (6 species), the family of *Aceraceae* (3 species) and the family of *Oleaceae* (2 species). Even though it is impossible to completely avoid pollen, there are measures which could be used to reduce its allergy causing effect. Constant monitoring of schools green areas, their changes and tendencies, is very important and necessary. One of the most important measures is regular maintenance of green areas. Also, timely mowing the lawn is very important because it reduces the presence of pollen of grass and weed in the air. When designing green spaces of newly built schools in suburbs and villages across Serbia, as well as the reconstruction of existing green areas, species that do not have allergenic properties of pollen should be chosen.

In addition, during the maintenance of green areas of schools, ill, old, and in any way inappropiate tree should be successively changed with tree species that are not allergenic. Control and monitoring the state are of essential importance in the effective minimization of the negative impact of allergenic species and allow timely action in case of need for suppression of these species.

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CALCULATION OF WATER BALANCE FROM THE HYDRO-GEOLOGICAL PRESPA LAKE BASIN

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ABSTRACT

In this work the available hydro-meteorological, hydrological and hydro-geological data from three neighbors Countries: Republic of Macedonia, Greece and Albania were collected for Prespa Lake basin and selected for water balance calculation. The water balance calculations were carried out for hyro-geological catchments area using the specific discharge coefficient, specific coefficient of evapo-transpiration and specific coefficient of infiltration, for each geological structure

Key words: Prespa Lake basin, hydro-geology, water balance.

SYMBOLS

p_{CAV} – average specific coefficient of precipitation over the catchments area *(l/s/km²)*
Q_{pi} – quantity of precipitation over the each *(i)* geological structure (m^3/y)
A_G – geological catchments area (km^2)
Q_{Ri} – quantity of run-off from each *(i)* geological structure (m^3/y)
q_i – specific discharge coefficient from each *(i)* geological structure *($l/s/km^2$)*
Q_{ETi} – quantity of evapo-transpiration from each *(i)* geological structure *(m^3/y)*
e_{ETi} – specific coefficient of evapo-transpiration *($l/s/km^2$)*
Q_{Ii} – quantity of infiltration from each *(i)* geological structure *(m^3/y)*
i_f – specific coefficient of infiltration *($l/s/km^2$)*

INTRODUCTION

The ecosystem of three lakes: Ohrid, Big Prespa and small Prespa Lakes, for million of years coexist in natural harmony, creating a very beautiful environment with various kinds of flora and fauna and endemic fishes. These three lakes form the biggest water system on the Balkan Peninsula. Prespa region is the name of the water basin where two Lakes are sheared between: Republic of Macedonia, Greek an Albania.

Prespa is among the seventeen ancient Lakes on earth that are estimated to be more than three million years old. In 2002 the Prime Ministers of Republic of Macedonia, Greece and Albania declared the establishment of Prespa Park, as new protected area that includes Big and Small Prespa Lake with the surrounding forests, extending across three neighboring Countries.

The Prespa Lakes are supplied with water from underground resources and several rivers and streams that flow into the lakes from the Macedonian, Geek and Albanian side. The waters from the Big Prespa Lake are drained through the Galichica and Mali and Tate mountains and appear as a visible surface springs (St. Naum and Thushemisthy springs) at the southern coast of Ohrid Lake [1,2]. It has been calculated that about 11 years hydrological cycle is necessary for all the water in the Big Prespa Lake to be replace with new water.

During the last fifty years the hydrological data have shown significant fluctuation of the water level of Big Prespa Lake. The historical maximum of water level was recorded during 1963. In the period from 1988 to 2000 a continuing and fast decrease of the water level in the Big Prespa Lake was recorded. The further decrease of water level still continued with larger or smaller fluctuation and currently it is observed the drop of approximately 8 m from the historical maximum. Unfortunately it is still unclear whether the main reason for water level declination is human interference, meteorological or climate change, geological perturbation or some unknown factors. For finding the real reason for water level declination, so far many national, international, IAEA, NATO and FP projects were initiated, where the main tools in the performed researches were water balance calculations. In these calculations the catchments area has been delineated on the basis of the hydro-meteorological parameters, rainfall-runoff modeling, terrain slope, land cover an land use. It should pointed out that in literature data can be found big deviation in the values of sub-catchments area and whole catchments area, presented from various institutions and authors [3-7].

Table 1. Sub – catchments area of Big Prespa Lake

Sub-catchments	Previous old data Area (km^2)	GFA Area (km^2)	Hydro-meteorological Institute, Area (km^2)
North	430	314.97	405
East	270	272.47	246
West	210	271.97	181
South	250	254.38	225
Total	1160	1113.79	1057

In Table 1 the comparative values of some delineated sub-catchments area by GFA and Hydro-meteorological Institute in Skopje are presented. As it can seen from Table 1 there exists noticeable difference (more than 100 km^2) between the whole catchments area and sub-catchments area. These differences are especially accentuated for the North and West catchments area.

RESULTS AND DISCUSSIONS

The main parameters for water balance calculations are: estimations of the inputs and outputs of water for a water system. The inflow waters in the catchments area of the lake and in the lake consists: precipitation over the catchments area, direct rain-fall over the lake surface, surface water inflow in the lake, underground waters inflow in the lake and artificial waters inflow in the lake. Condensations over the catchments area and lake surface are the minor influencing factors on the water balance calculations. The outflow waters from the catchments area of the lake and from the lake consist: evapo-transpiration from the catchments area, direct evaporation from the lake surface, surface waters outflow from the lake, underground waters outflow, artificial waters outflow and irreversibly consumed waters (mainly irrigation).

Table 2. Distribution of water budget over the catchment area of Prespa Lake given in percentage

Geological structure	Surface area (km^2)	Precipitation P_C (%)	Run-off k (%)	Evapotranspration ET(%)	Infiltration I(%)
Sediments	280	100	24 %	63 %	13 %
Granites	420	100	34 %	60 %	6 %
Limestones	626	100	5 %	35 %	60 %
Total	1326	100			

As it can be seen from Table 2, the total precipitation over the Prespa Basin is distributed between: run-off, evapo-transpiration, and infiltration, using the equation

$$P_C(\%) = k(\%) + ET(\%) + I(\%) = 100\ \% \qquad (1)$$

The total precipitation is estimated as 100 % over each geological structure and a specific precipitation coefficient was calculated as the average values over the whole catchments area.

$$p_{CAV} = 27.279\ l/s/km^2 \qquad (2)$$

From this coefficient the (quantity) volume of precipitation over each geological structure is determined using the equation

$$Q_{pi} = p_{CAV}\ x\ A_{Gi} \qquad (3)$$

For sediments, granites and limestones

$$Q_{pS} = p_{CAV}\ x\ A_{GS} \quad Q_{pG} = p_{CAV}\ x\ A_{GG} \qquad Q_{PL} = p_{CAV}\ x\ A_{GL} \qquad (4)$$

$$Q_{pS} = 27.279\ (l/s/km^2)\ x\ 10^{-3}\ x\ 3600\ x\ 24\ x\ 365\ x\ 280 = 240.87x10^6\ m^3/y \qquad (5)$$

$$Q_{pG} = 27.279\ (l/s/km^2)\ x\ 10^{-3}\ x\ 3600\ x\ 24\ x\ 365\ x\ 420 = 361.31x10^6\ m^3/y \qquad (6)$$

$$Q_{pL} = 27.279\ (l/s/km^2)\ x\ 10^{-3}\ x\ 3600\ x\ 24\ x\ 365\ x\ 626 = 538.53x10^6\ m^3/y \qquad (7)$$

Determination the specific discharge coefficient *q*

From calculated values for *Qpi,* the specific discharge coefficients for each geological structure are determined by the equation

$Q_{Ri} = Qp_i\ x\ k_i(\%)$ and $q_i = \dfrac{Q_{Ri}}{A_{Gi}}$ (8)

For sediments

Q_{RS}= 240.87x10^6 *x* 0.24 = 57.81x10^6 m^3/y and

$$q_S = \frac{Q_{RS}}{A_{GS}} = \frac{57.81 \cdot 10^6\ (m^3/y) \cdot 1000}{280\,(km^2) \cdot 3600 \cdot 24 \cdot 365} = 6.547\,(l/s/km^2) \quad (9)$$

For granite

Q_{RG}= 361.31x10^6 *x* 0.34 = 122.84x10^6 m^3/y

$$q_G = \frac{Q_{RG}}{A_{GG}} = \frac{122.84 \cdot 10^6\ (m^3/y) \cdot 1000}{420\,(km^2) \cdot 3600 \cdot 24 \cdot 365} = 9.27\,(l/s/km^2) \quad (10)$$

For limestone

Q_{RL}= 538.53x10^6 *x* 0.05 = 26.92x10^6 m^3/y

$$q_S = \frac{Q_{RS}}{A_{GS}} = \frac{26.92 \cdot 10^6\ (m^3/y) \cdot 1000}{626\,(km^2) \cdot 3600 \cdot 24 \cdot 365} = 1.36\,(l/s/km^2) \quad (11)$$

Determination the specific coefficient of evapotranspiration e_{ET}

From calculated values for *Qpi,* the specific coefficients of evapotranspiration for each geological structure are determined by the equation

$Q_{ETi} = Qp_i\ x\ Et_i(\%)$ and $e_{ETi} = \dfrac{Q_{ETi}}{A_{Gi}}$ (12)

For sediments

Q_{ETS}= 240.87x10^6 *x* 0.63 = 151.74x10^6 m^3/y and

$$e_{ETS} = \frac{Q_{ETS}}{A_{GS}} = \frac{151.74 \cdot 10^6\ (m^3/y) \cdot 1000}{280\,(km^2) \cdot 3600 \cdot 24 \cdot 365} = 17.18\,(l/s/km^2) \quad (13)$$

For granite

Q_{ETG}= 361.337x10^6 *x* 0.6 = 216.784x10^6 m^3/y and

$$e_{ETG} = \frac{Q_{ETG}}{A_{GG}} = \frac{216.78 \cdot 10^6\ (m^3/y) \cdot 1000}{420\,(km^2) \cdot 3600 \cdot 24 \cdot 365} = 16.36\,(l/s/km^2) \quad (14)$$

For limestone

$Q_{ETL} = 538.53x10^6 \; x \; 0.35 = 188.48x10^6$ m^3/y and

$$e_{ETL} = \frac{Q_{ETL}}{A_{GL}} = \frac{188.48 \cdot 10^6 \;\; (m^3/y) \cdot 1000}{626\,(km^2) \cdot 3600 \cdot 24 \cdot 365} = 9.547\,(l/s/km^2) \tag{15}$$

Determination the specific coefficients of infiltration i_f

From calculated values for *Qpi,* the specific infiltration coefficients for each geological structure are determined by the equation

$$Q_{Ii} = Qp_i \; x \; I_{Ii}(\%) \qquad \text{and} \qquad i_{fi} = \frac{Q_{Ii}}{A_{Gi}} \tag{16}$$

For sediments

$Q_{IS} = 240.87x10^6 \; x \; 0.13 = 31.313x10^6$ m^3/y and

$$i_{fS} = \frac{Q_{IS}}{A_{GS}} = \frac{31.313 \cdot 10^6 \;\; (m^3/y) \cdot 1000}{280\,(km^2) \cdot 3600 \cdot 24 \cdot 365} = 3.546\,(l/s/km^2) \tag{17}$$

For granite

$Q_{IG} = 361.337x10^6 \; x \; 0.06 = 21.68x10^6$ m^3/y and

$$i_{fG} = \frac{Q_{IS}}{A_{GG}} = \frac{21.68 \cdot 10^6 \;\; (m^3/y) \cdot 1000}{420\,(km^2) \cdot 3600 \cdot 24 \cdot 365} = 1.637\,(l/s/km^2) \tag{18}$$

For limestone

$Q_{IL} = 538.53x10^6 \; x \; 0.6 = 323.12x10^6$ m^3/y and

$$i_{fL} = \frac{Q_{IL}}{A_{GL}} = \frac{323.12 \cdot 10^6 \;\; (m^3/y) \cdot 1000}{626\,(km^2) \cdot 3600 \cdot 24 \cdot 365} = 16.367\,(l/s/km^2) \tag{19}$$

Table 3. Summarized calculated data

Geological structure	p_i x 10^6 lit/s/km^2	Q_{pi} x 10^6 m^3/y	q_i x 10^6 lit/s/km^2	Q_{Ri} x 10^6 m^3/y	e_{Ti} x 10^6 lit/s/km^2	Q_{ETi} x 10^6 m^3/y	i_{fi} x 10^6 lit/s/km^2	Q_{Ii} x 10^6 m^3/y
Sediments	27.279	240.875	6.547	57.81	17.18	151.74	3.546	31.313
Granites	27.279	361.31	9.27	122.84	16.36	216.78	1.637	21.68
Limestones	27.279	538.529	1.36	26.92	9.547	188.48	16.367	323.12
		1140.72		207.57		557.6		376.113

The balance of incoming and outgoing water is

$$Q_{pi} = Q_{Ri} + Q_{ETi} + Q_{Ii} \tag{20}$$

CONCLUSIONS

Using the values for the hydro-geological catchment area of A_{CG} = 1326 km^2, the surface area of the Big Prespa Lake of 265 km^2 and the Small Prespa Lake of 39 km^2, as well as a total specific precipitation module over the whole catchments area of p_{AV} = 27.279 *l/s/km,*^{2} the water balance was calculated. The quantity of total precipitated waters of 1140.72x10^6 m^3/y, is distributed to: (i) run off (sediments 57.81 x10^6 m^3/y, granites 122.84 x10^6 m^3/y and limestones 26.92 x10^6 m^3/y) , (ii) evapotranspiration (sediments 151.74x10^6 m^3/y, granites 216.78x10^6 m^3/y and limestones 188.48 x10^6 m^3/y), (iii) infiltration (sediments 31.313 x10^6 m^3/y, granites 21.66 x10^6 m^3/y and limestones 323.12 x10^6 m^3/y)

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PHOSPHORUS LOSSES AND POLLUTION OF THE DNIEPER FROM KYIV WWTP AND POTENTIAL FOR THE RESOURCE SAVING

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ABSTRACT

The contribution of the waste water treatment plant (WWTP) of Kyiv to phosphorus (P) pollution of the Dnieper and P-losses has been analyzed for its operation in 2011 and 2012. A material flow analysis has been used to quantify P-flows. The effluent content of P exceeds the EU standard and contributes to eutrophication, while the sludge is landfilled and represents a loss of P. Appropriate pollution-prevention measures have been proposed to advance P-management and provide saving of the valuable resource.

Key words: WWTP, P-flows, water pollution, sludge, P- losses.

INTRODUCTION

Human intrusion in natural processes of the Earth resulted in substantial violation of the global biogeochemical cycles, first of all, nitrogen (N) and phosphorus (P) flows [1]. A growing disposal of N and P into aquatic environments aggravates the problem of eutrophication of surface waters and generates their hypoxia/anoxia. A new research [2] identified 535 low-oxygen "dead zones" worldwide, and additional 248 sites were identified as areas that are at the risk of developing hypoxia. The Sea of Azov and the Black Sea South-West Shelf are included to the list of hypoxic zones of the world [3].

P is considered to be a main driver influencing the ecological state of marine systems. At the same time P, as phosphate rock, is a non-renewable resource that is irreplaceable for agriculture and food production [4, 5]. The commercial deposits of phosphates are limited, and a major part of them (83%) is situated in Morocco, China, South Africa and the USA [6]. Two thirds of the world P requirement is produced in three countries, the USA (30%), Morocco (17%) and China (14%) [4]. There is a concern that the exploitation of this valuable resource to meet current demand for food production is not sustainable [5,7]. Hence, a decrease in P-losses and maximizing its recycling in different spheres of human activities is an urgent task for providing both food security and environmental protection.

For the last decade, P-flows, sources of its losses, as well as options for P recycling, are intensively studied at different scales: local, regional, national, and global [8, 9, 10].

The water industry is an essential sink of P and source of surface water pollution. In Europe, 50-75% P goes to the aquatic environment from point sources, such as municipal and industrial WWTPs, and 20-40% from agriculture [4]. At a global scale, on average 50% P of sewage effluents goes to water bodies, and only 10% P is recycled for food production [9]. At the national scale these characteristics are different. For example, in UK (2009) around 40% P entering sewage treatment works was discharged to water bodies and 50% recycled to agriculture [10], whereas in the Netherlands about 18% P coming to WWTPs goes to surface waters, the most of P contained in the sludge is incinerated or landfilled, and only 5% is used in agriculture [8].

A study of P-flows at a local level, such as at WWTPs, is of importance for estimation of the contribution of the water sector to surface water P-inflow and for development of more sustainable P management in Ukraine.

The paper is devoted to analyzing P-flows and its losses to the environment at the greatest WWTP of Ukraine, Bortnytska aeration plant (BAP) in Kyiv, including evaluation of its contribution to P pollution of the Dnieper and recommendations of necessary measures to reduce P- losses and water pollution.

METHODS

A simple material flow analysis has been performed on data of BAP operation in 2011 and 2012. Mean input and output of waste water (WW) and the amount of P in the flows have been calculated on average monthly values. At BAP, P is monitored as phosphate (PO_4^{3-}) in the incoming and treated WWs, and as total P (P_{tot}) in the sludge using standard spectrometric method [11]. Values of P_{tot} in the incoming WW have been roughly estimated using the relationship: $P_{tot}/(PO_4\text{-}P) \approx 1.21$, where ($PO_4$-P) is P of phosphates [12].

A variety of primary and secondary sources has been used to compare and evaluate the results, as well as for the recommendations, such as EC and academic articles, monographs and handbooks, EU and Ukrainian standards, EFMA, WHO materials, papers of specialized international conferences, UA statistics, technical documentations of BAP and others.

RESULTS AND DISCUSSION

BAP processes a mixture of household and industrial (5-7%) WWs from Kyiv and some adjacent settlements (about 4 %). The plant consists of three equal treatment blocks that were introduced in 1965-1987. The designed capacity of each bloc is 600,000 m^3/day of WW. BAP uses the conventional technology of 1950s-60s, including primary (mechanical) and secondary (biological activated sludge) treatment of WW. This is also characteristic for other WWTPs of Ukraine. The treated effluents from the three blocks are mixed and discharged to the Dnieper. The sludge from the primary sedimentation tank and the following digester, and the superfluous sludge, after aerobic stabilization, go to the sludge drying fields and are accumulated there without being utilized.

The total annual input of WW to BAP has increased from 48.9 million m^3 in 1965 to its peak of 525.5 million m^3 in 1991, and then decreased to around 300 million m^3 in 2011-2012.

Despite a drastic decrease in the amount of WWs for the last decade, the level of contamination of incoming WWs, including P-input, is rising. The increased P-input to the municipal WWs is mainly due to the use of P-containing detergents. It is estimated [13], some 40 to 50% of P in the household WWs in Ukraine originates from the detergents. The original technology at the existing WWTPs, such as BAP, is not intended for a high removal of P. Accordingly, the concentration of phosphates in the Dnieper water, receiving P from both point and non-point sources, has doubled in the past ten years [12].

The water and P-flows to and from BAP in 2011 and 2012 are summarized in Tables 1 and 2.

On average, the phosphate concentration in the incoming WW for the whole plant (all three blocks) was 17.7 mg/l, but in some months it was much higher (to 23 mg/l). For the studied period, the average P-removal rates were rather high, and made up on phosphates 70% in 2011 and 74.3 % in 2012. These rates were achieved, firstly, because of not full load of the plant on the incoming WW (not more than 50% of the projected capacity), and, secondly, thanks to a high concentration of active sludge maintained in the aerotanks ($\approx$ 3.5 g/l), a high degree of active sludge recycling (70-80%), and timely removal of superfluous sludge.

However, this achievement requires a high energy usage and generates large volumes of sludge (Tables 1and 2), which makes such technological process non-sustainable and, moreover, the achieved results cannot be stable.

The results of BAP operation show that the achieved degree of P-removal (70-74%) and the P- content in the treated effluent (see Table 1 and 2) do not meet the EU standard [14].

According to the Directive 91/271/EEC, for WWTPs serving $\geq$100,000 p.e. (people equivalent), a P-removal rate is stipulated $\geq$80%, and a total P (P_{tot}) in the discharged effluents must not exceed 1 mg/l. BAP serves a p.e. of 3,977,470 (2011) and 3,637,890 (2012), so that the P- concentration in the discharged effluents (the average PO_4-P of 1.73 mg/l and 1.51 mg/l in 2011 and 2012 respectively, and taking into account that a total P (P_{tot}) must be even more high) does not ensure this norm. Moreover, some mean monthly PO_4-P concentrations in the discharged effluents much exceeded the annual average and reached, for example, 2.7-2.8 mg/l (June-September). At the same time, the phosphate content in the Dnieper water in May-October 2012 varied within 0.18-1.0 mg/l and 0.25-0.88 mg/l (500 m upstream and downstream from the disposal point) [12], that is, at average was 0.5 mg/l PO_4^{3-}, or about 0.17 mg P/l. In comparison, to avoid a risk of eutrophication, the US EPA recommends $\leq$0.05 mg P/l in sensitive zones of water sources receiving WWs [15].

Hence, the discharged effluent from BAP and the Dnieper water quality produce conditions for eutrophication. Additionally, the existing rate settings in Ukraine do not further an improvement of surface water state.

Table 1. Average annual values of P-containing flows at BAP in 2011

Characteristics of flow	Input to BAP with waste water	Output from BAP: Treated effluent into Dnieper	Output from BAP: Sludge to sludge fields
Mean amount of wastewater or sludge, m^3/day Input/output per year, m^3	806,244 (+-10%) 294.28 $\cdot 10^6$	806,244 (+-10%) 294.28 $\cdot 10^6$	≈ 12,000 ≈ 4.38 $\cdot 10^6$ (≈109,500 ton d.m.)
Mean phosphorus content in water or sludge - phosphate (PO_4^{3-}), g/m^3 - PO_4 - P, g/m^3 - total phosphorus, g/m^3	 17.76 (13.83-23.04) $^{x)}$ 5.92 (4.61-7.68) $^{x)}$ 7.16 (5.58-9.29) $^{x)}$	 5.31 (2.49-8.35) $^{x)}$ 1.73 (0.83-2.78) $^{x)}$ -	 - - ≈6%(2-11%) $^{xx)}$
Mean amount of phosphorus - phosphate (PO_4^{3-}), ton/day - PO_4 - P, ton/day - P_{tot}, ton/day	 14.32 (11.15-18.6) $^{x)}$ 4.77 (3.72-6.2) $^{x)}$ 5.77 (4.6-7.5) $^{x)}$	 4.28 (2.01-6.73) $^{x)}$ 1.43 (0.67-2.24) $^{x)}$ -	 ≈ 6570 ton P/year
Presumable P-balance, ton P/year	2,106	522	1,574 $^{xxx)}$

$^{x)}$ min and max average values per month; $^{xx)}$ % in dry matter; $^{xxx)}$ from material balance

Table 2. Average annual values of P-containing flows at BAP in 2012

Characteristics of flow	Input to BAP with waste water	Output from BAP: Treated effluent into Dnieper	Output from BAP: Sludge to sludge fields
Mean amount of water or sludge, m^3/day Input/output per year, m^3	801,734 (+-10%) 292.6325 $\cdot 10^6$	801,734 (+-10%) 292.6325 $\cdot 10^6$	≈ 12,000 ≈ 4.38 $\cdot 10^6$
Mean phosphorus content in water or sludge - phosphate (PO_4^{3-}), g/m^3 - PO_4 - P, g/m^3 - total phosphorus (P_{tot}), g/m^3	 17.66 (13.1-22.76) $^{x)}$ 5.89 (4.37-7.59) $^{x)}$ 7.3 (5.29-9.18) $^{x)}$	 4.54 (0.91-8.15) $^{x)}$ 1.51 (0.3 -2.72) $^{x)}$ -	 - - ≈6 % (2-11%) $^{xx)}$
Mean amount of phosphorus - phosphate (PO_4^{3-}), ton/day - PO_4 - P, ton/day - P_{tot}, ton/day	 14.16 (10.5-18.25) $^{x)}$ 4.72 (3.5-6.08) $^{x)}$ 5.71 (4.2- 7.35 $^{x)}$	 3.64 (0.73-6.53) $^{x)}$ 1.21 (0.24-2.18) $^{x)}$ -	 10.52 $^{xxx)}$ 3.51 $^{xxx)}$ ≈ 18
Presumable P-balance, ton P/yr	2,085	442	1,643 $^{xxx)}$

$^{x)}$ min and max average monthly values; $^{xx)}$ % in dry matter; $^{xxx)}$ from material balance.

For example, temporary norms for the discharged effluents have been coordinated for BAP (for 2011-2014) [12] that stipulate a permissible concentration of phosphates (PO_4^{3-}) in the treated effluent at the level of 8 mg/l (about 2.66 mg/l PO_4-P). Moreover, the National Standard of Ukraine [16] admits 0.051-0.2 mg P/l in surface sources meant for centralized water supply (3 class quality)), which does not conform with the EU Directive on integrated pollution prevention and control [17].

As a whole, for the years 2011-2012, the total inflow of P to the Dnieper with the discharged effluents from BAP is estimated (Tables 1 and 2) around 1000 ton.

Very rough estimation of P-amount in the sludge was made on the data [12] of P_{tot}-content of 2-4% (in dry matter) in the primary sludge and its volume of about 5,000 m^3/day, and P_{tot}-content of 6-11% (in dry matter) in the superfluous sludge and its volume of around 7,000 m^3/day. Average water content in the sludge is determined to be 97.5% [12]. The values of P-amount in the disposed sludge calculated on these data are 3.5-4 times higher than that calculated from the material balance (see Tables 1 and 2). This reflects a great uncertainty with volumes and composition of the disposed sludge, which, in turn, is a result of irregular monitoring and, above all, of extremely non-stability of the process.

However, it is clear that daily disposal of around 12,000 m^3 of liquid sludge with 97.5% wet and its accumulation at the sludge fields generate an additional pollution of the environment and represent a great P- wastage of more than 1,500 ton P per year. Moreover, a long-term accumulation of the sludge (9-10 million m^3 since 1985) at the sites has exhausted their accumulating capacity and threatens to become an ecological catastrophe.

Thus, at present it is impossible to make more exact estimation of P- flows at BAP (and so at other WWTPs in Ukraine). The main problems concerning improved estimates of P-flows at BAP are as follows:

1) lack of data on P_{tot} content in the incoming and discharged WWs;
2) uncertainties of the volume and P-content in the discharged sludge (accuracy of the data)
3) because of 1) and 2), inconsistencies of the results on P-flows calculated on the material flow balance basis and on the data of BAP operation;
4) and the accuracy of the results on P-flows for the whole plant.

CONCLUSION AND SUGGESTIONS

The water sector of Ukraine is a major source of P-discharge to aquatic environments and P-wastage. A total of over 2 billion of assumed purified WW is discharged by municipal WWTPs to the Dnieper (2011) [18]. BAP discharges annually (2011-2012) about 0.3 billion m^3 of effluents containing around 500 ton of P (20 % of total P-discharge by the WWTPs).

The BAP operation delivers a quality of the discharged effluent that does not meet the EU standard for P-disposal to sensitive surface waters from WWTPs, and about 70-75% of sewage P (on the data of 2011-2012) is wasted in the unutilized sludge. A similar situation is characteristic for all other municipal WWTPs of Ukraine.

The following measures in the water sector are suggested to reduce P-losses and P-pollution of the Dnieper:

1. To decrease P-content in the household WWs by way of legislative ban on phosphate-based detergents in Ukraine. This single measure could reduce the inflow of P to the WWTPs by about 40-50% and thus decrease the phosphate

concentration in the discharged effluents. A bill was prepared in 2012 to the Parliament, and its approval will promote an improvement of the ecological status of surface waters in Ukraine.

2. To introduce the best available technologies for P-removal at WWTPs, first of all, advanced biological treatment and/or chemical P-precipitation by reagent treatment [12, 19]. Advanced biological treatment provides for the application of an anaerobic process of WW treatment side by side with an aerobic one, which results in an increase of P-accumulating bacteria in the activated sludge. This, in turn, increases the P- concentration in the superfluous sludge and P-removal up to 90% and more (at a high ratio of BOD/P in the incoming WW), and simultaneously decreases the volume of the sludge. This process stipulates the superfluous sludge treatment only in aerobic conditions and quick dewatering of it [12]. For the BAP conditions and the incoming WWs quality, such advanced biological treatment would be quite acceptable. It was estimated that improving sewage treatment (to achieve 90 % P-removal from WW) in all countries could lead to a decrease in P-load on surface waters by 33% [20].
3. For new housing districts, to project updated sewage systems based on separation of different household waters to decrease P-loading to WWTPs [21]. A long-term measure is to collect nutrient-rich urine or blackwater separately for treatment and reuse in agriculture. This separation has a potential to halve the P-content in the remaining household grey water. There are urine-diverting toilets on the market that can reduce the P-content in the sewage by 60% [21].

The most serious problem experienced by BAP is sludge accumulation at the sludge-drying fields. About 9-10 million m^3 of sludge has been accumulated since 1985, and at present some 12,000 m^3 of liquid sludge containing presumably 4-5 ton of P is daily discharged to the sludge fields.

All appropriate pollution-prevention measures must be used in order to fulfill the EU IPPC Directive:

- as the first step, to introduce mechanical dewatering of the newly generated sludge followed by its thermal treatment and utilization to stop sludge disposal to the sludge fields;.
- as the second step, to realize the treatment and utilization of the accumulated sludge, including possible P-recycling in agriculture. The potential is thousands ton of P per year.

At present, there are different methods and practical solutions for P-recycling from the household sewage, such as direct recycling of sewage nutrients (if the quality of sludge is good enough), specific processes for P-recovery from sewage liquors, e.g. struvite recovery to produce a commercial fertilizer, P-recovery from sewage sludge incineration ashes, e.g. to substitute phosphate rock, and others [19, 22].

It is estimated that up to 80% of P is theoretically accessible in the total sludge [23].

According to a recent analysis [24], P-recovery from the sewage sludge for using in agriculture `will be an ordinary process in the industrialized countries over next 20 years.

The emergency and options for P-recycling of sewage sludge in Ukraine should be considered at the national level. In this way, Ukrainian environment legislation would comply with the European requirements on integrated pollution prevention and control.

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TWELVE YEARS OF INTERLABORATORY STUDIES OF DANUBE WATER: RESULTS FOR IRON, CADMIUM AND LEAD

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ABSTRACT

Ten interlaboratory studies were organised in the period 2002-2014 in order to improve the quality of chemical analyses of water in South-Eastern Europe. About seventy laboratories from Greece, Montenegro, Republic of Srpska - Bosnia and Herzegovina, Romania and Serbia took part in them. In all regional interlaboratory studies the task for participants was to determine some or all trace elements (Al, As, Cd, Cu, Mn, Fe, Pb and Zn) in the samples based on Danube water. Furthermore, the participants had also to determine some other parameters important for water quality.In this paper the results for determination of iron, cadmium and lead were discussed.

Key words: Interlaboratory study, Intercomparison, Danube water, Trace element, Cadmium, Iron, Lead.

INTRODUCTION

The environmental analyses as well as the globalization of trade require accurate and precise chemical analyses. In order to achieve such goal, the principal solutions are wide use of reference materials, accreditation of laboratories, participation in interlaboratory studies and the introduction of quality system based on the ISO 9000 standards in chemical laboratories [1]. Laboratory accreditation can be at national, regional or international level. The criteria for accreditation cover all aspects of laboratory's operations. It includes also the obligation for applying laboratory to participate in interlaboratory studies. As the consequence, the number of interlaboratory studies increased considerably, mostly in developed countries [1]. The interlaboratory studies could be organised at national, regional or international level. Consultations among several scientists and the Round Table Discussion on Interlaboratory Measurements organised within the 2nd International Conference of the Chemical

Societies of the South-Eastern European Countries "Chemical Sciences for Sustainable Development" [2] stressed the need for permanent long-term activities in the region as well as the organization of the regional interlaboratory studies.

Therefore, ten regional interlaboratory studies were organised in the period 2002-2014 in order to improve the quality of water analyses in South-Eastern Europe. The International Scientific Committee with professor dr. Anastasios Voulgaropoulos as the Chairperson organised and evaluated regional interlaboratory studies. In all regional interlaboratory studies the task for participants was to determine some or all trace elements (Al, As, Cd, Cu, Mn, Fe, Pb and Zn) in the samples. Furthermore, participants in regional interlaboratory studies the participants had also to determine choride, sulphate, phosphate, nitate, nitrite, ammonium ion, oil, phenol and chemical oxygen demand (COD) in samples based on Danube water. In some regional interlaboratory studies they also had to determine sodium, potasium, magnesium, calcium and selen in mineral water. About seventy laboratories took part in ten interlaboratory studies organized in the period 2002-2014. Three laboratories were from Greece: Department of Analytical Chemistry, Aristotle University of Thessaloniki; Department of Chemistry, University of Ioannina, Ioannina and Thessaloniki Water Supply and Sewerage Organisation, Thessaloniki. Three laboratories were from Montenegro: Hydrological and Meteorological Service of Montenegro, Podgorica; Institute for Public Health, Podgorica and PI Centre for Ecotoxicological Research of Montenegro, Podgorica. Two laboratories were from the Republic of Srpska - Bosnia and Herzegovina: Institute for health protection of the Republic of Srpska, Banja Luka and Water supply and sewerage organisation, Bijeljina. Eleven laboratories were from Romania; Administratia Nationala Apele Romane - Directia Apelor Prut Iasi; ICIA CLUJ NAPOCA, Cluj Napoca; Institute for Energy Research and Development – ICEMENERG, LAICA, Faculty of Chemistry, AI.I. Cusa University of Iasi, Iasi, Bucharest; National Research and Development Institute for Industrial Ecology (ECOIND), Bucharest; R.A. APA - CANAL "Aquatim", Timisoara; RA AQUASERV, Tg. Mures, Jud Mures; S.C. APA CANAL 2000 S.A., Pitesti; SC APA NOVA, Comuna Chiajna, Jud Ilfov; S.C. ROMPETROL REFINING, Navodari and S.C. RULMENTUL S.A., Brasov). Other laboratories were from Serbia: A.D. Bio-ecological Center, Zrenjanin; ANAHEM, Belgrade; Copper Mill, Sevojno; DP HIP Azotara - Pančevo, (Nitrogen fertilizer plant), Pančevo; DP HIP Petrohemija – Pančevo (Petrochemical plant), Pančevo; Enoloska stanica, Vršac; Faculty of Chemistry, University of Belgrade, Belgrade; Faculty of Technology and Metallurgy, Belgrade; Faculty of Technology, Novi Sad; Geoinstitute, Belgrade; Holding Institute of General and Physical Chemistry, Belgrade; IChTM – Center of Chemistry, Belgrade; Institute for Safety and Preventive Engineering, Novi Sad; Institute for Technology of Nuclear and Other Mineral Raw Materials, Belgrade; Institute for Water Development "Jaroslav Černi", Belgrade; Institute of Public Health (Belgrade, Čačak, Kosovska Mitrovica, Kraljevo, Leskovac, Niš, Novi Sad, Pančevo, Podgorica, Požarevac, Subotica, Šabac, Užice, Vranje, Zaječar, Zrenjanin); Institute of Public Health of Serbia, Belgrade; "Knjaz Miloš" - Laboratory, Arandjelovac; "MOL", Joint Stock Company for Chemistry, Biotechnology and Consulting, Belgrade; NIS – Naftagas, Central Laboratory, Novi Sad; NIS – Oil Refinery Pančevo, Pančevo; Petnica Science Center, Valjevo; Serbian Environmental Protection Agency, Belgrade;Sojaprotein A.D., Bečej; "ZORKA" – Chemical Industry, Research Center, Šabac; "ŽUPA" – Chemical Industry, Kruševac; Veterinary institute, Belgrade; Veterinary institute, Kraljevo; Water Supply and Sewage, Belgrade; Water Works "NAISSUS", Niš; Water Works, Kruševac; Water Works, Novi Sad; Water Works, Pančevo; A.D. Bio-ecological Center, Zrenjanin**.**

The results for determination of some trace elements were presented earlier [3, 4]. In this paper the results for determination of iron, cadmium and lead are discussed.

MATERIALS AND METHODS

The samples for all regional interlaboratory studies were prepared from filtered water of the river Danube near Belgrade by addition of corresponding substances. The task for participants was to determine some or all trace elements (Al, As, Cd, Cu, Mn, Fe, Pb and Zn) in two samples (A and B) and some other parameters (in samples C, D, E and F). In this paper the results for determination of iron, cadmium and lead were discussed. Participants could freely select the elements for analysis and the analytical methods. Full confidentiality was guaranteed with the respect the link between results and participants' identity. All participants who submited their results in time received the certificate of participation. All participants also received CD with several scientific papers and other literature relevant for interlaboratory studies of water and traceability in chemical analyses.

All results were analysed using the same methods as in the interlaboratory studies organised by IRMM-JRC (Institute for Reference Materials and Measurements: EU-Joint Research Centre, Geel, Belgium) within IMEP (International Measurements Evaluation Programme) [5, 6, 7, 8]. Cochran and Grubbs test were also used as well as graphic presentation of results using the Youden method [9]. Reproducibility (R) and repeatability (r) were calculated according to the British standard BS 5497: Part I: 1987 (ISO 5725: 1986) [10].

RESULTS AND DISCUSSION

Interlaboratory studies are important for the improvement of the quality of determination of various chemical parameters. Accurate chemical analyses are neccessary for the investigation of the quality of natural or wastewater as well as for the monitoring of wastewater treatment. In this paper the results for determination of iron, cadmium and lead in regional interlaboratory studies were presented. Different methods were used for determination: spectrophotomertry, AAS, ICP and ASV.

Results for determination of cadmium and lead obtained in the '1st South-Eastern European Interlaboratory Study: Water Analysis 2003' were presented in Fig. 1. It is convenient to present results in the ascending order as in IMEP studies [5, 6].

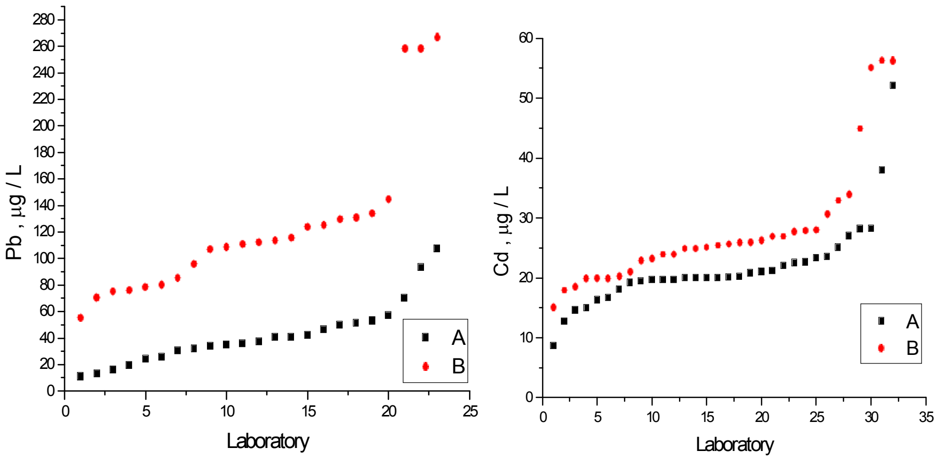

Figure 1. Results for determination of lead and cadmium (µg/L) in samples A and B (Water Analysis 2003)

The results which were obviously too low or too high were discarded. The remaining results were subjected to Cochran and Grubbs test which also eliminated some results. The results which were not eliminated in such way became the accepted results and they were used for calculation of the median, mean and standard deviation which are used for further analysis. Better information on the quality of remaining results couuld be obtained by the use of Youden graphical method [9]. The same method was applied for evaluation of international interlaboratory studies of water (IMEP-3, IMEP-6 and IMEP-9) organised by experts of the European Commission – Institute for Reference Materials and Measurements [5, 6]. For example, the Youden diagram for determination of lead (Fig. 2) was constructed by drawing the x-axis and laying off the results for sample A on this scale. Similarly, the y-axis corresponded to the scale with the results obtained for sample B. In such diagram each laboratory was represented with one point (its results for sample A and B were the coordinates). New coordinate system was then made by adding two lines: one, parallel with y-axis was made to go through the median of the results for sample A and another, parallel with x-axis, was made to go through the median of the results for sample B. The results of good laboratories had the position close to the crossing of median lines. In the same way the Youden diagram for determination of cadmium was constructed (Fig. 2).

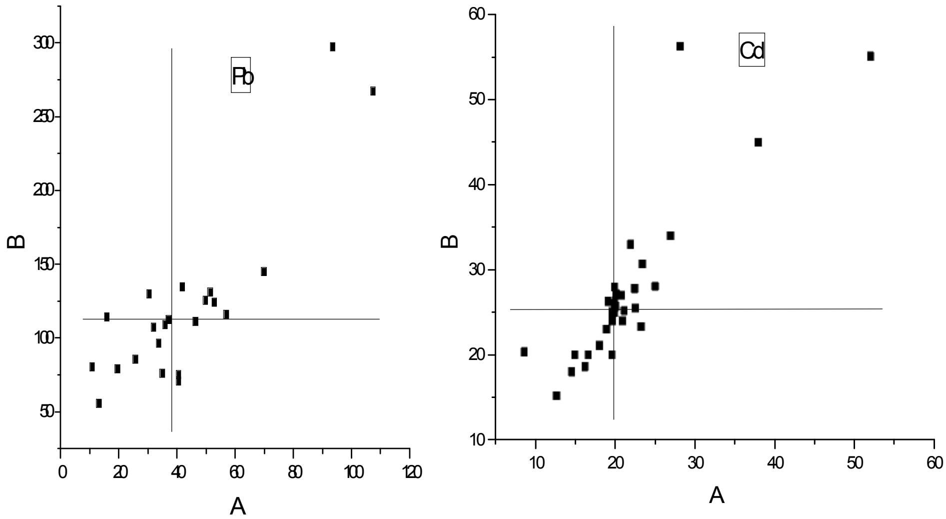

Figure 2. Youden diagrams for determination of lead and cadmium (µg/L) in samples A and B (Water Analysis 2003)

Radial distribution of results indicated that random errors prevail in determination of lead (Fig. 2). Oh the other hand, diagonal grouping of results in determination of cadmium indicated that some laboratories had systematic errors, i.e. they found too low or too high values for both samples (Fig. 2). Considerably better results for determination of cadmium were obtained in later interlaboratory study, 'The 9th South-Eastern European Interlaboratory Study: Water Analysis 2013' (Fig. 3).

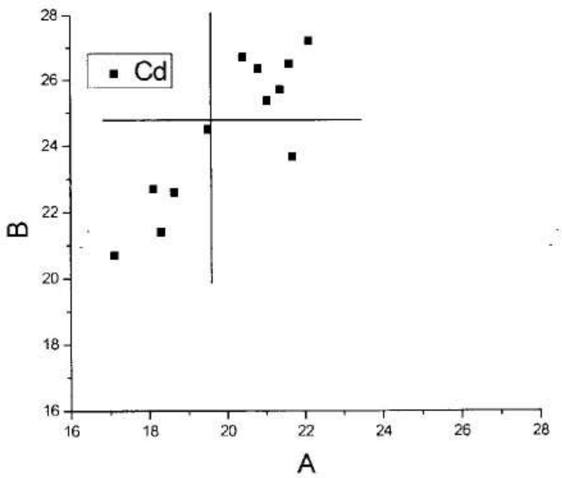

Figure 3. Youden diagram for determination of cadmium (µg/L) in samples A and B (The 9th Regional Interlaboratory Study Water Analysis - 2013)

It was of interest to compare the results in this regional interlaboratory study with the results obtained in international interlaboratory study IMEP-9 organised by experts of the European Commission - Institute for Reference Materials and Measurements [6]. Results of IMEP-9 presented in Table 1 correspond for lead and cadmium determination in water samples obtained by laboratories from Balkan countries (which are not exactly the same laboratories from South Eastern European countries which participated in the regional interlaboratory study 'Water Analysis 2003). In both cases results $\pm$ 50% of the target values were considered as 'accepted results' (Table 1). Higher percent of accepted results was obtained for both elements in the regional interlaboratory study.

Table 1. Determination of lead and cadmium in two interlaboratory studies

	ELEMENT	SAMPLE	NUMBER OF RESULTS	NUMBER OF ACCEPTED RESULTS	PERCENT OF ACCEPTED RESULTS
IMEP-9	Pb	1	22	11	50.0
IMEP-9	Cd	1	24	14	58.3
WA-2003	Pb	A	27	16	59.3
WA-2003	Pb	B	27	20	74.1
WA-2003	Cd	A	34	29	85.3
WA-2003	Cd	B	34	28	82.3

Better results for determination of iron were also obtained in later interlaboratory study (The 9th regional interlaboratory study "Water Analysis 2013', Fig.3).

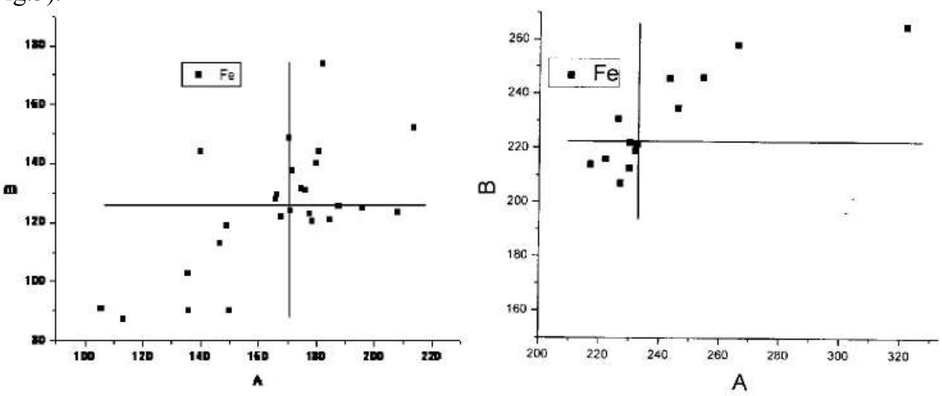

Figure 3. Youden diagrams for determination of iron in the 7th and 9th regional internaboratory studies 'Water Analysis 2011' and 'Water Analysis 2013'

CONCLUSION

Interlaboratory studies are important for the improvement of the quality of chemical analyses, accreditation of laboratories and the introduction of quality system based on the ISO 9000 standards in chemical laboratories. Ten regional interlaboratory studies, which included determination of trace elements in Danube water as the sample matrix, were generally successful and useful for all participants. There was a good agreement between the results of most laboratories obtained for determination of lead and cadmium. The achievement was better than in some earlier interlaboratory studies. Better results for determination of lead, cadmium and iron were obtained in later interlaboratory studies.

Acknowledgements

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PROTECTION OF WATER RESOURCES BY IMPLEMENTING CLEANER PRODUCTION - A CASE STUDY

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ABSTRACT

Strategy for Sustainable Development with the introduction of cleaner production is the current management philosophy that involves achieving economic growth without environmental damages. Application of cleaner production in manufacturing processes includes rational use of raw materials, water and energy, substitution of hazardous materials with less hazardous ones and reducing the quantity and toxicity of emissions and waste in water, air and soil. The Cleaner Production Centre of Serbia (CPCS) on behalf of the Faculty of Technology and Metallurgy, University of Belgrade and the United Nations Industrial Development Organization (UNIDO) conducted a project entitled "Cleaner Production" in 2008, which involved a joint stock company HIPOL from Odzaci in Serbia. The project included a plant for the production of polypropylene (PP) and Facilities of Maintenance and Energy - Boiler room, compressor stations, chemical treatment of water (CTW) and wastewater treatment (WWT) in the HIPOL Company. This paper presents the analysis of the quantity of all types of water (raw water consumption and wastewater release) before and after the introduction of cleaner production in the observed time period (from 2007. to 2008). Effects of the implementation of cleaner production are reflected in the reduction of the quantity of raw water and wastewater release of 18,305 m^3 (11.7%) and 23,584 m^3 (21%), respectively. Benefits of implementation of cleaner production have been presented through the reduction of both energy and water consumption in a total savings worth of € 120,000. The case study shows that a good environmental performance also provides a significant economic development.

Key words: cleaner production, sustainable development, environmental performance.

INTRODUCTION

Hipol JSC from Odžaci in Serbia is Chemical factory which produces polypropylene granules from liquid propylene homopolymer, signed as HIPOLEN P trademark, in total capacity of 33,000 tons per annum. Production of polypropylene granules done by classical suspension polymerization process in heptane as solvent ensures a high purity product. For many years HIPOL JSC Company is operating in accordance with ISO quality system, which is confirmed in 2008 with the certification of ISO 9001 [1]. UN agency UNIDO (*United Nations Industrial Development Organization*) promotes industrial development for poverty reduction, including globalization and environmental sustainability [2]. Cleaner Production Centre of Serbia emerged in 2007, on the initiative of UNIDO Agency wherin Ministry of Science and Environmental Protection, Department of Environmental Protection, Ministry of Environment, Chamber of Commerce and Faculty of Technology and Metallurgy, University of Belgrade also participated [3].

In 2008 Cleaner Production Centre of Serbia (CPCS) along with UNIDO conducted the project entitled "Cleaner Production". The project included a plant for the production of polypropylene (PP) and Facilities of Maintenance and Energy - Boiler room, compressor stations, chemical treatment of water (CTW) and wastewater treatment (WWT) in the HIPOL Company [4]. Cleaner production as a responsible choice for the environment arises from the definition given in the Environment Programme of the United Nations (*United Nations Environment programs - UNEP*) which states that "Cleaner Production is the continuous performance of a comprehensive preventive environmental strategy to processes and products in order to reduce negative impacts on people and the environment" [5].

This paper presents the analysis of the quantity of all types of water (raw water consumption and wastewater release) before and after the introduction of cleaner production in the observed time period (from 2007. to 2008).

RAW WATER CONSUMPTION AND WASTEWATER RELEASE IN HIPOL JSC INDUSTRY

For industrial purposes Hipol uses the Danube-Tisa-Danube Canal (DTD) for water supply which is also the recipient of discharged wastewater. Distribution of water from the canal DTD is done in two systems: fire alarm system and raw water system. Chemical treatment of water (CTW) with design capacity of 115m3 / h produces three different types of water quality for cooling tower (RT), boiler and plant (PP), while drinking water and sanitation needs in 2007 used the tap water.

The total amount of water consumed in 2007 in the amount of 287.724 m3 is shown in Figure 1 using percentage structural balance of water consumption [4].

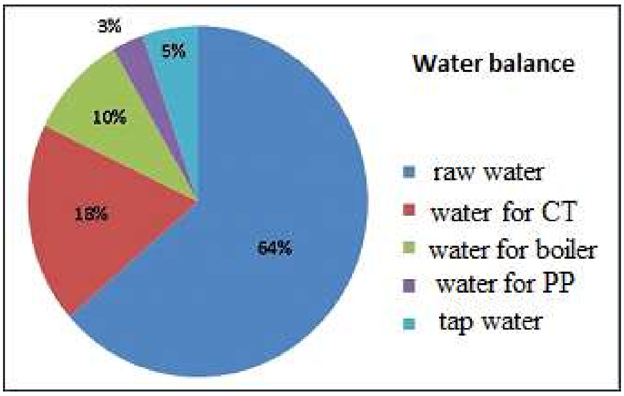

Figure 1. Structural balance of water consumption in 2007

Plant for the treatment of waste water (WWT) in Hipol with designed capacity of 40 m3 / h, consists of four technology units as follows: 1) Biological treatment of wastewater from sanitary sewers, 2) the treatment of oily wastewater from the sewer into which the water from oily surfaces is flowing, 3) the final treatment of wastewater from storm sewers, purified water with biological treatment and treated water from the oily water treatment and 4) sludge treatment - all of the sludge that is allocated on the plant is distributed in the filter field. There is a sewer network stretching over the entire area of Hipol factory. It is composed of three separate parts: Sanitary sewer - wastewater from toilets and kitchens of restaurants, Storm sewer - wastewater sludge removal from the cooling tower, washing sand filters and rainwater and Oily sewage - wastewater from all surfaces where a possibility of oil spills (base plant, decanting of fuel oil, boiler rooms, mechanical maintenance workshops, etc.) exists. Treated water from the plant is discharged into the DTD canal in the amount of 133.779 m3 during 2007 and corresponds to the second class of the watercourse quality [6, 7]. Figure 2 shows the percentages ratio of abstracted raw and treated wastewater in the canal [4].

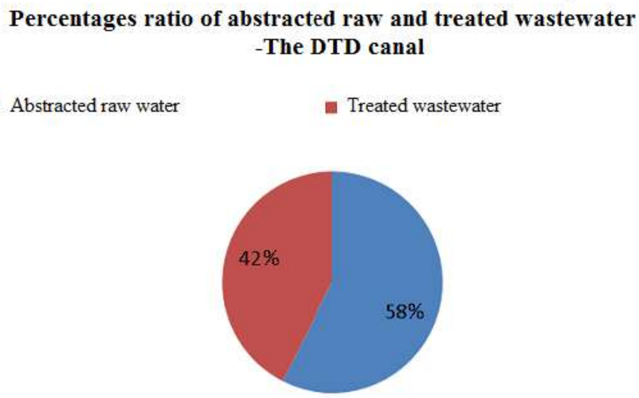

Figure 2. Structure of abstracted raw and treated wastewater in 2007

The amount of all types of water (raw water consumption and discharged wastewater) before and after the introduction of implemented CP options was analyzed for the given time period aimed at protecting water resources.

RESULTS AND DISCUSSION

UNIDO project and implementation of cleaner production in Hipol imply defining a total of eleven cleaner production program options with a clear explanation of the positive effects of environmental impact. From the contents of the entire program of integrated environmental protection system three major options that directly affect the ecological profile of the water balance were singled out (Table 1).

Table 1. Options of the Program for Cleaner Production (1-3) concerning Water balance

Options	The value of investments (€)	Cost savings (€ / y)	Return (y)	Environmental impact
OPTION 1 Reducing the amount of water - Abstracted raw water - discharged wastewater	/	/	immediately	Decrease in the consumption of chemicals for water treatment, reducing electricity consumption and the amount of waste water.
OPTION 2 Own supply of Hipol with technical water instead of water from the municipal water supply system	3 900	12 000	4 months	Reduced amount of abstracted water from underground aquifers to 15000 m^3 / y.
OPTION 3 Merging WWT and CTW in one technological unit	20 000	25 000	10months	Reduction of carbonate sludge for min. 150 t / y. Decrease in consumption of chemicals for treatment of up to 50%.

The effects of these options at the time of realization of investment in the industry of Hipol JSC were observed. The deadline for the return of the investments of proposed options (1-3) is the first ten months (from January to October) in the observed 2008. A concrete result of the environmental impact of the implementation of Option 1 involves reducing the amount of all types of water. Firstly, it should be noted that the restoration of losses and rationalization during 2008 reduced consumption of raw water compared to the same period in the year before. The amount of raw water for the CTW has been reduced by 18,305 m^3 or 11.7% (Figure 3). Decrease in consumption of raw water resulted in a decrease in the consumption of chemicals for its treatment by 10%, reducing the consumption of electricity for the pumps and transport raw water (113,000 kWh) together with the reduction of fees for water supply from the DTD canal. Overall effects of reducing the consumption of raw water amounted to € 6,500 [4].

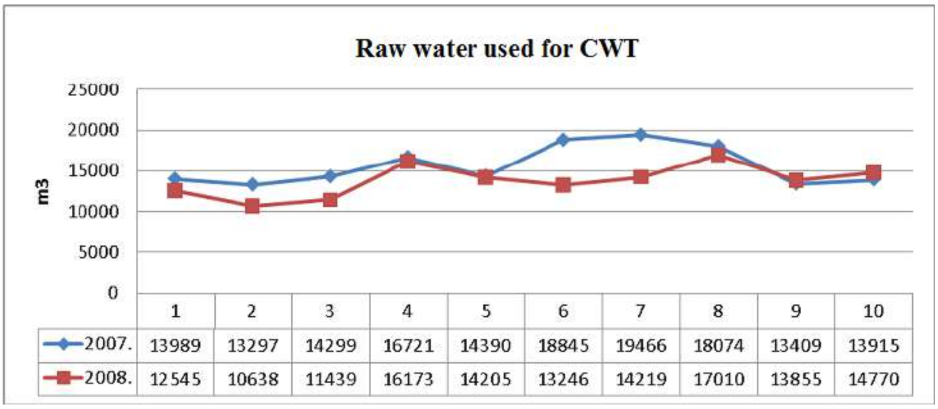

Figure 3. Reduction of the volume of water (raw water)

It is important to emphasize that the rationalization of raw water and other types of water that are produced in CTW largely influenced on decrease in the amount of waste water, and thus reduce the amount of treated water discharged from wastewater treatment (WWT). The amount of water discharged in the first 10 months of 2008 is reduced by 21% compared to the same period in the previous year (Figure 4). The effects of reducing the amount of discharged water are lower consumption of chemicals for waste water treatment in 20%, less power consumption for the operation of the plant and less expenditure on fees for waste water. Overall effects of reducing the amount of treated wastewater estimated at 7.500 € [4].

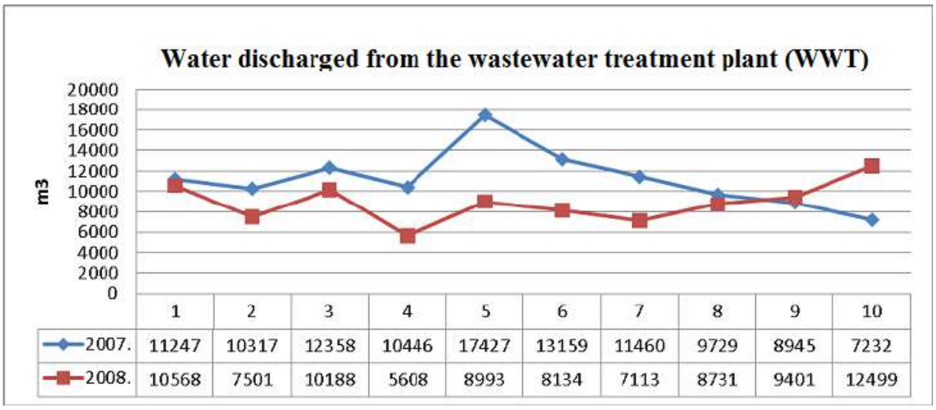

Figure 4. Reduction of purified water (water discharged)

Implementation of Option 2, concerning own supply with technical water for sanitary, washing and personal hygiene, was achieved in June 2008. Chemical treatment of water can produce filtered water to be used as technical water in Hipol water supply system. It is necessary, previously, to connect plumbing equipment with the CTW and provide equipment for the correction of pH and water disinfection. Results of the analysis of technical water showed that the water quality is in accordance with the Regulation on the hygiene of drinking water and can be used for their intended purpose. In addition to the expected financial effects (savings of € 5,148.9), Option 2 gives another dimension in the form of reducing the amount of water that can derive from underground aquifers as its source.

There is a legitimate interest why the treated water discharged from the WWT Plant should be used in CTW instead of raw water withdrawn from the canal. It is because of the high fees that Hipol must pay for the abstraction of water from the canal and for discharge of water into the canal. WWT Plant with its efficiency contributes to the same quality of treated water at the exit of the plant, and to some indicators, even better quality than the raw water quality withdrawn from the canal DTD for CTW use. Thus, using the circular flow of water, Option 3 was carried out, and the two systems are merged into a single technological unit. Environmental protection and thus the protection of water resources is achieved by reducing the actual amount of carbonate sludge to 150 t / year [4].

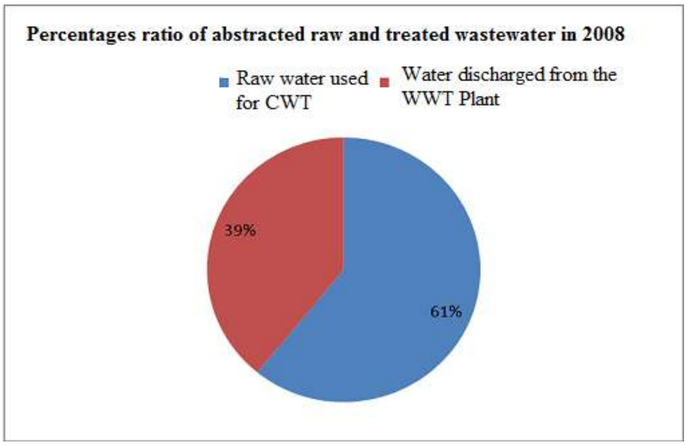

Figure 5. Structure of raw and waste water in 2008

CONCLUSION

HIPOL's commitment to implementation of the UNIDO project of the Center for Cleaner Production in Serbia represents a qualitatively different attitude towards the economy, development, energy efficiency, improvement of working conditions and the environmental problems. The case study shows that a good environmental performance also provides significant economic development. This paper presents the analysis of the quantity of all types of water (raw water consumption and wastewater release) before and after the introduction of cleaner production in the observed time period (from 2007. to 2008). Effects of the implementation of cleaner production are reflected in the reduction of the quantity of raw water and wastewater release of 18,305 m3 (11.7%) and 23,584 m3 (21%), respectively. Benefits of implementation of cleaner production have been presented through the reduction of both energy and water consumption in a total savings worth of € 120,000 where savings for the analyzed amount of all types of water (raw water consumption and wastewater release) worth € 19,148. Achieved solutions of ecological problems are shown in a significant improvement of environmental performance confirming the advantages of an integrated system for environmental protection. In this way, a balance between economic development and environmental conditions is achieved with respect to the Law on the protection of the environment as a human right to live and develop in a healthy environment.

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USAGE OF ANTHRACITE IN DRINKING AND WASTEWATER PURIFICATION

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ABSTRACT

Anthracite is as good as absorción means, and it is widely used for purification of drinking water and wastewater.

Key words: anthracite, waters, ecology.

INTRODUCTION

AM “Vrška Čuka” Avramica located in the Eastern part of Serbia, around 10 km SE from the city of Zajecar. Mine is producing high-quality anthracite coal. Coal have black – gray colour, metallic-glass shine and depending on its metamoprhosisit can appear as a graphite. It is brittle and easy to break, rarely save a whole pieces. Scratch mark is black. Fracture is irregular and with sharp edges. It occurs in two macroscopically different types of coal, such as amorphous carbon and crystalline carbon. These physical properties of anthracite are suitable for the purification of water.

USE OF ANTHRACITE IN PURIFICATION OF DRINKING WATER

Elemental analysis by Institute of General and Physical Chemistry anthracite showed good coal quality with more than 80% C and less than 1% S. These features indicate that anthracite has a good filtration and sorption characteristics, qualifying it for purification and filtration of drinking water.

Based on these research results have shown that the anthracite very good for purifying drinking water. Anthracite from mine "VrškaCuka” with an ash content below 6% and a grain size of 0.6 mm to 5.00 mm was used in further studies.

An anthracite samples were sent to the Institute for Public Health “Dr. Milan Jovanović – Batut” - Center for Toxicological diagnostic, Belgrade to investigate its applicability for purification drinking water. Results of analysis are written down in a Report No. 6283/ per u.896 from 14.05.2002.

The study included the determination of the characteristics of the coal (volatility and metal content), the discharge of substances soluble in water (to simulate conditions superiors in the planned use of anthracite: coal ratio, the water and the contact time), changing the characteristics of the water after contact with anthracite and dynamic migration of total organic matter (TOC), PAHs (polyaromatic hydrocarbons), and benzo (a) pyrene content after 24, 48 and 72 hours of contact. Based on the results of these studies it was concluded that the extraction of organic and inorganic substances distilled and deionized water from anthracite equal and very small. After contact of water (distilled and deionized) to the anthracite has not been any significant migration of the tested compounds videlicet, all the parameters are within the expected values Regulation on the hygiene of drinking water (Official Gazette no. 42/98). The extraction of polyaromatichydrocarbons, and benzo (a) pyrene is negligible, and below the detection limit.

Further down the report states:" due to results of the performed analysis it can be concluded that anthracite prepared as in samples should not pose any threat to consumers.Given that according to studies and under conditions simulating real applications, there are no changes in a drinking water, which could jeopardisehealth of consumers".

For the purpose of purification of drinking water Anthracite is incorporated into fewwater systemsex. Makis - Belgrade, plumbing Lazarevac and Negotin as well as pilot plant in Elemir near Zrenjanin.

PROCESSING MARKET AND THE NEED FOR ANTHRACITE

Due analysis of the surveys, we can conclude that more than 50% of the water in the technological line do not have represented filtration on a two-layer filters. Mostly represented filtration in sand filters. Only 10% of respondents confirmed that they have completed or in the near future can complete necessary documentation needed for a water treatment technologies. These water supply systems have expressed the interest of anthracite as filtering material. interested systems are Belgrade water supply (Makis II, reconstruction of existing facilities), Leskovac (Barije) and Arandjelovac. Estimated anounts are around 600 $m^3$of product.

Further analysis are showing much higher potential due to physical - chemical and bacteriological - biological quality of drinking water. It can be concluded that the needs for a product are much higher..

Republika Srpska has expressed its needs for Banja Luka's water supply system. Amounts are around 400 qubic meters related to the reconstruction of existing and extention of piping systems.

Summarasing above stated, estimated amounts of the product are around 1,000 qubic meters. If we include sanitary control Regulations amounts are significantly higher.

THE COST OF PRODUCTION

ROM costper tone is95 EUR processing , separation and washing are adding additional 35 EUR per metric tone totaling in 130 EUR per tone. Additional costs costs for thermical treatment are40 EUR plus wrapping and packaging 20 EUR per tonne, transportation and handling is 10 EUR per tone of product. According to stated finalized product can be estimated at level of 240 EUR per metric tone of anthracite

Survey shows that retail price of world famous manufacturers are somewhere between 750 EUR per Mt (China) to 950 EUR per Mt(England without VAT) respectively.Recommended price for our product can be between those values.it should be emphasized that our product have better performance than world manufacturers in the range of 10% regarding sorption analysis.

USE OF ANTRHRACITE AS FILTRATING – SORPTION AGENT IN PURIFICATION OF WASTEWATER CONTAINING OIL AND CRUDE OIL

The Power plant Industry of Serbia, as a biggest problem emphasizes oily wastewaters.. None of the existing power plant don't have implemented a system for purifying oily wastewater, regardless of the type of liquid fuel used. The evacuation of the water, from object to object, performed, depending on the place of origin in the rain sewage, landfill coal, recipient, tracked station, the return chilled water, city sewer, etc. Unsolved problem at the start of thermal power plant and insufficient maintenance during the operation is leading to the fact that the amount of this water are increased on daily basis., regardless of the content of oils and fats in them. Attempts to introduce, or build, adequate facilities for water treatment have not been satisfactory. And those thermal power plants that posses required the projects hence they are not implemented due to various reasons such as lack of space,bulking, lack of funds etc. Some thermal power plants permission is conditioned with a construction of purification facilities.

It is the fact that inside JP PEU is existing mine Vrska Cuka with a production of anthracite as a hight quality coal. Worldwide usage of anthracite in water purification is one of the reasons why beneficiation of ROM product is considered. Obtained results are in the range of world famous manufacturers. During the research, it is noticed that product is showing some sorption characteristics. Those finding led to idea that product itself or with some additives can be used in treatment of oil polluted wastewaters generated in Thermal Power Plants.

The fact that anthracite itself is efficient removal of trace organic substances from water, drive to a preliminary reserch of the possibility to use anthracite in removing the oily fragments from wastewater. During those analysis it was found that anthracite can be efficient agent in sorption. This is where idea came from.

Based on the results estimated costs for a wastewater treatments can be found in table below:

Table 1. Price of filtration / sorption mass

Activated carbon	150	din/kg	150.000	din/t
Zeolite 13x	250	din/kg	250.000	din/t
Anthracite	15	din/kg	15.000	din/t

It is a fact that the sorption capacity of activated coal is around 4 times higher than the sorption capacity of anthracite, and a cost comparison of those sorbents is putting anthracite as favorable product. Price of activated coal is also at least 10 times higher than the price of anthracite This can say that at the same cost anthracite can be purify 2.5 times more wastewater.

Assumption is that wastewater contain oil in a concentration of 5mg per liter and it need to purified until concentration of oil is 1mg per liter. According to calculations, we can assume that for 1 qubic meter of water we will need 0.5 kilogram of anthracite. That results in a cost of sorption agent as 7.5 RSD per cubic meter of oily water. I we consider that after purification we can use anthracite as a fuel in Power Plant that also decrease cost and remove waste disposal.

Implementation of chemical treatment of oily wastewaters can extend anthracite sorption life up to ten times.

Based on surveys in the Institute, ROM anthracite can be used as oily wastewater purifying agent. It decreases cost significantly due to avoiding classification and any further treatment.

At the end of the assessment of the effectiveness was made of selected filtration / the sorption agents, and has been shown to be very suitable anthracite, not just as efficiently and as cost-effective for filtration / sorption agent.

Mine already produced anthracite for filtration of wastewaters and delivered thermal power plant with a pilot facility. Purifying facilities are already built is Heating Plant Zrenjanin and Power Plant Drmno. Results from purifying facilities have shown that the oil contain is decreased below 0.2 ppm. Results from both plants are the same as per results given by laboratory.

Technical Faculty in Bor done research and series of laboratory testing in treatment of oily wastewaters from RTB "Bor" using the fine class of anthracite coal produced "VrškaČuka" mine. For this puroposefine anthracite class (FK) size is used. Classification is as follows:

- (-1+0)mm with an ash content of 38.17% and
- raw coal (RC) size class (-10+0)mm ash content of 39.52%.

Experimental results are shown in Table 2 .

Table 2. Absorption capacityregardingthe initial concentration of oil in wastewater.

Initial concentration of oil in waste water Co (mg/l)	Apsorption capacity Q (mg oil/g coal)
135	0,42
104	0,31
120	0,36

The results of analysis of concentration of oil in purified water, and the degree of absorption depending on the range and quality of the test class fine anthracite coal are given in Table 3.

Table 3. Concentration of oil in the purified wastewater and the degree of absorption depending on the quality class of the fine coal.

Sample class coal	Mass of solid (g)	Concentration of oil in purified water C (mg/l)	Degree of absortion A(%)
FK	22,25	40	79,37
RU	22,15	37	72,59

Reserch of absorption under dynamic conditions showed that fine class raw coal and anthracite from RA, Vrška Čuka, Avramica can successfully be used for the treatment of oily wastewaters produced by RTB "Bor".

The treated water contains oir and grease in concentrations within the permitted limits, according to the Regulation .After treatment waste waters are safe to be drained in sewer system From aspect of economy it is important to say that used class of is not adequately valorized by mine and it usage in purification can contribute to better mine performance.

Technical Faculty in Bor also performed research about absorption of metal ions by fine anthracite fractions. Research shown promising results for anthracite fines from Anthracite Mine "Vrska Cuka". According to research fines can be used for removal of metals from various efuenats to prevent pollution of natural watersheds. Crucial for this research is availability of fines and its very low cost.

CONCLUSION

Mine anthracite, Vrška Čuka, is one of the eight anthracite mines in the world that has a very good quality of coal. It is used as a raw material and technology: for purification of drinking water and wastewater to produce carbon cathodes, silicon carbide, graphite, etc. after processing of coal low quality cola is used as fuel in smelters, brick factories, power stations etc.

Anthracite mine "Vrska Cuka" produces high quality coal. Mine operates underground using room and pillars mining method. Ash content of ROM coal is in the range from 30 to 35 %Processing facility includes wet coal separation plant with gravitation and flotation line. Processing the ROM coal separation plant can decrease the ash content to ranges between 2% and 6% respectively. This is high quality concentrate which is base for filtration materials used in purification of drinking water, wastewaters and industrial wastewaters.

Separation plant is processing the coal ash content up to 6%. This coal is used to produce anthracite for drinking water purification. It is necessary to build a facility with a set of sieves, mill and dryer to improve classification of ROM coal. Total investment is around 100,000 Eur with a capacity of 2.5 tone per hour.

Construction of a plant for the production of anthracite mine gets a new technological product that is used for purification of drinking water, oily and wastewater. Byproducts are to be used as energy sources in cement plans, Power stations, Smelters and Brickyards. Construction is about to increase utilization of ROM coal to number which excesses 95% of all production.

ROM coal price is 9384 din per tone. Utilisation and implementation as explained above is multiplying the price of the product./ Investment in preparation plant is the only possibility with no further increase in costs. The cost of ROM coal production is the same. For the increased production investment need to be increased for exploration and development cost. It should be noted that the operation of the plant for the production of anthracite will engage the existing workforce (i.e. will employ workers who are already working in the mines or separation). All this will allow increasing economy of the mines.

As stated above, the vital interest is construction of plants for the production of anthracite, which will be produced technological raw material. This product has a very important place in the market, and our country is importing it. Investment and further construction of the mine plant will produce sufficient quantities for domestic needs. With this production and processing of coal, mine will achieve profitable results, which will favorably affect the area where it is found,videlicet on the border with Bulgaria in underdeveloped areas.

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ASSESSMENT OF HEAVY METALS POLLUTION IN THE BOR RIVER (SERBIA)

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ABSTRACT

This paper contains analysis of heavy metals in The Bor river for the period from 2009 to 2013. The main source of waste waters in Bor is waste water created in mining and metallurgical activities for copper production. Based on the measured concentraction of Fe, Pb, Zn, Cu, Cd, Ni, Cr and As in The Bor river and the conducted characterization of river sediment, the impact of the copper production industrial combine on the quality of The Bor river is provided.

Key words: river pollution, industrial waste water, heavy metals, sediment.

INTRODUCTION

Influence of antthropogenic agents on pollution of waste waters is one of the most serious issues during the last several years worldwide. Development of industry, urbanization and increase of population make the water pollution issues become more obvious and they lead to serious environmental issues [1-3]. Many research studies have showen a close relationship between water quality and urban development [4-7]. Heavy metals are serious pollutants becouse of their toxicity, persistence and non-degradability in the environment [8-10].

The increased content of heavy metals and arsenic in surface waters have a negative influence on the flora [11-12] and fauna as well on the health of people [13-15].

Determination of the concentration of heavy metals (Cd, Cr, Cu, Ni, Pb, Zn) in the river and river sediment and their influence on polluting the entire region have been a subject of investigations by many authors [16-20].

Influence of mining and outdated procedures for obtaining copper as well as irrational water consumption are seen in a high level of water streams pollution [21,22].

Contemporary trends and environmental standards are transformed by pyrometallurgical plants into industrial-environmental facilities. Development of metallurgical combines is reaching for application of the best available technologies which have a considerable effect on imporvement and environmental protection [23-27].

MATERIAL AND METHODS

The main sources of the waste waters created in Bor are the waste waters from the undergound operationsin the mine (blue water) and the drainage water that is collected around the open pits (Bor, Veliki Krivelj and Cerovo), waste water from the smelter plant i.e. waste water from the sulphuric acid plant, used electrolytic solutions and the cooling system water; discharges from the waste dumps [28].

Mining and metallurgical activities have had a significant impact on the natural water streams in Bor region. The Bor and Krivelj river present an open waste water collector (for industrial and communal waste water) and they are degraded. After the confluence of The Bor river into The Krivelj river, The Bela reka river is formed which goes into the Timok. Waste industrial water goes into a collector without prior treatment, from where it is sent to The Bor river which severely pollutes the river itself and affects the quality of the Timok [29,30].

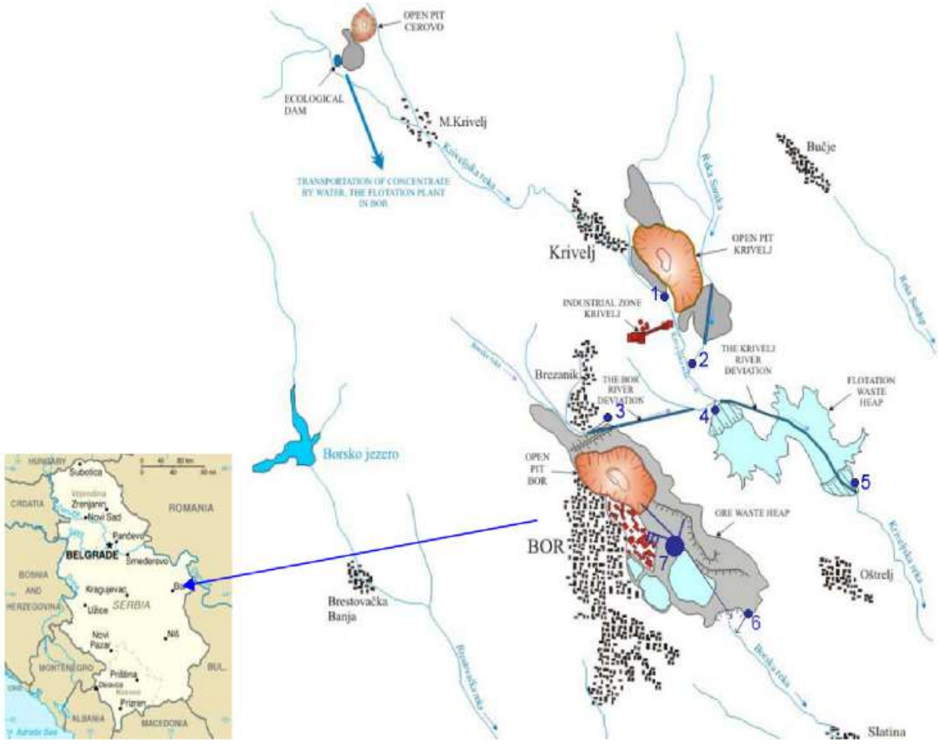

Figure 1. Map of Bor copper mine (Bor-Krivelj-Cerovo)[28,31,32]

As it can be seen in Fig 1. there are 7 different places where wastewaters enter natural water streams of Krivelj and Bor Rivers.

They are presented as:

1. Wastewater from open pit "Veliki Krivelj",
2. Wastewater of Saraka stream,
3. Open pit Bor wastewater,
4. Wastewater of flotation dam 1A of flotation tailings pond "Veliki Krivelj",
5. Wastewater of flotation dam 3A of flotation tailings pond "Veliki Krivelj",
6. Wastewater from lake "Robule",
7. Collective wastewater from open pit Bor and copper smelting and refinery plants.

Public Health Institute Timok analyses The Bor river four times per year at the measuring point "Slatina". Effluent samples were analysed by using the Atomic Absorption Spectrophotometer Perkin-Elmer's Model 403. This analysis includes current and realistic concentrations of heavy metals in The Bor river.

RESULTS AND DISCUSSION

Charts 1-9 present average annual pH values and heavy metals contents in The Bor river at the measuring point "Slatina".

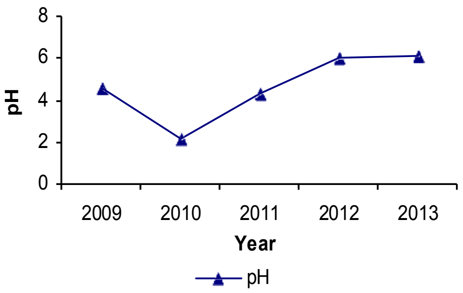

Figure 1. Average annual pH value in the Bor river from 2009 to 2013

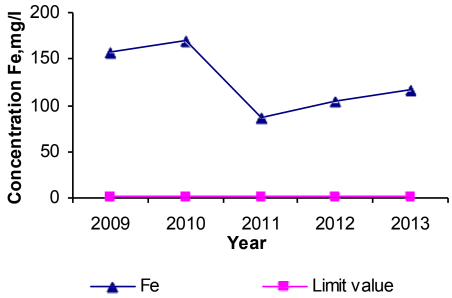

Figure 2. Average annual content of Fe mg/l in the Bor river from 2009 to 2013

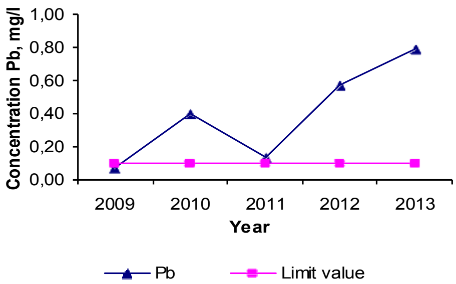

Figure 3. Average annual content of Pb mg/l in the Bor river from 2009 to 2013

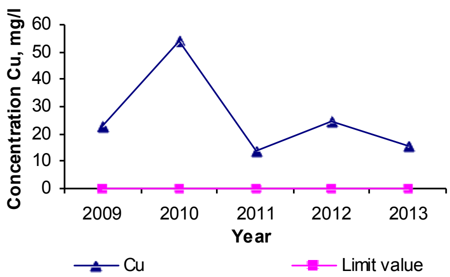

Figure 4. Average annual content of Cu mg/l in the Bor river from 2009 to 2013

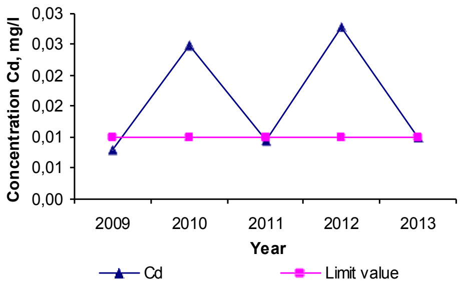

Figure 5. Average annual content of Cd mg/l in the Bor river from 2009 to 2013

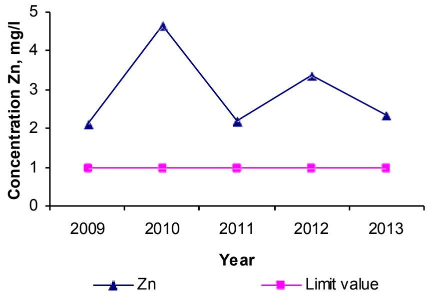

Figure 6. Average annual content of Zn mg/l in the Bor river from 2009 to 2013

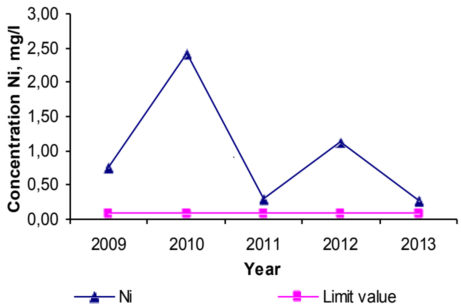

Figure 7. Average annual content of Ni mg/l in the Bor river from 2009 to 2013

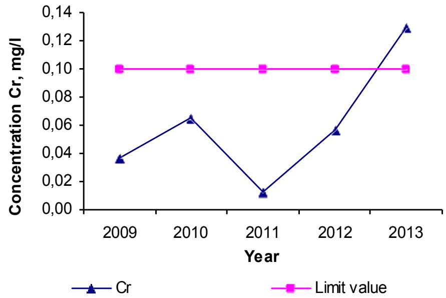

Figure 8. Average annual content of Cr mg/l in the Bor river from 2009 to 2013

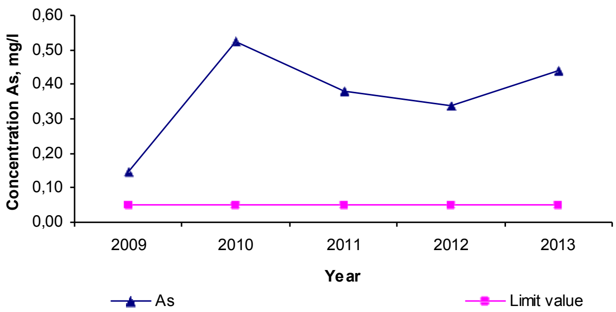

Figure 9. Average annual content of As mg/l in the Bor river from 2009 to 2013

Many authors have addressed the impact of water pollution with heavy metals on the river sediment [33-35].

Characterization of the river sediment in Bor was done within the UNEP Project. Determining the capacities for environmental monitoring in Bor in September 2002 at the following locations:

- Sediments in the Bor river before the confluence with the Krivelj river (sample ID 10-33)
- Sediments in the Krivelj river at the confluence with the Bor river (sample ID 10-34)
- Sediments in the Bor river after the confluence with the Krivelj river (sample ID 10-33)

Table 1. Analytical results of the Bor river sediment in 2002 (36-39)

Parameters / sample ID	10/33	10/34	10/35	Serbian Standards, mg/kg		
				MDK in soil	Soil (mg/kg absolutely dry matters)	
					Limit value	Remedial value
pH	7,69	4,56	6,39	/	/	/
Heavy metals, mg/kg:						
Lead, Pb	38,3	105	41,2	100	85	530
Cadmium, Cd	< 1,25	< 1,25	< 1,25	3	0,8	12
Zink, Zn	133,5	92	101,2	300	140	720
Copper, Cu	2937	3257	2688	100	36	190
Chrome, Cr	8,9	9,2	9,2	100	100	380
Nickel, Ni	8,9	9,2	9,0	50	35	210
Arsenic, As	315	291	310	25	29	55
Mercury, Hg	0,472	< 0,15	0,406	2	0,3	10

UNEP's report (2002) shows that the analyzed samples have indicated higher pollution with copper and arsenic, as well as increase of soil acidity.

CONCLUSION

Mining and metallurgical activities for copper production have had a significant impact on the quality of the Bor river making it acid and extremelly polluted with heavy metals. The increased contents of Fe, Pb, Zn, Cu, Cd, Ni, Cr and As are a consequence of outdated technologies for copper production and inadequate waste water tretment before discharge into the recipient. The analysed soil samples have shown increased pollution with copper and arsenic, as well as increased soil acidity. By applying BAT technology within the New Flash Smelter and Sulphuric Acid Plant Project an effluent treatment plant will be constructed which will significantly improve the environment. Treated water will not be discharged into the recipient, instead it will be used in the industrial process. Thus, considerable improvement in the quality of the Bor river should be expected.

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NATURAL RESOURCE MANAGEMENT

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ABSTRACT

A new wave of concern for the environment occurred during the 90s by launching claims that environmental problems are global in character. In fact, it is no longer enough that a country conducts proper environmental policy. Neither can polluted air be ordered not to cross the state border nor can an international river be informed not to flow in its bed through all the countries which it has been flowing for centuries. New findings about ozone depletion in the '90s were not announced to the world public for fear of the consequences for all of humanity, because nobody really knew how many centuries are needed for recovering waste. Even the problem of "acid rain" in Germany, "the greenhouse effect“ in the United States and "waste impact" in Great Britain have not sufficiently sobered up environmental policy makers who cannot seem to understand that the market is not able to determine the price of resources such as water, air, clean environment and nice view, and that the state intervention is, therefore, necessary, as a complementary force which contributes to improving the functioning of markets [1].

Key words: economy of nature, environmental economics, environmental management, environmental taxation, ecological equilibrium.

THE ECONOMY OF NATURE

Theorists of Ecological economics offer two solutions for this: (1) it is necessary to know who the holder of a particular natural resource is, and (2) it is necessary to force producers and consumers to pay the actual costs in proportion to their share of environmental pollution. In the first case, the owner and the potential pollutant could negotiate, because if, for example, a private fishpond is in question, then the owner would take care to avoid over-fishing. In the other case, however, if it had been common, the producer's and the consumer's calculation would include in the price of gasoline and the cost of remediation of harmful effects of exhaust gases. In this context, the economists' task would be to determine the price of the environment, like the price of any other resource, so the economic policy would be reasonable in terms of official state policy towards current and potential pollutants on the principle of cost-benefit analysis. However, the governments are now acting quite the opposite; they encourage energy consumption by subsidizing prices. Agricultural subsidies encourage the use of pesticides and fertilizers. Permanently entrenched lobbies do not care why the U.S. subsidize the state industry, why Germany subsidizes coal mines, why Great Britain subsidizes the use of vehicles that are owned by companies, etc.. This in turn shows that the economic compromise between subsidies and environmental costs is not reached. Even less has been done on the problem of formulating development strategy that allows limited use of existing resources (with the idea of "sustainable development"). And it is the sustainable development which does not exhaust the reserves so the respective reserves would remain for future generations to use. Therefore, it is a question of relation towards the present, as well as an ethical issue within the current environment policy. This is why, for most people today, the most important environmental issue in a market economy with a combination of private sector interests and government regulations is: "how to leave to posterity a world that is, if not better, at least the same as it was when the present generation inherited it"[2].

For logistical entrepreneurs reliability is more important than speed. From an economic point of view, it is about goods to be in the right place at the right time; environmentally, this needs to be done with the least possible burden on the environment [3]. Criteria of "speed" is no longer of prime importance. The transition to a slower, but environmentally favorable means of transport, is quite acceptable to so-called 'ecologistics'. The combination of ecology, economics and logistics in the structural projection of ecologistics prompts the modern society to solve the problem of mutual harmonization of road, rail, air and maritime traffic, so the traffic problem would not become a hindrance of economic growth. The structure of the mass transport must now choose the most environmentally advantageous mode of transport, particularly when it comes to the introduction of fees for heavy transport, increase of taxes on mineral fuels and the introduction of tax on carbon emissions. Ecologistics now pleads to significantly reduce costs through greater reliance on the maritime and railway transport, which provide environmentally friendly and better treatment of goods and more environmentally reliable transport[4].

"GREEN" ECONOMY MANAGEMENT

Goal of the II UN Conference on Environment and Development (Brazil, from 1 to 12 June, 1992) was the interaction between the economy and environment, and balancing economic and environmental objectives within economic decision-making and business management. These ideas are not new, because their intellectual foundation was formulated as early as 1971 in Switzerland, which served for the preparation of the so-called Stockholm conference. Then, however, it was dramatically emphasized that poverty is a major source of environmental pollution because a billion of the world population that lives in poverty, misery and deprivation, are forced, out of desperation, to assault their environment just to survive. The cumulative effects of the devastating onslaught of individuals on nature are big and dangerous, especially when destruction and poverty are combined. That is why the Brundtland commission rejected the so-called zero growth, since zero growth is a consequence of the development of destructive processes to the environment. To meet the needs of growth, the concept needed to include the so-called sustainable development, within the United Nations Conference (calledECO '92.). The concept of sustainable development implies change of climate, cross-border expansion of the air pollution, waste management, protection and management of land resources, conservation and biodiversity, protection of oceans and coastal areas and the quality of supply of freshwater resources. Global risks in the field of biological and genetic resources are forcing the accelerating transition onto balanced development, which must be done through incentives and regulatory measures. In market economy, this means that the cost of the environment is built into the prices of products that induce the growth of costs. This is the so-called "polluter pays" principle. The solution, through regulated action, involves the formation of environmental funds which gather resources intended strictly for the rehabilitation of the environment. The aim is clear: the environmental protection measures must integrate into economic growth and business management, and an economic basis for cooperative global alliance must be formulated, if there is a will for the EARTH to remain a safe home for humans and a common future.

In order to restore the healthy relations of the world trade flow, it is inevitable to incorporate environmentally-protective mechanisms in international trade. In this context, cheapening of agricultural products is not a central goal, if it happens at the expense of nature. Therefore, reduction of subsidies for "green products" does not necessarily mean the preferred policy of reduction of inherited environmental protectionism if the substance of ecology is not incorporated into the structure of market prices. The cost of production of organic food can can no longer be irrelevant, because they are already part of the structural reality. After all, market-competitive prices in international trade cannot protect natural resources of a country. Therefore, the environmental protection requires long-term financial and technological investments that would pay off most in the field of environmentally sound agricultural production.

The EU Commission has, after a process that lasted two years, proposed the introduction of a tax whose basis (subject to taxation) would be „the carbon content in fuel." The aim of the new tax, according to the proposal, is that the emissions of carbon dioxide be stabilized 1 on their level in 1990, but also the encouragement of energy efficiency and stability of supply.

Institutionally speaking, the European Union is not entitled to the introduce taxes, because it does not have fiscal sovereignty (in itself); therefore, the tax on energy can be introduced only by the member states in the form of a national tax, which would be included in fiscal policy harmonization. However, the fiscal (and economic) trend is such, that the new increase in tax burden is not an option. The solution is, therefore, found in reducing "other" taxes.

ECOLOGY AND ECONOMY

Green economists are already producing models for the valuation of environmental costs and benefits in national economies, so the national accounts would also show the changes in natural resources. Effects of consumption of natural resources should be empirically verified through the change of SNA (System of National Accounts and Methodology of UN), into the concept of national income, including those natural resources that are under the control of man. The goal is, therefore, for national income balance sheets to "turn green" in order to treat plants and animals in the same way ("increase in a country's livestock is included when it occurs, but the growth of commercial forests recorded when they are cut down)"[5].In the present calculation, the national income is often artificially increased by including the cost of preventing pollution. This, in turn, means that the pollution does not count as a loss of gross domestic product. Likewise, the decline in the value of natural resources is presented as an item that exaggerates the net national product. It is clear, in fact, that it is extremely difficult to say how much idyll costs. But deforestation, according to market criteria, is certainly the sum of loss of value of uncut trees and revenues from timber that could be achieved. But, this criterion does not include the value of forests as a wildlife habitat and a recreation area. Therefore, it is important that the development of the national balance sheet adapts to the needs of environmental protection. In the initial stage, it is important to build so-called balance satellites in the form of parallel balances (in addition to the official ones). These "new" balances would include the change in the quality of the environment (for example, increase of air pollution, extinction of certain species of plants and animals), and the evaluation of the damage to natural resources that are not commercially valued. For resources that do not have a market value, the controversial issue is what should be measured:(a) what is the cost of restoring the environment to its original state or (b) the amount of funds that consumers would be inclined to spend to improve environmental quality. All in all, the conventional models for the determination of wealth should be expanded and enriched in order to give adequate answers to the environmentalists who popularize the new calculations. Economists from the Division for the Advancement of rural areas at the University of Newcastle have already made a calculation model for British agriculture and forestry, "Set funds apart for the pleasure that green belts and national parks provide, add some more funds for the planting of trees to absorb the effect of the planet heater- carbon monoxide, and this supported net product is 25% greater than the net product". Low prices in mining, grotesque economy of scale and national subsidies have negative implications for the ecology. Intended sale of state (public) land to mining companies for a pittance ($ 12 per hectare), public funding of mining research results and tax deductions, which reduce the real costs of mining in the United States have significantly contributed to the degradation of eco-balance. Japan offers a wide range of incentives (from loans and subsidies to tax incentives) for the exploration and exploitation of mineral reserves. It is the same in Canada and Australia. German and French governments guarantee assistance and direct financial investments, and they also subsidize foreign projects of domestic mining companies [6]. Even the World Bank is financing the increase in mining production through the provision of loans under favorable conditions. Such a policy of exploitation of natural resources poses a serious environmental threat, because the real costs of world mining are hidden in the extensive producer subsidies as well as in unrecognized environmental damage. Low prices of ore today reflect the extraction-distribution economy, for which there are no costs of restoring denuded forests, eroded land, destroyed or polluted rivers. "The implementation of the stringent environmental laws suggests channeling part of the funds collected through taxation from industrialized countries into the mining countries of the third world. This mechanism would be facilitated by the World Bank through commissions on loans, which would be conditioned by nature conservation. A higher degree of recycling raw materials and substituting them by less "malignant" materials, in the long term, are additive mechanisms in the reduction in demand that environmentally stumbles. Gradual replacement of copper communication cables by more efficient optical fiber made of glass [7]also represents the future, which should be supported by tax rewards (not just by basic subsidizing of mining).The establishment of new companies for waste sorting and companies for thermal processing and construction of devices for waste incineration plants and systems for the production of packaging for recycling are a new challenge to the Ministry for the Environment, which, through tax benefits, features instruments from the Ministry of Finance. Also, placing the green dots on new products should be funded from the state budget.

In the economic and ecological theory and practice, it is considered that most of the natural resources are of a regenerative nature: rational use can renew a resource, and efficient use can increase the total volume of the resource. Mineral resources or raw materials of mineral origin "excavated from certain deposits or ore body" cannot be regenerated, nor can other mineral concentrations be formed. In mineral materials, therefore, only what is created by nature in the unique manner can be used. Therefore, attention should be focused on economic measures in order to protect the environment in the philosophy of sustainable development. Economic instruments, in order to protect the environment, are used as an effective form of replacement of regulations and as a complement to legislation, since legislation cannot always influence the rational use of resources and effective protection against pollution [8].

The "polluter pays" principle actually reflects the need to institutionalize environmental taxes (fees), as follows [9]:(1) differentiated taxation of regular and lead-free gasoline, (2) differentiated sales tax and customs duty on import of cars and trucks with higher consumption compared to cars with lower fuel consumption and the use of unleaded gasoline, (3) differentiated tax on goods with packaging that can be recycled, (4) additional sales tax and customs duty on cigarettes, (5) sales tax and customs duty on import of fertilizers, detergents and pesticides, (6) selective taxation of goods (in order to establish such price ratio that will stimulate the consumption of products whose production and use is less polluting) (7) exemption from corporate income tax (for polluters and manufacturers who, by new technology, reduce emissions and the use of polluting materials), (8) the exemption from value added tax and the introduction of tax on the use of natural resources through the income tax with the abolition of tax on the sale of secondary raw materials (so as to encourage the collection and processing of waste materials), (9) the introduction of fees for pollution, as compensation for the costs of the waste material, (10) introduction of tax for manufacturers whose products pollute the environment during the production process or use, (11) the introduction of penalties for polluters so as to be forced to introduce new technologies, (12) the existence of subsidies to help invest in clean technology and (13) the introduction of pollution charges, for the use of landfills, for the use of natural resources and space (which would be applied for the discharge of pollutants into the air, water and soil, disposal of solid and hazardous waste at the landfills, and to cover the cost of rehabilitation of natural resources and space).

In general, almost all countries of the modern world are seeking out and finding instruments and mechanisms for the implementation of the so-called Bergen Declaration on Sustainable Development (1990), which insists on the economic respect for commitments based on taking from nature - so-called debt towards nature. In industrialized countries, the fees for so-called mineral wealth have already been introduced (fees for mineral resources and mining fees), which essentially reflects the allocation of the portion of assets (calculated per unit of product) as reimbursement for the renewal of the available natural resources, for goods taken from the available natural reserve funds and for the repayment of debt towards nature. However, sand and gravel are present in almost all regions of the world, whereas oil and diamonds can be found only in "some" regions (because of uneven geographical dispersion of minerals). Therefore, the existence of so-called fees for mineral resources on selective basis, depending on the type of mineral resources, is economically justified. These allocations would be included in the cost of products, and would be used to repay debts to the nature. Debt for nature would incorporate a fee for use of mineral resources and compensation for damage caused to the environment.

ECOLOGICAL STRATEGY OF GLOBAL COMPANIES

For each transnational company (corporation), business success is becoming increasingly dependent on accurate predictions of future trends in the business environment of the company. Today, it is of great importance for the managers who are trying to create a picture of business environment for the twenty first century. Managerial structures in developed market economies are forced to respect the widespread opinion of the population which already refuses to accept a high degree of environmental degradation. And when environment is taken into consideration, companies are forced to respond more responsibly to public concern for the inevitable warming of the planet. Forthcoming financial years are future challenges for business dealings, because ecology is becoming a decisive factor in the future of business. The world's leading managers are already preparing to meet the strict requirements of environmental legislation and the demands of consumers, who increasingly insist on the organic components of the product quality[10].

Businessmen feel their vital role in protecting the environment, as they have already realized that the business processes are the dominant source of pressure on the environment. The same as employment is the key prerequisite of social security, the protection of the environment has become a leading prerequisite for doing business. Environmentally sensitive public is giving a chance to profit-oriented managers to color their business planning "green" and to diversify approaches to business organization, accounting, balancing success, corporate finance, marketing, management and public relations, in order to obtain environmental reputation, which predominantly determines consumer decisions about buying (environmental quality) products. Environmentally enlightened consumers in civilized societies with market orientation are ready to use (in an organized way) their purchasing power on the market and put pressure on the industry. Manufacturers have already felt that the demand for environmentally friendly products has an upward trend in the developed markets of the modern world. At the international level, a dramatic shift in consumer preferences "swallows" additional environmental expense burden. And, lo and behold, it is considered a new chance for competitive success, pressuring the leading managers to recognize the need to formalize the new development strategies of the companies, which includes a new marketing view of the world. New business philosophy must take particular account of the relatively strong segment of the population that is willing to pay for products that meet environmental standards. However, managers must take into account the inevitable truth that certain products will become unacceptable to consumers of ecological quality. In the short-time sequences, multinational companies can achieve high profits by bypassing investments into ecological research of product quality. But in the long run, these companies acquire the image of environmentally insensitive companies, lose their place in the highly competitive market, run late in the restructuring of the production programs and endure future rigorous environmental standards more difficultly.

SUMMARY

Environmental pressures of the public have forced the acceleration of the transformation of the evaluation of managerial success, which, in addition to the usual management performances based on the quantum of profit growth, incorporates long-term component of the ability to develop teams, who, business -wise and environmentally, introduce a company into the 21st century, focusing the company on environmental problems, with high environmental awareness of employees and with developed production of so-called green products. The public opinion of modern Western civilization goes in the direction of the topic for the same reason as the companies are fully responsible for the impact of their products and technologies and pressure that their products put on the environment. Managers are, environmentally, burdened by public opinion, and companies are faced with environmental responsibility by law. In this sense, the companies, along with their managers, formulate internal environmental programs and thereby assume full responsibility for the pollutants emitted and recycling. Many companies are already looking for eco-perfection and the reduction of environmental risks that are inherent in the production processes and products. Future environmental monitoring will be tasked to observe the negative impacts on the environment and comply with environmental standards, with derived effects in terms in terms of raising the level of environmental awareness and savings of companies. Monitoring teams will have the opportunity to compare the environmental performances of production processes and products with environmental standards and to ensure their compliance, irrespective of the fact that ecological confrontation of costs and benefits creates problems in the company. But nevertheless, the future of the market will belong only to companies with strong ecological product development strategy whose industrial-production cycle envelops four stages in terms of (1) the extraction of raw materials, (2) the production of goods, (3) use of product, and (4) disposal of products after use (and recycling). It is now accompanied by the requirements for minimizing the environmental impact of products which expired, and for eliminating the perceived problem of waste disposal. In ecologically redefined business strategy, the companies are becoming fully responsible for the product life cycle, from the stage of production to the stage of waste and reuse. Production processes of the future, therefore, must be adjusted to recreating

the roundabout and the inputs and outputs with a modular design, which combines relatively short technology cycles and long-term use of products by means of recycling [11].

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STRATEGIC ENVIRONMENTAL ASSESSMENT (SEA) AS AN INSTRUMENT FOR ENVIRONMENT PROTECTION IN BOR MINING-INDUSTRIAL REGION

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ABSTRACT

SEA is one of the most important control instruments for achieving sustainable development in urban and spatial planning. When SEA is fully (methodologically, timely and legislatively) integrated in the planning process, it enables consideration of environmental effects equally with the economic ones. This is of particular importance in polluted and degraded areas as Bor and its surrounding. In the last few years several SEAs have been compiled (or adopted) for this area on different hierarchy levels, i.e. for: Master plan of the City of Bor, Spatial Plan for the Municipality of Bor and Spatial Plan for the Special Purpose Area of Bor and Majdanpek Mining Region. The paper will address evaluation of environment protection in these documents.

Key words: Strategic environmental assessment (SEA), environment protection,urban and regional planning, Bor, Serbia, mining & industry.

INTRODUCTION: SIGNIFICANCE OF STRATEGIC ENVIRONMENTAL ASSESSMENT FOR BOR MINING & INDUSTRY REGION

Strategic Environmental Assessment (SEA) represents a significant tool to ensure that environmental protection considerations are fully included and properly addressed in the development of plans, programmes and policies. Inclusion of mandatory SEA in Serbian national legislation was important prerequisite for harmonisation with *Acquis communitaire*, i.e. with the Directive 2001/42/EC on the Assessment of Certain Plans and Programmes on the Environment (SEA Directive) [1]. After the Law on SEA (2004) was adopted, compilation of SEA in Serbia was requested quite extensively for almost all types of plans [2].

The significance of SEA is non-questionable, especially for the areas with degraded nature and poor environmental conditions. The main positive results of SEA implementation include [3]: helps to incorporate sustainability principles in the policymaking process; it can influence and improve decision-making contributing to establish an environmentally and sustainable integrated context for the development of policies and plans; enables tiering of environmentally structured actions; provides better context for assessment of cumulative effects; provides screening context to lower levels EA, particularly project' EIA; anticipates impacts that can occur at project level, improving and strengthening project' EIA.

Compilation SEA of Spatial Plan for the Special Purpose Area of Bor and Majdanpek Mining Region started simultaneously with compilation of SEAs for Master plan of the City of Bor and Spatial Plan for the Municipality of Bor [4], [5], [6]. All mentioned SEAs are a result of review, clarification and improvement in implementation of environment protection and sustainable development principles in compilation of those plans, along with respecting requirements and expert recommendations of agencies, institutions and other stakeholders regarding the necessity of eliminating or limiting negative effects of dominant activities (exploitation and processing of minerals, industry) on environment. The main aims, in this regard, were: rational utility of non-renewable energy resources and sustainable development based on utilizing mineral resources; discontinue with further degradation of the area; endangering and destroying natural resources and welfare; preventing resource overuse, unplanned spatial use and construction; revitalization of endangered areas; environment protection including protection of natural and cultural heritage, as well as economizing, rationally using and protecting the natural resources.

The main imperative during compilation, and especially realization of mentioned SEAs was absolute respect of top down and bottom-up planning principles, as that is the only way to provide adequate implementation of protection measures emerged from expert multicriteria evaluation of environmental protection variables made during the SEA process.

ENVIRONMENT IN BOR MINING&INDUSTRIAL REGION: STATE AND MAIN IMPACTS

The present condition of environment in Bor region can be described as unsatisfying. The combination of different synergetic and cumulative environmental impacts of various (mainly mining and industry) activities during the last several decades resulted in severe pollution of air, water and soil, whose revitalisation will assume implementation of mitigation measures and monitoring of all environmental parameters. Environment quality in this area is dominated by mining and metallurgy development (for more than 110 years) in Bor and Majdanpek, as well as different industry installations, while measures for limiting the emission of polluting substances have not been properly practiced (due to several reasons, as inadequate regulation, small fines, low ecological awareness, lack of control, etc.). These facilities have negative impact on the quality of main environment factors, population health, ecosystems, flora and fauna, landscape. Extremely bad economic situation in Serbia during last 25 years, along with lack of investment in industry technologies and protection measures, low employment level and absence of remediation and revitalisation measures had additional negative impact on environment conditions in major part of Bor region. Environment quality is better only in the area of the National park „Đerdap“. The main environmental „black hot spots“ include: V. Krivelj, Field 2 and Old Bor tailings, surface mines in Bor, Krivelj and Majdanpek, flotation tailings Valja Fundata and Šaški creek, tailings dumps in Bor, Krivelj and Majdanpek, metallurgy complexes in Bor [5], [6].

Environment quality in Bor region is under direct impact of activities in:

1. **mining** - activities of MTB Bor Group and MTB Majdanpek, including cumulative effects they induce (surface mines of copper, limestone, quartz sand and sandstone; landfills and flotation tailings; underground copper mine): occupying agricultural land; change of area morphology; industrial waste; noise and vibrations; contamination of air, water and land; lowering level of underground water; flotation tailings: contamination of water and land;
2. **metallurgy** and flotation (melting house, industrial waste, waste waters, etc.):pollution of water and air with SO_2, suspended particles, soot, Pb, As, Ni, Cd, etc.
3. **industry** - factories for copper and processing of precious metals: copper pipe industry and gold production (dust emissions and wastewater), enamelled wire factory (organic compounds emission, wastewater), electrical products factory (toxic trichloroethylene), timber industry (noise and vibrations); activities in industry (dust, suspended particles),
4. **energy** facilities (thermal power plant, power plant): dust, soot, CO_x and SO_2;
5. **traffic**: dust, suspended particles, SO_2, noise and vibrations;
6. **charcoal production**: dust, CO_x;
7. **agriculture**: overuse of pesticides and fertilizers, waste from large farms;
8. **inadequate waste management** (soil degradation by leachate form non-sanitary landfills) etc.

Due to inadequate monitoring in the Bor region, determination of basic environment variables was based on conditions and opinions of competent institutions and public enterprises and existing documentation on environment.

METHODOLOGY OF SEA IN SERBIA

The methodological approach is based on the fundamental concept of simultaneous development of objectives of the plan and the solutions developed within the SEA on one hand, and a holistic set of goals that support environmental protection and sustainable development on the other, which are then discussed in relation to the initial decision of the plan. Thus, the application of SEA in the planning process helps promoting equal representation of environmental, social, economic and other impacts, which further implies that the implementation of such plans enables implementation of sustainable development strategy. Serbia has a huge problem in lack of detailed elaboration and verification of unique methodology for the development of this type of assessment, so all the evaluation must rely on foreign methodologies and experiences, respectively guidelines, instructions and case studies [7], [8], [9], [10] .

In its practice of elaborating strategic assessment of effects of various activities in space on the environment, the Institute of Architecture and Urban & Spatial Planning of Serbia has originally used and developed a method within scientific project entitled „Method for Strategic Environmental Assessment in Planning the Spatial Development of Lignite Basins" (Project Manager B.Stojanović, PhD) and also supported by the SOTAVENTO method which has been implemented for the first time in determining effects of wind turbines (eolic fields) on the environment in Spain [11]. For the needs of carrying out strategic environmental assessment in Serbia, the mentioned methodology has been adapted and adjusted to the needs of multi-criteria analysis for spatial plans of higher level and spatial plans for special purpose areas [12], [13], [14]. During the analysis, basic problem was a modest national information base about the environment and the lack of a system of indicators - indicators for assessing and monitoring the environment.

The effects that planning decisions can have on the environment are quantified by utterances of (-3) to (+3) (also including utterance (0) denoting a fact that certain activity does not affect environmental quality parameters). Their territoriality is uttered at the level of trans-border, national, regional, municipal and local level. In a final utterance, and after having carried out multi-criteria analysis of planning solutions relative to previously defined goals of strategic environmental assessment (related to the protection of air, water, land quality, etc.), the quantitative/qualitative characteristics of planning solutions are combined. This utterance is defined in the form of table, through description of impact strength, territorial distribution and likelihood of occurrence. The mentioned conclusions of the multi-criteria analysis are used for establishing the measures for neutralization and reduction of environmental effects of certain activities in space. On the other hand, the process of detailed spatial plan elaboration it is necessary to implement additional methods for elaborating the multi-criteria analyses [12]. For the needs of carrying out SEA in Serbia, the SOTAVENTO methodology has been adapted and adjusted to the needs of multi-criteria analysis for spatial plans of higher level and spatial plans for special purpose areas [13], [14] .This method is used for more detailed determination of characteristics of effects of certain activities on the environment, so that it may also be used independently of the level of planning, particularly when higher level of detail in impact analysis is required. Like with previous mentioned methodology, it is also possible to identify the impact type (without its quantification), i.e. positive, negative or zero impact. This is, at the same time, a shortcoming of SOTAVENTO method considering that there is no variability in quantitative utterance, because of which it is necessary to combine this method with the basic one. The SOTAVENTO method is also used to define impact length (temporary, permanent), impact relative to its territorial dispersion, as well as level of cumulativeness, i.e. synergistic effect it may have together with other effects. Precisely due this specific feature, the SOTAVENTO method may have a significant advantage over previous mentioned methodology, particularly in evaluating the effects of certain planning activities in space with extremely degraded environment having several direct polluters. Furthermore, the SOTAVENTO method is used for determining the impact source, i.e. its directness, where the impact may be considered either as a direct or indirect. Besides, the method is also used to determine the level of reversibility of effects of certain activities, impact duration, continuity, importance, as well as level of necessary intervention. More complex processes, which may have cumulative or synergistic action on the environment, and which may be a result of certain activities planned in space, should be elaborated through this method in more detail in order to determine specific measures for reducing or neutralizing their effects. In this connection, the level of detail of this method directly affects the validity of measures for preventing the negative effects of the planning activities.

IMPACTS OF PLANNED DEVELOPMENT

Compilation of SEA for mining regions can contribute to achievement of sustainable development, especially regarding valuing the (usually neglected) environment protection, because it [15]:

- evaluates the alternatives with potentially different environmental consequences, with equal emphasis on ecological, social and health aspects, and helps to derive the best decision;
- analyses expected effects, their character (irreversible or not), durability: long/middle/short-term, possibility, scope (local, regional, global), and induces activities stemming from a major development;
- considers cumulative impacts (caused by several projects);
- analyses direct and indirect activities and their impacts;
- focuses on maintaining a chosen level of environmental quality (instead on mitigation measures).

Multicriteria expert analysis of Bor region by two different methodologies has identified special positive effects of planned development, as: preservation and revitalisation of natural values, remediation of SO_2 emissions, emissions of ash, dust, heavy metals and other pollutants, with the application of precautionary principle for new investments; reclamation of flotation tailings and landfills: old Bor tailings, Southeast plan, gangue landfill Saraka, Brana 3 and field 2 of tailings Veliki Krivelj; conduction of an inventory of damaged soil; reparation and implementation of the program of reclamation and remediation of degraded land and environmental remediation programs and vulnerable nature of the city and the whole area of "RTB Bor group"and RTB Majdanpek (remediation of contaminated geology, reclamation of inactive tailings and mines, increasing protection, the park and recreational greens, etc.); reduction of air pollution, water and soil products exploitation and processing of mineral resources through construction of a new smelter and sulfuric acid plant in Bor and revitalize other parts of the industrial complex in Bor and Majdanpek;correction of existing borders sanitation and monitoring zones; preparation and implementation of the project environmental monitoring and monitoring of seismic impacts of mining in the copper mines etc.

These analyses have shown that there are many positive environmental effects of planned development, which demonstrates high degree of sustainability of all considered plans. But, there are still impacts which depend on the degree of applied solutions and protection measures. This means that planned development has to be followed by adequate environment protection – especially in ecologically endangered areas (areas of intensive exploitation of mineral resources, erosion areas etc.).

Especially important are cumulative impacts, formed as a result of sum of existing and planned activities (see Table 1).

Table 1. Cumulative environmental impacts in Bor region [3], [4], [5]

SEAs aims	Cumulative impacts of Plans
1. Protection and sustainable natural resource utilisation	Planned economic development, especially further exploitation of mineral resources, development of SMEs and tourism, can lead to cumulative pollution of air, water and soil, especially in already environmentally degraded areas (hot spots) and sensitive areas. Air, soil and water quality can be maintained by using renewable resources, applying protection measures during copper exploitation and processing, improving waste management and balanced development in settlements network
2. Decreasing pollution and environment pressures	Planned development in field of balanced settlement network, improvement of transport connections, balanced population disposition, improvement of life quality and balanced urban and rural development have cumulative positive effect.
3. Promoting waste management and use of mineral and energy resources	Rational exploitation of mineral resources and renewables have positive cumulative impact. More exploitation of mineral resources and tourism development can have negative cumulative effects.

SEAs for Bor region have proposed a set of measures aimed at efficient prevention, reduction and elimination of possible negative impacts of proposed development on nature, environment, cultural heritage and quality of life. Proposed measures are based on national regulation in the area of nature and environment protection, construction, urban and regional planning, tourism, forestry, water and agriculture, etc. The main precondition for success of these measures is organisation and qualification of governing structures (on local and national level), as well as support of public, NGOs and local population.

CONCLUSIONS

Based on the previous experiences in the practice of SEA compilation in Serbia, among other things, it can be concluded that there is usually a sufficient level of coordination between the development of strategic plans and SEAs, but the process of strategic environmental assesment starts only after planning solutions have been defined and established.

Though it should be a key document of environmental planning, SEA in Serbia is expected to confirm the pre-determined planning solutions, rather than to discuss and evaluate previously offered variants. This largely negates the importance of this document which could play a key role in decision-making on issues that may have negative repercussions on environment.

In the case stydy of three different SEAs in Bor mining industrial region it has been shown how and with which specific instruments is possible to direct development without violating environmental, nature and cultural protection. Some planning solutions given within spatial/urban plans for Bor mining industrial region have shownsignificant negative impacts in the initial stages of the SEA (during multicriteria evaluation), and they were exempt from further elaboration. On the other hand, for the individual solutions whichcould also generate slightly less pronounced negative effects, there has been set the system of measures and instruments for neutralizing them in a short period of time, thus enabling the realization of some seemingly environmentally unjustified interventions in space.

Therefore, SEA in this case was accepted as the primary method for supporting decision-making process from the perspective of environmental protection and sustainable development in the planning area, and the planning has done a huge step from deterministic to environmental approach which is the basic imperative of applying the principles of sustainable development.

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PUBLIC PARTICIPATION IN DECISION-MAKING AND ACCESS TO JUSTICE IN ENVIRONMENTAL MATTERS IN EU LAW

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ABSTRACT

The environmental legislation of the Union includes provisions regarding participation of public authorities and other bodies in certain actions which may have a significant effect on the environment as well as on personal health and well-being.Therefore it is important to enable participation of public in decision-making and access to justice in environmental matters, by providing for public participation as regards the drawing up of certain plans and programmes in the environmental field, and improving public participation and making rules on access to justice.

Key words: European Union, envitonmental impact assessment, public participation.

INTRODUCTION

In 1985 Council of the European Communities adopted Directive on the assessment of the effects of certain public and private projects on the environment (EIA Directive) which applies to a wide range of defined public and private projects, which are defined in Annexes I and II. The EIA Directive has been amended three times: 1. Directive 97/11/EC brought the Directive in line with the UN ECE Espoo Convention on EIA in a Transboundary Context. The Directive of 1997 widened the scope of the EIA Directive by increasing the types of projects covered, and the number of projects requiring mandatory environmental impact assessment (Annex I). It also provided for new screening arrangements, including new screening criteria (at Annex III) for Annex II projects, and established minimum information requirements; 2. Directive 2003/35/EC was seeking to align the provisions on public participation with the Aarhus Convention on public participation in decision-making and access to justice in environmental matters; 3. Directive 2009/31/EC amended the Annexes I and II of the EIA Directive, by adding projects related to the transport, capture and storage of carbon dioxide (CO2). The initial Directive of 1985 and its three amendments have been codified by Directive 2011/92/EU of 13 December 2011. Adopted 25 years ago the EIA Directive should be adapted to reflect the experience gained as well as changes in EU legislation and policy, and European Court of Justice case law. As a result of a review process, on 26 October 2012, the Commission adopted a proposal for a revised Directive.

PUBLIC PARTICIPATION IN EIA PROCEDURE

The EIA Directive requires that the developer (the person who applied for development consent or the public authority which initiated the project) must provide the authority responsible for approving the project with the minimum information. With due regard for rules and practices regarding commercial and industrial secrecy, this information must be made available to interested parties sufficiently early in the decision-making process: the competent environmental authorities likely to be consulted on the authorisation of the project; the public, by the appropriate means (including electronically) at the same time as information (in particular) on the procedure for approving the project, details of the authority responsible for approving or rejecting the project and the possibility of public participation in the approval procedure; other Member States, if the project is likely to have transboundary effects. Each Member State must make this information available to interested parties on its territory to enable them to express an opinion.

Reasonable time-limits must be provided for, allowing sufficient time for all the interested parties to participate in the environmental decision-making procedures and express their opinions. These opinions and the information gathered pursuant to consultations must be taken into account in the approval procedure.

At the end of the procedure, the following information must be made available to the public and transmitted to the other Member States concerned: the approval or rejection of the project and any conditions associated with it; the principal arguments upon which the decision was based after examination of the results of the public consultation, including information on the process of public participation; any measures to reduce the adverse effects of the project.

In accordance with national legislation, Member States must ensure that the interested parties can challenge the decision in court.

In implementation and interpretation of the EIA Directive CJEU has so far an important role especially in relation to cases on access to justice in the Member States of the EU.

TIMING OF THE CONSULTATIONS – STATUS OF THE OPINIONS

While Article 6(1) and (2) of the EIA Directive require Member States to hold a consultation procedure, in which the authorities likely to be concerned by the project and the public are invited, respectively, to give their opinion, the fact remains that such a procedure is carried out, necessarily, before consent is granted. Such opinions – and further opinions which Member States may stipulate –form part of the consent process and are aimed at assisting the competent body's decision on granting or refusing development consent. They are therefore preparatory in nature and not, generally, subject to appeal (C-332/04, Commission v. Spain, paragraph 54).

PARTICIPATION IN THE DECISION-MAKING PROCEDURE AND ACCESS TO JUSTICE

Article 6(4) of Directive 85/337 guarantees the public concerned effective participation in environmental decision-making procedures as regards projects likely to have significant effects on the environment. Participation in the decision-making procedure has no effect on the conditions for access to the review procedure. Participation in an environmental decision-making procedure under the conditions laid down in Articles 2(2) and 6(4) of Directive 85/337 is separate and has a different purpose from a legal review, since the latter may, where appropriate, be directed at a decision adopted at the end of that procedure (C-263/08, Djurgården, paragraphs 36 and 38).

SETTING CONDITIONS ON PUBLIC PARTICIPATION

The levying of an administrative fee is not in itself incompatible with the purpose of the EIA Directive. It is apparent from the sixth recital in the preamble to the EIA Directive, as it is from Article 6(2) of that directive, that one of the directive's objectives is to afford the members of the public concerned the opportunity to express their opinion in the course of development consent procedures for projects likely to have significant effects on the environment. In that regard, Article 6(3) allows Member States to place certain conditions on participation by members of the public concerned by the project. Thus, under that provision, the Member States may determine the detailed arrangements for public information and consultation and, in particular, determine the public concerned and specify how that public may be informed and consulted. A fee cannot, however, be fixed at a level which would be such as to prevent the directive from being fully effective, in accordance with the objective pursued by it. This would be the case if, due to its amount, a fee were liable to constitute an obstacle to the exercise of the rights of participation conferred by Article 6 of the EIA Directive. The amount of the fees at issue here, namely 20€ in procedures before local authorities and 45€ at the Board level, cannot be regarded as constituting such an obstacle (C-216/05, Commission v. Ireland, paragraphs 37-38, 42-45).

PUBLICATION OF THE DECISION TO GRANT OR REFUSE DEVELOPMENT CONSENT

Under Article 9 of the EIA Directive the public is to be informed once the decision to grant or refuse development consent has been taken. The purpose of issuing this information is not merely to inform the public but also to enable persons who consider themselves harmed by the project to exercise their right of appeal within the appointed deadlines. It follows from the foregoing that the publication by a Member State of an environmental impact statement issued by a competent administrative authority in environmental matters, an action not required under Community law, is no substitute for the obligation, under Article 9 of Directive 85/337/EEC as amended, to inform the public of the granting or refusal of consent to proceed with a project under Article 1(2) of the Directive. This interpretation is supported by the purpose of Directive

85/337/EEC, in its original version, which is, according to the first recital, to prevent the creation of pollution or nuisances at source, rather than subsequently trying to counteract their effects. This purpose was confirmed by Directive 97/11/EC, which recalls, in its second recital, that, pursuant to Article 130r(2) of the EC Treaty (Article 174(2) in the amended Treaty), Community policy on the environment is based on the precautionary principle and the principles that preventive action should be taken, that environmental damage should as a priority be rectified at source and that the polluter should pay. By imposing, in Article 9, the obligation on Member States to inform the public when a decision granting or refusing development consent is adopted, the amended Directive 85/337/EEC is intended to involve the public concerned in supervising the implementation of these principles. Informing the public only of the content of the opinion which is to be taken into account by the competent authority before adopting its decision is a less effective way of involving the public in supervision than informing the public of the final decision which concludes the consent procedure. Inasmuch as national law does not require the publication of the decision to grant or refuse consent for the project, Article 9(1) of Directive 85/337/EEC as amended has not been correctly implemented (C-332/04, Commission v. Spain, paragraphs 55-59).

PARTICIPATION IN AN ENVIRONMENTAL DECISION-MAKING PROCEDURE AS A CONDITION TO HAVE ACCESS TO A REVIEW PROCEDURE

Article 10a [11 as per codification] of the EIA, taking account of the amendments introduced by Directive 2003/35 which is intended to implement the Aarhus Convention, provides for members of the public concerned who fulfil certain conditions to have access to a review procedure before a court of law or another independent body in order to challenge the substantive or procedural legality of decisions, acts or omissions which fall within its scope. Thus, according to the wording of that provision, persons who are members of the public concerned and either have sufficient interest, or if national law so requires, maintain that one of the projects covered by Directive 85/337 impairs their rights, are to have access to a review procedure. It is also apparent therefrom that any non- governmental organisations which promote environmental protection and meet the conditions which may be required by national law satisfy the criteria, with respect to the public concerned who may bring an appeal, laid down in Article 1(2) of Directive 85/337 read in conjunction with Article 10a. The right of access to a review procedure within the meaning of Article 10a of Directive 85/337 does not depend on whether the authority which adopted the decision or act at issue is an administrative body or a court of law. Second, participation in an environmental decision-making procedureunder the conditions laid down in Articles 2(2) and 6(4) of Directive 85/337 is separate and has a different purpose from a legal review, since the latter may, where appropriate, be directed at a decision adopted at the end of that procedure. Therefore, participation in the decision-makingprocedure has no effect on the conditions for access to the review procedure. Members of the "public concerned" within the meaning of Article 1(2) and 10a [11 as per codification] of the EIA Directive must be able to have access to a review procedure to challenge the decision by which a body attached to a court of law of a Member State has given a ruling on a request for development consent, regardless of the role they might have played in the examination of that request by taking part in the procedure before that body and by expressing their views (C-263/08, Djurgården, paragraphs 32-39).

COST OF THE REVIEW PROCEDURE

It is clear from Article 10a [11 as per codification] of the EIA Directive that the procedures must not be prohibitively expensive. That covers only the costs arising from participation in such procedures. Such a condition does not prevent the courts from making an order for costs provided that the amount of those costs complies with that requirement. A national practice under which the courts may decline to order an unsuccessful party to pay the costs and can, in addition, order expenditure incurred by the unsuccessful party to be borne by the other party is merely a discretionary practice on the part of the courts. Such a practice on the part of the court which cannot, by definition, be certain, cannot be regarded as valid implementation of the obligations arising from those articles (C-427/07, Commission v. Ireland, paragraphs 92-95).

ACCESS TO JUSTICE FOR NON-GOVERNMENTAL ORGANISATIONS (NGOS) WHICH PROMOTE ENVIRONMENTAL PROTECTION – MINIMUM NUMBER OF MEMBERS

It is clear from Directive 85/337 that it distinguishes between the public concerned by one of the projects falling within its scope in a general manner and, on the other hand, a sub-group of natural or legal persons within the public concerned who, in view of their particular position vis-à-vis the project at issue, are, in accordance with Article 10a [11 as per codification], to be entitled to challenge the decision which authorises it. The directive leaves it to national law to determine the conditions for the admissibility of the action. Those conditions may be having 'sufficient interest' or 'impairment of a right', and national laws generally use one or other of those two concepts. As regards non-governmental organisations which promote environmental protection, Article 1(2) of Directive 85/337, read in conjunction with Article 10a thereof, requires that those organisations 'meeting any requirements under national law' are to be regarded either as having 'sufficient interest' or as having a right which is capable of being impaired by projects falling within the scope of that directive. While it is true that Article 10a [11 as per codification] of the EIA Directive, by its reference to Article 1(2) thereof, leaves to national legislatures the task of determining the conditions which may be required in order for a non-governmental organisation which promotes environmental protection to have a right of appeal under the conditions set out above, the national rules thus established must, first, ensure 'wide access to justice' and, second, render effective the provisions of the EIA Directive on judicial remedies. Accordingly, those national rules must not be liable to nullify Community provisions which provide that parties who have a sufficient interest to challenge a project and those whose rights it impairs, which include environmental protection associations, are to be entitled to bring actions before the competent courts. From that point of view, a national law may require that such an association, which intends to challenge a project covered by the EIA Directive through legal proceedings, has as its object the protection of nature and the environment. Furthermore, it is conceivable that the condition that an environmental protection association must have a minimum number of members may be relevant in order to ensure that it does in fact exist and that it is active. However, the number of members required cannot be fixed by national law at such a level that it runs counter to the objectives of the EIA Directive and in particular the objective of facilitating judicial review of projects which fall within its scope.

In that connection, it must be stated that, although the EIA Directive provides that members of the public concerned who have a sufficient interest in challenging projects or have rights which may be impaired by projects are to have the right to challenge the decision which authorises it, that directive in no way permits access to review procedures to be limited on the ground that the persons concerned have already been able to express their views in the participatory phase of the decision-makingprocedure established by Article 6(4) thereof. Thus, the fact that the national rules offer extensive opportunities to participate at an early stage in the procedure in drawing up the decision relating to a project is no justification for the fact that judicial remedies against the decision adopted at the end of that procedure are available only under very restrictive conditions (C-263/08, Djurgården, paragraphs 42-52).

ACCESS TO JUSTICE FOR NON-GOVERNMENTAL ORGANISATIONS (NGOS) WHICH PROMOTE ENVIRONMENTAL PROTECTION – INTERESTS PROTECTED

Non-governmental organisations promoting environmental protection, as referred to in Article 1(2) of that directive, can derive from the last sentence of the third paragraph of Article 10a of Directive 85/337 a right to rely before the courts, in an action contesting a decision authorising projects 'likely to have significant effects on the environment' for the purposes of Article 1(1) of Directive 85/337, on the infringement of the rules of national law flowing from Article 6 of the Habitats Directive, even where, on the ground that the rules relied on protect only the interests of the general public and not the interests of individuals, national procedural law does not permit this (C-115/09, Trianel Kohlekraftwerk Lünen, paragraph 59).

Injunctive relief: injunctive relief is recognised by the case-law of the Court of Justice as a cornerstone to access to justice. In order to enhance the effectiveness of the legal protection of rights, it was specifically referred to by the Court in case C-213/89, Factortame (see also case C-432/05, Unibet). The courts have consistently held that the principle of effective judicial protection requires the national court to be able to grant interim relief as necessary to ensure that rights derived from EU law are respected. Thus, the right to apply for injunctions are considered inherent in the concept of effective access to justice, guaranteeing effective interim protection of rights. Therefore, independently of Article 9(4) of the Aarhus Convention which requires injunctive relief to be provided where appropriate, injunctive relief can be considered an essential element for ensuring effective judicial protection, to avoid irreversible damage to the environment amongst other reasons. This has been confirmed by AG Kokott in case C-416/10 Križan (paragraphs 170- 177), where she concluded that the right to effective access to justice under the Environmental Impact Assessment Directive and the IPPC Directive also includes the right to apply for injunctive relief. The Court went on to follow the Advocate-General in its ruling delivered (paragraphs 105-110).

AVAILABILITY TO THE PUBLIC OF PRACTICAL INFORMATION ON ACCESS TO JUSTICE

It must be borne in mind that one of the underlying principles of Directive 2003/35 is to promote access to justice in environmental matters, along the lines of the Aarhus Convention on access to information, public participation in decision-making and access to justice in environmental matters. In that regard, the obligation to make available to the public practical information on access to administrative and judicial review procedures laid down in the sixth paragraph of Article 10a of Directive 85/337, inserted by Article 3(7) of Directive 2003/35, and in the sixth paragraph of Article 15a of Directive 96/61, inserted by Article 4(4) of Directive 2003/35, amounts to an obligation to obtain a precise result which the Member States must ensure is achieved. In the absence of any specific statutory or regulatory provision concerning information on the rights thus offered to the public, the mere availability, through publications or on the internet, of rules concerning access to administrative and judicial review procedures and the possibility of access to court decisions cannot be regarded as ensuring, in a sufficiently clear and precise manner, that the public concerned is in a position to be aware of its rights on access to justice in environmental matters (C-427/07, Commission v. Ireland, paragraphs 96-98).

CONCLUSION

Implementation of EIA Directive on access to justice in the Member States of the European Union differs while effective access to justice for members of the public includes many factors. The possibilities for the public to challenge environmental decisions may be improved in different ways, e.g. by relaxation of the standing criteria for individuals or NGOs or increased possibilities to go to court. In addition to this, the development of case law in the CJEU has played a positive role for the development of access to justice in many Member States.

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INDUSTRIAL IMPACT ON THE ENVIRONMENT

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ABSTRACT

The paper lists and analyzes the processes of industrial productions as well as the pollution sources of the environment. The most important among them are: metallurgy, chemical industry, oil industry, food processing industry and building material industry. What needs to be emphasized is that large quantities of service water, even though they are treated, should be let out downstream of settlements. Industrial facilities locations should be planned using preventive principles and including environmental factors in investment decision-making process.

Urban sustainable development comprises development of new production technologies, products and services which are in accord with economic and social principles of environmental protection.

Key words: industry, production, ecology, protection, sustainable development.

INTRODUCTION

Urban ecology employs a complex methodological apparatus consisting of analysis, synthesis, experiments, induction and deduction, analogy and applied mathematical methods based upon the theory of the system.

The objective of urban ecology as a particular scientific discipline is the establishment of a healthy life in all existing and future settlements. This includes full alignment and balancing between effect of biological, social and other natural laws according to which healthy life of every human individual and specific human community is going on. The thesis is that the causes of degradation of the urban environment should be sought in inadequate planning. This is reflected in the fact that planning often does not cover the entire territory of the city, and that the whole settlements have been erected in spite of the plan and some industrial facilities have not been properly located, which all adversely affects the conditions and the quality of the environment. It should be borne in mind that the industrial production of the old technology greatly pollutes the natural environment. New technologies, however, use the radioactive, toxic, infectious, explosive, flammable or other dangerous substances. In many cases, the application of modern protective measures does not result in a risk of an accident at a level that it would be justified to build the facilities in which the hazardous materials are stored nearby buildings for other purposes. Thereby the problem of determining safety distances occurs, and often fires occur when many dangerous products of combustion ensue that are not categorized as hazardous. Therefore, there is a significant violation of the environment and heavy consequences for the ecological balance.

URBAN SUSTAINABLE DEVELOPMENT AND INDUSTRIAL PRODUCTION

Industry is one of the basic economic branches, but it is one of the most important sources of endangering environmental quality. The impacts of the industry are reflected in the processes of using natural resources (raw materials, energy, water), emission of pollutants in parts of biosphere (water, air, soil) and waste production. Reducing or eliminating the negative impact of industry on the environment involves the development of new production technologies. Environmental management in industry takes place on a global level, the company level and the level of wider or narrower spatial areas or towns (settlements).

Urban sustainable development means development of new technologies, products and services, which are in accordance with the principles of economic efficiency, social justice, political democracy, cultural diversity, and environmental protection. These include the conditions and manner of use of construction land (location for the industry), the method of providing energy , water and resources for manufacturing, human resources , created capacity (infrastructure), providing communication system and transport, conditions and the way of solving the problem of industrial waste, spatial organization of industry and other functions of the urban area. The practice of environmental management in industry, especially in the EU countries, has evolved significantly in recent years. Evolution of approach to environmental protection in the planning of industrial projects has been performed in three phases: the traditional approach, the newer approach and preventive approach. The recent practice of environmental management in Europe has been changed significantly. Raising environmental consciousness of society influenced by the pressures of different actors, there was a change in the approach and the inclusion of environmental factors when making investment decisions.

A large number of industrial plants are filthy and noisy. Locating of these industrial plants is influenced by the radius of propagation of physical-chemical emanations and the field of propagation of unallowed sound influence.

SOURCES OF ENVIRONMENT POLLUTION

Functional zoning of cities is a complex planning process because of the residential and industrial areas location depending. For example, industries with high consumption of water also discharge a large amount of process water into receiving waters (rivers, lakes, etc..). Although the water is treated, the most favorable position of industry with wastewater in relation to the settlement is downstream of the settlement.

In the following some sources of environmental pollution of the city will be listed.

Metallurgy

Slag is produced during the process of obtaining aluminum from ore, and red mud as waste material of ore that is beside the pyralene from transformer very dangerous pollutant. Also aluminum dust may lead to Shafer's disease and aluminosis that is manifested as difficulty in breathing, choking, pain, loss of appetite and losing the weight.

Sulfide ores are crumbled in the process of obtaining copper, while a large dust is produced, so that splashing with water is carried out in order to reduce its emissions.

The manufacture of iron and steel pollute the air, water and substantial amounts of slag or dross generated during the manufacturing process are rejected, while of the harmful gases carbon monoxide is most released (dangerous blood poison).

Metallurgical process of getting a lead is among the dirtiest technologies, because hazardous materials in the form of gases are released in the process, as well as in the form of dust containing lead and arsenic.

In the production of zinc from sulfide ores, ore is first roasted and then is synthesized, when it is released the dust, smoke and sulfur-dioxide.

Chemical Industry

Production of sulfuric acid 70% is used for the preparation of phosphate fertilizers. Its production is carried out in an oxidizing and compact process from raw materials: elemental sulfur, hydrogen sulfide and sulfide ores.

Ammonia production is based on the catalytic reaction of hydrogen and nitrogen at high temperatures and pressures, by using natural gas or coke and nitrogen.

During production of ammonia may be emitted into the atmosphere up to several kilograms per ton of ammonia, as well as during transport and storage.

Production of chlorine, hydrogen and sodium hydroxide is carried out mainly by electrochemical process, and environment is polluted by the wastewater containing mercury salts that are removed by chemical means, i.e. by the deposition of mercury.

Explosives are divided into high and low explosive substances. The most commercially used is trinitrotoluene (TNT), the production of which is very complex.

Paints and varnishes process includes weighing, grinding, sifting ingredients, mixing and packaging. Contaminants are dry powdered pigments which are poured in the low boiling solvents from which 1-2 % are going into the atmosphere. During manufacture of paints, as well as a lot of colors organic substance in the form of steam are released, and the loss of raw materials can range from 1-6 %.

Manufacture of soap and detergents do not pollute the environment to a large extent because in the production of soap there are no heavy metals and hazardous organic substances. Pollution that occurs during the manufacturing process of detergents is by fine dust particles from dry detergent and gases from the chamber for spraying and drying.

Oil and Natural Gas

Side effects of the oil industry are reflected through: the emission of gases and vapors, releasing fluids and wastes coming from drilling in oil extraction, the use of holons to extinguishing fires, accidental oil spills, etc., so that great environmental pollution is possible. Refining of crude oil is made up of five basic processes, each of which has operations that are potential polluters of the environment. Natural gas is obtained from the oil-field boreholes, and the desulfurization is one of the major refining process of natural gas. Petroleum and natural gas industry is very complex.

Food Industry

In the production of flour can be said that there are no polluting agents. In the production of alcoholic beverages there are several stages and there is a lot of organic waste after completed fermentation (husk, kernels, seeds, etc.). In the process of roasting coffee pollution of the environment is negligible. Industry of oils and vegetable fats uses as raw materials sunflower seeds, canola, corn, flaxseed, soybeans, olives, etc. Significant contamination originates from the waste water generated in the cooling process and emulsified organic matter (fats, etc.).

Processing of fish includes canning, production of fish oil and fish meal and usually there are no significant environmental pollutants.

Industry of building materials

Production of bricks and similar ceramic products

The basic raw material in this industry is brick clay or kaolin, and fluoride and sulfur dioxide are emitted in the air at a temperature of 1370°C during the kilning of bricks and ceramics. In waste water of the production of ceramics there are heavy metals.

Production of glass

Basic raw material in the production of glass depend on of the types of glass, whereas common glass form 90% of total production at the temperature of 1480°C to melt the mixture of materials giving the glass. In the waste water that follows glass production there are: phosphates, sulfates, suspended particles, chromates, zinc, copper, iron, chromium, silver, nitrates, tin, etc. Arsenic, barium, cobalt, nickel, titanium, vanadium and boron can be found as the heavy metals.

Concrete production

In the production of concrete contamination originates mainly from the presence of relatively large quantities of cement. During the transport and loading of cement into concrete mixers cement wastage into the environment happens (air, soil). Its wastage over the land causes the impregnation of soil and reduces its permeability. Cement in surface waters increases their alkalinity.

Lime production

Lime is a product of high temperature calcination of limestone. Two types of lime are produced: lime with a high content of calcium and dolomitic lime (calcium - magnesium). In the production of lime as the final stage often hydration of lime is performed. Basic operations of production of lime are: limestone crushing, limestone preparation, its transportation and storage. Some pollutants are emitted in the production of lime among which the most dust and gaseous pollutants from lime kilns. The major source of particulate matter is kiln for calcination. From kiln also are emitted nitrogen oxides, carbon monoxide and oxides of sulfur. Emitters of solid particles are crushers and mills that are used in the production process.

Production of Portland cement

For the production of cement about 30 different basic raw materials are used. They can be classified into four groups: lime, silicon - dioxide, aluminum - oxide, and iron oxides. In this production process, the basic raw material is crushed and mixed. After crushing and mixing it goes to the processing by dry or wet procedure. In the dry procedure the moisture content in the primary raw material is reduced to less than 1%, when it is grinded to powder. This powder is then brought into the rotary kiln. Milled material entered at one end of the furnace and comes out at the other end of the furnace. Hot gases pass through the material. Drying, decarbonization and calcination are performed by passing of the material through hot zones while the clinker is created. Clinker is cooled and mixed with about 5% gypsum and then transported to the warehouse. The main pollutants which occur during production of the Portland cement are solid particles. In the course of cement production emitted are also gases generated during fuel combustion: oxides of nitrogen and sulfur oxides.

CONCLUSION

It can be concluded that industrial production as the main economy branch is one of the most important source of threats to environmental quality. The most important pollutants are briefly presented and analyzed in the paper, those being: metallurgy with the production of aluminum, copper, iron, steel and zinc; the chemical industry with the production of sulfuric acid, ammonia, chlorine, hydrogen and sodium chloride, explosives, paints and varnishes, and soap and detergent; oil and natural gas industry; the food industry which pollutes the environment the least; industry of building materials producing bricks and other similar ceramic products, glass and concrete, lime and Portland cement, which as mass production emits into the environment and air the different pollutants, even those that are not expected to be released in this production such as arsenic or heavy metals .

It should be noted that a large number of industrial plants is unclean and noisy. Locating of these plants is conditioned by the urban environment taking into account radius of propagation of physical-chemical emanations and the propagation field of unallowed sound impacts, so that the protection of which should be adequate. Almost all of the aforementioned technological processes create a large amount of process water (polluted), which is discharged insufficiently purified into recipients.

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COST AND FINANCIAL MANAGEMENT ASPECTS OF REMEDIATION ACTIVITIES

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ABSTRACT

Protection of environmental components, such as soil, is a paramount issue for all stakeholders, because of its basic functions for humans and ecosystem. Remediation process as one ways for improving the current state of contaminated sites is necessary, but on the other side is very costly. Because of this proved statement in numerous reports, financial management and cost leadership becomes increasingly significant in the light of trend that signifies funding decrease which is a result of global economic problems. These facts, motivated authors to highlight the urgent need to consider cost and financial effectiveness and efficiency of each chosen remediation technique. Authors in article presented necessity of creating cost estimation process for remediation activities, Social aspects of cost-benefit analysis and at the end alternatives for site remediation financing. After examination of all documents regarding this issue, it is clear that cost-benefit analysis and financial management has to be included in the decision of policy makers and to become equally important as other principles that are already accepted in the process of remediation.

Key words: remediation, contaminated sites, cost, funding, cost-benefit analysis.

INTRODUCTION

Soil is essential environmental component and its health is priority task for global world. Nevertheless, soil resources in many parts of Europe and in the world are being over-exploited and irreversibly lost due to inappropriate management practices. In many countries regarding soil management and priority task of its v it is obvious that two issues attached the greatest attention. First: shortage of financial resources devoted for this purposes regarding great number of locations, and second monitoring of effectiveness of remediation techniques and knowledge about cost benefits linked with policy makers decision are still poorly developed. Hence, the number of sites where potentially polluting activities take place now stands approximately 3 million is clear how this issue is serious for future implementation of concept of sustainable development.[1]

[1] The State of Soil in Europe, JRC Reference Reports, European Environment Agency, European Commission, 2012. http://ec.europa.eu/dgs/jrc/downloads/jrc_reference_report_2012_02_soil.pdf

Management of contaminated sites is 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, environmental impacts are defined and finally implementing remedial and after care measures.[2] This process is constantly followed by one fact and this is cost. Funding represents one of the key issues in remediation of contaminated sites and its management process which is becoming increasingly important.

The main objectives of this paper is to analyze and structure costs of remediation of contaminated sites, consider social cost-benefit analysis as one of primary benefits that derive from remediation activities and finally to describe funding options for remediation of contaminated sites, which importance arise from the fact that there is a lack of environmental funding on a global scale. Bond between three objectives in this paper lies in aspiration of authors to emphasize importance of financial element in remediation of contaminated sites.

The Republic of Serbia is presented it need for 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.[3]

COST ESTIMATION PROCESS FOR REMEDIATION ACTIVITIES

One among important and hard task in remediation processes is to understand a complex process regarding the magnitude of cost and benefits of remediation techniques. In practice and theory still are ongoing discuss about a number of variables that could have a significant impact on magnitude of additional remediation costs and public health benefits that may be generated by remediation in the future. In order to have successful cost estimation and calculations it is imperative that remediation goals are set and that is clear what objectives are. When it is certain that the general principle is understood, organization, operationalization, activities and actions need to be accounted and recognized. After the identification of most important cost elements next step is to map the activities and actions so that they can be categorized into cost list. After formation of needed information, valuation of these parameters should be done in monetary terms. These estimations are important in order to have stabile cost structure and to be able to evaluate different remediation options. Also, cost structure can vary in different remediation options both in financial and structure terms.

In the process of contaminated sites management, it is sufficient to estimate 'ball park' figures for each of the cost headings listed below. However, it is important to ensure that key costs are not overlooked – for example, long-term monitoring and maintenance may be a significant cost element for some remediation options.[4]

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[2]Radović V., Rakić S."*The management of contaminated sites and soil remediation in Serbia"*, Page: 323-330, ISBN: 978-86-6305-007-5, Publisher: University of Belgrade, Technical Faculty in Bor, Republic of Serbia; Scientific Proceedings XXI International Scientific and Professional Meeting "Ecological Truth" Eco-Ist '13. (4-7 June, 2013, Bor Lake, Hotel "Jezero", Bor, Serbia).

[3] National Environmental Approximation Strategy for the Republic of Serbia (Official Gazette of the Republic Serbia No 80/2011)

[4]Model Procedures for the Management of Land Contamination, Environment Agency, Department for Environment, Food and Rural Affairs, United Kingdom, 2004. http://www.doeni.gov.uk/niea/clr11-4.pdf

Table 1. Cost information required for detailed evaluation of remediation options

Site preparation	Provision of hard standing, access roads, site security, accommodation for remediation personnel
Regulatory approvals	Application for licenses and approvals to install and/or operate the method
Project management costs	For management and supervision of remediation
Equipment	Materials handling and processing plant, pumping wells and associated equipment
Mobilization and start-up	Transport and assembly of plant, equipment and materials, calibration of equipment and other preoperational checks
Maintenance	Plant modification, repair and long-term performance
Demobilization	Disassembly of plant and equipment, decontamination measures
Financing	Working capital, interest, depreciation, insurance, taxes, contingency
Labor costs	Salary and expenses
Consumables	Sampling equipment, construction materials, replacement parts
Utilities	Power, water, telecommunications
Health and safety measures	Protective clothing and equipment, project-specific training, independent audit
Environmental protection measures	Containment of dusts, vapors, noise, effluents and similar emissions and associated monitoring procedures (ambient air quality, discharge of effluents)
Waste disposal	Solid and liquid waste arisings, pollution-control residues
Analytical support	For verification purposes during, on completion and over the long-term if required, to support health and safety and environmental protection needs

Source: Model Procedures for the Management of Land Contamination, Environment Agency, Department for Environment, Food and Rural Affairs, United Kingdom.

COST-BENEFIT ANALYSIS – SOCIAL ASPECT

Every country needs to assess the economic feasibility of chosen soil remediation process for contaminated sites regarding their own needs and possibilities, but also following useful examples from practice. The estimated economic benefits include both direct benefits, resulting from the increase in the land value of the remediation site, and indirect benefits, arising from the increase in nearby property value, human health etc.[5]

Remediation problems can be complicated. There may be a range of options, the most appropriate of which is not so obvious to decision-makers. The aim of cost-benefit analysis is to consider the diverse range of impacts that may differ from one proposed solution to another such as the effect on human health, the environment, the land use,

[5]Radović, V,. Rakić S. *„The risk srategy in a future remediation activities – how to avoid the failure"*, Publisher: University Donja Gorica, Podgorica, Montenegro: Scientific Proccedings 3rd Climate Change Economic Development and People Conference – CCEDEP 2013 (5-7, December 2013, Podgorica, Montenegro).

and issues of stakeholder concern and acceptability by assigning values to each impact in common units. Monetary or quantitative values may not be appropriate for all issues, so cost-benefit analysis can involve a combination of qualitative and quantitative methods. Many practitioners use a wide definition of cost-benefit analysis, encompassing a range of formal and semi-formal approaches.[6]

Basic principle in cost-benefit analysis is trade off. This kind of analysis helps make difficult choices which can't be done any other way. When considering social cost-benefit analysis there are numbers of questions that need to be answered such as number of people living in the contaminated area, risk of sickness, which technology should be used etc.

Cost-benefit analysis is used in environmental regulation to determine acceptable levels of risk. Acceptable risk denotes a level that maximizes the difference between total social cost and total social benefits, or in other words, where the marginal social benefits associated with the risk reduction are equal to the marginal social costs of pollution abatement.[7]

CB analysis involves six steps:[8]

- quantifying the health outcomes associated with waste exposure before and after regulation;
- assigning monetary values to the number of cases potentially averted by regulation;
- quantifying the cost of regulation;
- accounting for the timing of costs and benefits;
- comparing the resulting estimates;
- sensitivity analysis to evaluate the effect of parameter uncertainty on the study results.

Policy makers should consider implementation of all above mentioned steps in a process of CB analysis, even it is clear that sometimes it is a hard task because of insufficient scientific data about current state of health status of population in vicinity of remediation sites, as well as future benefits on it. This kind of analysis suggests constant monitoring of health status of population before, during and after remediation.

FINANCING ALTERNATIVES FOR SITE REMEDIATION

Financing remediation activities, in the light of constant decrease in funding, is becoming increasing challenge. Countries need to address this issue with better care. European example shows that countries that joined EU in 2004 and 2007 had significant problems attracting cohesion and structural funds because of lack of preparation, application and implementation of projects. In the first three years of membership,

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[6]EUGRIS, Portal for soil and water management in Europe. Site accessed 26th April, 2014. http://www.eugris.info/FurtherDescription.asp?e=467&Ca=1&Cy=1&T=Cost%20benefit%20analysis

[7]Guerierro C., Cairns J., Cost-Benefit Analysis of the Clean-Up of Hazardous Waste Sites, Integrated Waste Management - Volume I, Publisher: InTech, ISBN 978-953-307-469-6, 2011. http://cdn.intechopen.com/pdfs-wm/17447.pdf

[8] Ibid

Romania and Bulgaria attracted less than 10% of available funds in the area of environmental protection, including remediation activities.

In the case of Canada, public expenditure is expected to increase in the following years. In 1995, Canadian government formed the Contaminated Sites Management Working Group to develop interdepartmental strategies. In 2002, the Treasury Board launched the Federal Contaminated Sites Inventory, and in 2004, the federal government of Canada committed \$3.5 billion through the Federal Contaminated Sites Action Plan (FCSAP) to clean up contaminated sites. The action plan started in 2005-2006 and will run through 2019-2020. As of March 2013, the total remaining environmental liability associated with federal sites was reported to be \$10.6 billion. This amount consists of \$4.7 billion in liabilities for the contaminated sites in the inventory; \$0.2 billion for other contaminated sites not tracked in the inventory; and \$5.7 billion for asset restoration, all of which, except \$4 million, is for nuclear facility decommissioning.[9]

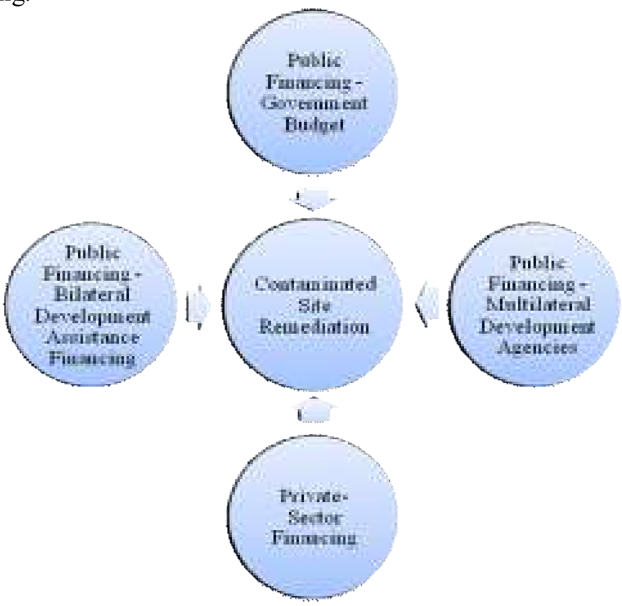

Figure 1. Site Remediation Financing

Source: Persistent organic pollutants: Contaminated site investigation and management toolkit, United Nations Industrial Development Organization, 2009.

When making remediation plans for Contaminated Sites, one of the decisions which have to be made is funding strategy. There are few possible ways of funding (Figure 1), but the basic division is to see will the project be funded publicly or privately. It depends on different factors, which are ownership of the site, responsibility, liability, legislature etc.

[9] Federal Contaminated Sites Cost, Office of the Parliamentary Budget Officer, Ottawa, Canada 2014.http://www.pbo-dpb.gc.ca/files/files/Federal%20Contaminated%20Sites%20Cost.pdf

If public funding is being considered there are three main options that can be taken into account. First of them is governmental funding which arise from different forms of taxes, such as environmental taxes and it can be in the form of subsidies and/or grants. Second source of funding can be from foreign governments through their aid agencies and the third ways of funding is from multilateral agencies which include global funds. Projects can be fully financed or co-financed.

Private funding has significant rise in the recent years, especially in developed countries. According to Report on Progress in the management of Contaminated Sites in Europe from the Institute of Environment and Sustainability from 2014, private funding is 58% of total funding while public funding is 42% of total funding for remediation activities which represents increase of 7% from 35% in survey taken in 2006. Developed countries such as France, Belgium and Switzerland have significant share in private funding of the remediation activities. Reasons for this trend are vast, but the most significant are:

- Higher GDP in developed countries which allow higher private funding.
- Implementation of Systems for Social and Environmental responsibility within corporations.
- Governments of developed countries have efficient legislative, regulatory and monitoring systems.
- Governments provide economic incentives for environmental funding.

Table 1. Estimated allocation of public and private expenditure for management of contaminated sites

Country	Breakdown (%)		Annual management expenditures (mil€)	Reference Year
	Public	Private		
Estonia	90%	10%	42.5	2011
Austria	75%	25%	32.6	2011
Slovakia	75%	25%	49.5	2006
Denmark	58%	42%	118.7	2009
Netherlands	50%	50%	324.0	2009
Finland	41%	59%	60.0	2011
Switzerland	40%	60%	131.0	2011
France	30%	70%	470.0	2010
Belgium	25%	75%	159.6	2011
Average	**42%**	**58%**	**1,387.94**	

Source: European Environment Agency, Progress in management of contaminated sites, 2014.

Public-Private partnership (PPP) also represents one of the forms for funding remediation activities. Attractiveness of the combined public and private partnership in sharing resources, funding, risks and benefits is becoming increasingly significant. Public and private partnership can bring positive synergetic effect in optimizing resources and benefits for all participants in remediation process. There are good examples of PPP projects such as, "Wessling/GIZ – Project on Remediation of Contaminated Soils and Groundwater in China".

The Remediation of Contaminated Soils and Groundwater in China project was implemented by DHC Consulting GmbH, WESSLING Beratende In-genieure GmbH, GIZ. The PPP ran from Nov. 2008 to Jun. 2010, with the Corporate social responsibility (CSR) Project acting as a cooperation partner by co-organizing activities, providing contacts to local and regional Chinese companies and authorities, particularly for urban planning.The goal of the project was to provide environmental authorities, industrial companies and companies of the waste sector in two pilot regions in China with knowledge in environmental risk assessment, remediation of contaminated sites and brownfield reactivation and to have access to trainings and consulting on brownfield reactivation, waste management and procuring environmental protection. To achieve the objective, trainings and information meetings were prepared and held for members of Chinese environmental authorities and waste management companies in Zhejiang Province and the city of Jiangsu. Trainers were also trained to educate additional authorities, waste management companies and industrial companies. In order to better understand the complexity of the topic and all applicable assessment and a remediation plan at a concrete site in each of the participating provinces.[10]

CONCLUSION

There are numerous considerations for the future management in remediation activities, especially in terms of cost management and funding both for developed and developing countries.

Most significant obstacles in funding that need to be overcome are political will of the government, economic and social conditions, global economic and financial conditions, extent of the pressure from domestic and international stakeholders for a government to be proactive in environmental matters that impact the health of the population and financial position of bilateral and multilateral development agencies.[11]

Emerging issues, such as cost-benefit analysis will be the topics of future research in the field of economic aspects of environmental protection. Rising requirements for cost cutting and decrease in funding for remediation activities are pushing projects to become as efficient and effective as possible.

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[10]SinoGerman Corporate Social Responsibility Project, Public-Private Partnership, http://www.chinacsrproject.org/Highlights/PPP_EN.asp

[11]Persistent organic pollutants: Contaminated site investigation and management toolkit, United Nations Industrial Development Organization, 2009. http://zayedprize.org.ae/uploads_en/files/Contaminated%20Site%20Toolkit.pdf

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RESTOCKING- SUSTAINABLE MODEL MANAGEMENT AQUATIC ECOSYSTEMS

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ABSTRACT

Introduction/ Today, restocking and its effects on the ecosystem dedicates great care. Rotary Club of Sombor restocking the Grand Backa Canal whose pollution is considered one of the biggest environmental problems in Serbia.

Objective/ to preserve the ecological balance, prevent pollution and contribute to the revitalization of the canal.

Method / Restocking is completed with one-attested pieces of young fish, under strictly controlled conditions, with the support of formal and informal organizations, local communities and neighboring Rotary district.

Results and Discussion / Since 2007. till 2013's were discharged from 700 to 1.000 kg of fingerlings of grass carp and common carp (from 10,000 to 16,000 units).

Conclusion / Restocking becomes important ecological and economic links.

Key words: fish stocking, fish juveniles, The Great Backa Canal, Rotary Club of Sombor.

INTRODUCTION

The reduction of native fish species in the lakes of America, was the reason that in 1871, The State of America will form a commission whose task was to deal with researches the causes of fish stock and suggest corrective measures. So restocking has become a practice that was initially used only recreational fishing. (1) Today, the worldwide stocking and its effects on the ecosystem, to take great care. Experiences from semi-urban environment in Sweden (during the 1970s. Till 2000.), Saying the practice of discharging fish into waterways from the perspective of ecosystem management, and within the environmental and economic context. (2) The goal is to increase the fish catch by the user of the local resources. Organizers stocking are usually commercial enterprises, hydropower and local sports associations of fishermen.

Rotary Club of Sombor for ten years continuously implemented restocking Great Backa Canal , changing the location of stocking schedule of 5 years. In the West

Bačka District , based in Sombor, The North-West of Vojvodina , Serbia , the main hydrographic feature makes Danube. With its meanders , " Gin ", many branch of the lake as, backwaters , ponds , marshes gives an impressive hydrographic situation . There are also small rivers Plazović , Mostonga channels and Danube- Tisa -Danube network, which includes large and small Backa canal. Pollution of the Grand Backa Canal is considered one of the biggest environmental problems in Serbia . On hauls channels , concentrated food industry , which has for decades without treatment waste waters in the recipient and the same contaminants. Pollutants are 400.000 cubic meters of mud and include organic and inorganic waste. According to the study by the Norwegian Institute for Water Research, NIVA , Great Backa Canal is the most polluted waterway in Europe. (3,6) have seen growth in the development of cancer in people near the canal is threatened wildlife in the water and especially reduced fish stocks .

Reduction of fish in this channel also contributed to the drought because of which failed flooding areas around the Danube, very good carp hatcheries.

The amount of fish in the water is reduced as a consequence of uncontrolled fishing carp fish that has not reached sexual maturity, weighing about 350 g, which when caught by fishermen, not back into the water. Carp their sexual maturity and spawning capability is achieved in the second year of life. Water pollution, drought, uncontrolled fishing and as a result of this drastic reduction of fish stock in the channel, and the consequent disruption of the entire ecosystem of channel contributed to the Rotary Club of Sombor understand that the actions of restocking of the utmost importance to maintain the quality of these waters and the balance of wildlife in it .

OBJECTIVE

This paper is to present an example of solving environmental and economic problems by informal, non-governmental organization that uses the existing formal and informal social resources, in order to preserve the ecological balance and prevent pollution of the Grand Backa Canal, to contribute to its revitalization and its function as a tourism and economic waterway times and point to the economic benefits of restocking.

METHOD

Rotary Club of Sombor is off stocking the Grand Backa Canal began 2006th year, letting over half a ton of fish fry perch, catfish and carp. The action was supported by other Rotary Clubs, local and provincial authorities and civic associations. The main partner from the beginning of a Public company Vojvodina water. With stocking continued the following year, and 2007a. Recesses 700 kg. young grass carp and common carp. The action was joined by Roraty clubs from Hungary, and neighboring Baja NGO Young Friends of Nature in Sombor. Next, the 2008th channel is supplemented with 900 kg. (10,000 units) of offspring. As part of this action is represented by the newly formed cycling club Sombor, and the path along the canal is held promotional ride bikes Capriolo Backa Topola.

In 2009. . released over 12,000 pieces, about 1,000 kg . fish fry , again with the help of NGO Friends of Sombor and Environmental section comp. Elektrovojvodina . In addition to Hungary, this time it was yet and Macedonia . On the bank of the canal in the Bezdan, 2010. has put a significant amount of fish in the presence of guests from all over Serbia . Support was given by the company Tisa Sombor , Fishery Association pike and pheasant hunting society of the Bezdan. The 2011th and 2012. has sunken over 16,000 fry , over 500kg . certified fingerlings categories 150gr on the canal bank of the Bezdan. The action was supported by the Ecological Society of Ozone from the Bezdan.

Further action restocking Rotary Club Sombor has successfully continued its activities to restore fish stocks. Tenth action was 2013. The larvae from which it is produced fingerlings for restocking, produced were seeded in May of the same year . Set on a 800 kg one year younger in great shape average weight of 50 g . produced in Bezdan´s pond, under strictly controlled conditions . Restocking in Sombor has become a tradition .

In order to have an idea of the amount of fish which the Rotary Club of Sombor has realized restocking channels, in addition to the regular charge restocking conducted throughout Vojvodina, about 900 kilometers channels, when released 17.000 pounds of fingerlings per year, and 10.000 lakes California pounds of trout annually. (7)

Company Vojvodina Waters every year supported the Rotary Club of Sombor in the implementation and organization of these activities.

RESULTS

The first effects of the development of fish stocking are notable for two years when the young fish should be in their natural environment to reach around 1.5 kg mass each. It reaches a weight of about 20% of injected fish . With this action , we have to point out, one is a non-profit organization involved in a very serious commitment to water conservation and highlight the importance of stocking and some preserved ecological values .

Action during this decade, and both cycles restocking, in addition to enriching the canal water fish, complete contents on raising environmental awareness organization accompanying environmental workshops and professional conferences. So, restocking the waters of the Rotary Club Sombor 2007. year was promoted in counseling " Healthy water - the Millennium goal of Rotary ." Recognized experts in these fields have been talking about the quality of surface water and groundwater as well as measures to preserve and improve the quality. In September 2008th year, in a joint effort of the Rotary Club of Sombor and Baja, organized regatta Baja - Sombor , under the slogan BAJSKI CHANNEL, ecological project of the Rotary Club of Sombor and Baja. The program of action was presented at a meeting of European regions in Vienna and Geneva before the UN Commission for the Navigation closed waters.

In Santovo , Hungary , under the stocking 2013., was The Conference on Water . These two clubs are traditionally associated with water physical , medical hygiene (identical problems of water quality), economic (fishing and tourism) and friendly (love of the river Danube rivers Mostonga and Plazović and canals, recreation and sports on them). The conference was attended by top experts from the Faculty of state institutions and the two neighboring countries, as well as successful entrepreneurs in this area with very current issues .

Restocking activities at home and abroad have resulted in growing fish in hatcheries and releasing the same into river, lakes or oceans, for commercial and recreational purposesn, but also with the intention to increase the population of endangered fish and preserve native species .

At the annual World consultative meetings to discuss the mode of stocking and the results of management of fish resources.

He insists that all aquatic organisms that are stored in the internal waters must be in compliance with protocols for native species and translocation of fish .
Results restocking talk about the benefits of production possibilities and the importance of fish species that engage in water resources.

CONCLUSION

Restocking is becoming an important economic link with which to be seriously addressed multidisciplinary, including formal and informal institutions.

Restocking dealing with public authorities, private groups and NGOs.

The practice of stocking was to become viable.

Appendix:



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ENVIRONMENTAL MONITORING DURING THE CONSTRUCTION OF ADA BRIDGE SOUTH APPROACH ROADS - RADNICKA INTERCHANGE

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INTRODUCTION

Construction of the South approach roads to the bridge over Sava river in Belgrade- Radnicka interchange was a certain challenge in terms of planning and implementation due to complexity of space and existing infrastructure. Complexity also refers to the monitoring of construction works on environment due to the fact that the influence spread on the sanitary protection zone of the Belgrade waterworks, residential area Senjak and other vulnerable structures. The paper will present the results of the monitoring performed during the construction period (May 2011 till November 2013).

Key words: Ada bridge, monitoring.

MATERIAL AND METHODS

Before we started with environmental monitoring of the South approach roads SAR, we performed the State of the Art of the environment „Zero Study“. Measurement sites and locations which were set up during „Zero Study“ were used during monitoring under the construction works of South approach roads SAR. This was done in order to follow the trends of change „referent values“ to be able to compare according to „Zero Study“ („0 State“).

The size and dynamics of the sampling and the number and location of the measurement points were defined on the basis of the data from the Study of environmental impact assessment, the Zero Study, the Employer's requirement, conditions of the terrain and the expertise.

Monitoring was executed on the base on expert-methodological approach and in reference to the regulations in the field of protection of environment based on National regulation.

Sampling and laboratory testing were done by using accredited methods and expert opinion in accordance with current national regulations.

Environmental monitoring during the construction of south approach roads SAR, to the bridge over river Sava, was done during the whole period of those activities, from May 2011 to November 2013.

Table 1. Monthly scope and dynamics of environmental monitoring

Parametres of the environment	unit	Number & dynamics
I Surface waters		
The temperature, pH,electroconductivity, dissolved oxygen, % saturated O_2, suspended matter, COD, BPK_5, NH_3, NO_2, NO_3, sulphates, heavy metals (Cu, Cr, Pb, Hg, Zn, As, Ni i Cd), TOC, content of hydrocarbons (C_{10}-C_{40}), VOC, PAH	sample	Single sample (per month) of Topcider river upstream and downstream (total 2 samples)
II Outdoor Air		
rainfall (airsediment), particulate matter (PM10), analysis of heavy metals (Cd, Pb i Zn) in PM10, nitrogendioxide, BTEX	Sample and measurement sites	24hour measurement of PM_{10} at 2 measurement sites once a week; Continuous Airsediment 30 days at 2 measurement sites
III Soil		
% moisture, pH, loss ignition, clay, heavy metals (As, Ni, Cd, Cu, Cr, Pb, Hg i Zn), content of hydrocarbons (C_{10}-C_{40}), PCB and PAH	sample	One sample(per month) from each of 2 locations (total 2 samples)
IV Noise		
Measurement of the level of the noise in accordance with current regulation (standard ISO 1996-1,2,3) measuring: equivalent level of noise, impulsive level of noise, characteristics of the frequency of noise	Measurement sites	Measurement of level of noise at 2 locations once per week (two daily and 1 night measurement)

Locations for sampling

- Surface water:
  - Topčider river upstream, profile (Careva ćuprija)
  - Topčider river downstream, profile confluence of Čukarica estuary
- Ambient air:
  - Drinička 7, residential area Senjak
  - Belgrade horse race
- Soil:
  - Construction site - site between industrial tracks and railway Beograd-Bar (location 1)
  - Construction site - right bank of Topcider river near stone bridge (location 2)
- Measurement of noise:
  - Drinička 7b, residential area Senjak
  - Belgrade horse race (from August 2013. St. Lazarevačka 1, Senjak)

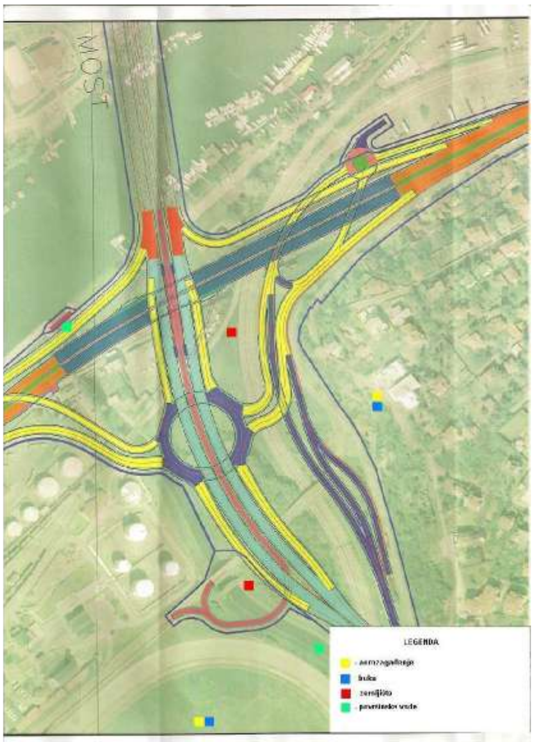

Figure 1. Sampling sites in relation to railway

RESULTS

This paper presents the results of environmental monitoring, which were analyzed and presented in monthly reports and six-months and final reports.

Surface water

Results of the surface water of river Topčider monitoring in the observed period (May 2011 to November 2013) showed the following:

- The most often deviations from the referent norms was registered in water quality at both locations-profiles in the following parameters: NH_4, NO_2, BOD_5, COD and suspended matter;
- The only significant difference between tested parameters at both monitoring sites during the investigation period was in the values of dissolved oxygen, where the value at profile upstream was all the time within norms, while at profile downstream from construction works the values of dissolved oxygen were over adopted norms showing the increasing trend during 3-years follow-up.

Air

Results of ambient air monitoring showed that

- The most often exceedance from the referent norm was registered in the values of PM10
- Concentrations of heavy metals were over the norms in the case of arsenic and nickel
- In few samples, concentration of benzene was over the limit value in the first 2 years, but in 2013 no exceedance was registered (on both locations).

Soil

The impact of the construction works SAR on soli was as follows:

- At location 1 the most often registered deviation was the concentration of heavy metals: nickel in almost all samples, then copper, zinc, arsenic, and lead. Other tested heavy metals were from time to time over limit value, while concentration of mercury was all the time within limit value. Organic parameters were very often over limit value, total hydrocarbons C10-C40 and PAH. Polychlorinated bipheniles (PCB) were not over limit value. Remediation values were exceeded for nickel in 15 samples, arsenic and copper in two and chromium and lead in one sample.
- At location 2 the most often registered deviation was increased concentrations of PCB in all collected samples. In the most of samples, increased content of total hydrocarbons C_{10}-C_{40} was registered and in lower percentage PAH. Regarding heavy metals, exceeded concentration of nickel and copper were registered in all samples, as well as the exceeded concentration of chromium and zinc in most of the samples. Remediation values were exceeded for PCB in 27 and copper and nickel in one sample.

Noise

Results of noise level monitoring in the period of monitoring are as follow:

- Location 1 (residential area Senjak) –level of noise in 89% of daily measurements were over limit value for certain acoustic zone. Level of noise in evening regime (18-19h) was over the limit level in 28% of the measurements.
- Location 2 (Belgrade horse race) - none of the measured noise levels were over the limit value for certain acoustic zone.

Generally, the most significant sources of noise in the vicinity were:

- road traffic in Radnicka street and bridge over river Sava and Vojvode Misica Boulevard
- traffic across bridge over river Sava and over built parts of approaching roads
- construction works on approaching roads

DISCUSSION

Surface water

Findings of increased values of the same parameters upstream and downstream from the construction works indicate that dominant reason for this is not connected to the activities of the construction works. The reason for this should be found in the stream of Topcider river i.e discharge of industrial waste waters and community sanitary waste water, upstream profile Careva Cuprija.

Having in mind obtained results from the monitoring we consider that construction works of south approach roads did not have significant negative impact on Topčider river and that they were of moderate and temporary character. In order to protect the surface water quality during the exploitation of interchange Radnicka, it should be considered to undertake the treatment of atmospheric waters from traffic, before its discharge into Topcider river.

Air

Obtained results are only partly due to the construction works. In should be taken into consideration the impact of other influence (current traffic in Radnicka St., Živojin Misic Boulevard, newly built roads on the Ada bridge, approaching roads, individual heating plants in winter period, activities on Belgrade horse race) that caused the increased concentration of some pollutants.

Considering that the construction works were lasting limited time, we do not expect cumulative negative effects on the air quality, except the influences derived from the traffic on the new roads.

Soil

Results of „Zero Study" which was done prior to construction works, have shown that most of the above stated results showed deviations from adopted norms for non-contaminated soil, what indicates the historical pollution in the area. Comparing the values of tested parameters (heavy metals and organic parameters) with „Zero study" and after finished works (November 2013) we can conclude that there was not increasing of concentrations of tested parameters. At location 2 we registered increased concentrations of heavy metals (Cu, Zn i Pb) and PAH what can be connected to: 1) removing of soil at location 2 which was done because of high concentrations of PCB-a, 2) applied technology (cutting of metal construction) during the construction works of the approach roads, and 3) the fact that in the final phase of works there were mixing of soil from other locations.

Removing of the soil i.e. its exchange at location 2 was done in order to perform remediation, since there were registered high concentration of PCB[12]. Study how to do remediation was prepared, and very detailed examination of the soil was done

[12] High values of PCB at location 2 (above remediation value) were registered in „Zero Study"

up to 2m depth. It enabled to define the borders of distribution of increased concentrations of PCB in soil. After the exavation of the soil, the characterization of waste-soil was done in accordance with national regulation. Remediation was done by filling in the empty space with soil brought from another place.

Noise

The level of noise measured during „Zero Study" at Location 1, expressed as mean value for day, was 56 dB, while mean value of noise level during the whole measurement period was 57 dB. The highest values of noise ere registered in the first year of construction works (2011), but in the following years (2012 and 2013) decreasing trend of noise level was registered.

Considering all above mentioned, the dominant source of noise in the period of monitoring was traffic on existing and newly built roads. The issue of setting up the sound barriers, in addition to the existing, toward the residential area Senjak should be considered.

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EXERGY ANALYSIS IN ENVIRONMENTAL PROTECTION – PRINCIPLES

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ABSTRACT

Exergy is a part of thermodynamic system energy that can be converted into useful work. Study of different energy forms transformation processes, based on exergy, could be used in order to estimate the effect of these processes on the environment. This approach gives more realistic picture than energy, allows detection of critical points of processes, and contributes to efficiency increasing, rational use of natural resources, development of green technologies and sustainable energy sources. Exergy analysis can determine which part of available energy could be converted into work, reaching a working substance in balance with the environment in a reversible manner.

Key words: exergy, exergy analysis, environment, useful work.

INTRODUCTION

Energy can be converted from one form to another, but these transformations are always in the direction of increasing entropy. It leads to degradation (dispersion) of energy, i. e. transition to less organized form of energy, unsuitable for conversion into useful work. Some forms of energy, such as heat, are impossible to be completely converted into mechanical energy, i. e. useful work. For example, heat is a lower grade of energy than mechanical or electrical energy. Exergy is a measure of energy form quality. When energy loses its quality, exergy value is also lost. It is defined as the maximum of useful work which can be produced by a thermodynamic system. Exergy analysis allows the identification of critical and inefficient points of the observed system, i. e. the plant. During development and design of energy systems, it is common to make trade-off between two main factors – the efficiency and the costs.

The consequences of energy conversion processes on the environment, e. g. climate changes and fossil fuels reduction have drawn more attention to the protection and preservation of the environment. Eventually, it is necessary to consider energy consumption and depletion of natural resources, i. e. the efficiency of the processes, the assessment of emission and reduction of its effects to the environment, as well as the development of new and less harmful technologies and sustainable energy resources use. Exergy efficiency is proposed as an indicator of environmental characteristic which includes the aspects of energy efficiency and environmental impact of the energy conversion processes, e. g. reduction of harmful impacts and environment degradation[1].

EXERGY ANALYSIS

Exergy is defined as the maximum work that can be produced by a stream or a system in a specified environment. Exergy is a quantitative measure of quality, i. e. usefulness of energy amount. It represents the maximum work of an open thermodynamic system that can be achieved by matter or energy flow with defined reference environment (described by its temperature, pressure, chemical composition and concentration), during the process which direction is the direction of establishing equilibrium[1]. Therefore, exergy is not a simple thermodynamic concept as it relates to the system and to the environment, i. e. it doesn't only depend on the state of a system and an energy transformation, but also on the state of the environment.

Exergy is based on the presumption that a working substance, whose initial state is not in an equilibrium with the environment, could reach the equilibrium with the environment in a reversible manner, i. e. through reversible state changes. Reversible processes imply that a thermodynamic system could be restored into initial state, after performed process, without any changes in the system, i. e. environment. These processes are infinitely slow processes, where system goes through a series of equilibrium successive states and could be carried out in an opposite direction with a very small (infinitesimal) change in external conditions, at any moment. When a system reaches the equilibrium with the environment, exergy becomes zero. Consequently, exergy of a system could be enlarged by increasing the differences, i. e. imbalance (mechanical, thermal, concentration – chemical) between a system and the environment in the observed thermodynamic cycle (thermodynamic cycle represents series of the thermodynamic processes, while a working substance undergoes series of state changes and, at the end of which, the system returns into its initial state). Fully reversible processes do not exist in the macro-world (nature), so the concept of reversibility is a thermodynamic idealisation. When a working substance or a thermodynamic system are in equilibrium with the environment they don't possess any exergy, considering that there are not any imbalance or any potential for any kind of thermodynamic process.

Exergy efficiency is a measure of entropy generation or exergy destruction by the system, i. e. a measure of irreversibility and it might indicate how close the actual process approaches the ideal case (reversible process). In spontaneous (irreversible) processes, exergy transforms into anergy, the part of energy which cannot be converted into any other form of energy. The increasing of thermo dynamic system entropy (ΔS_s) represents increasing of the amount of energy transferred to the environment, i. e. dispersed (waste) energy ($E_W = T_o \cdot \Delta S_s$) at the default temperature (T_o). This means that a greater amount of the released heat releases the greater degradation of energy. Exergy loss due to irreversibility of the process is a parameter which can be improved by changing technology or the process performing, in order to improve its efficiency, i. e. exergy efficiency. Therefore, exergy can be used as a measure of a thermodynamic process quality and could highlight the parts of the process where it could be possible to make some savings. Unlike exergy, the energy analysis does not provide any information of energy degradation or energy resources in the process, i. e. it does not show a quality of converting one form of energy into another. This is a classic method of energy use assessment in energy conversion processes, i. e. evaluation of energy efficiency and assessment of energy balance, based on the Principle of conservation of energy, i. e. The First Law of Thermodynamics and allows only the assessment such as heat losses or potential heat recovery.

The main characteristic of classical thermodynamic process is energy efficiency that represents the part of the heat converted into useful work, i. e. efficiency of heat conversion[1]. Many analyses of efficiency and process performances were made based on energy analysis pursuant to The First Law of Thermodynamics, which considers only the quantity of energy, regardless of its quality. In this case, the total input (additional) energy (Q_i) in a thermodynamic process is equal to the total sum of used energy, i. e. energy invested into useful (output) work (W_u) and unused (waste) energy (Q_w):

$$Q_i = W_u + Q_w$$

Energy efficiency of the cycle process is defined as the ratio of the useful (output) work (W_u) and input heat (Q_i) and it is always smaller than 1:

$$\eta = W_u / Q_i = (Q_i - Q_w) / Q_i$$

Exergy analysis method overcomes the limitations of The First Law of Thermodynamics. This concept is based on both laws – The First and The Second Law of thermodynamics. When it comes to exergy analysis, in addition to these energies, i. e. their exergies (used or unused), the calculation includes the loss (destruction) of exergy ($Ex_{dest.}$) caused by the irreversibility of the process:

$$Ex_i = W_u + Ex_w = W_u + Ex_w + Ex_{dest.}$$

The last two members of the equation are included in the exergy balance and they represent the cumulative exergy losses, while energy losses only include the unused emission of heat and gases into the environment.

In this case, the exergy efficiency (η_{Ex}) is equal to the ratio of the used (output) exergy ($Ex_o - Ex_i$) and input exergy (Ex_i):

$$\eta_{Ex} = (Ex_o - Ex_i) / Ex_i$$

Since in this case output exergy (Ex_o) is equal to the sum of unused (Ex_w) and lost ($Ex_{dest.}$) exergy, i. e. destructed exergy, the above equation takes the form stated below:

$$\eta_{Ex} = (Ex_i - Ex_w - Ex_{dest.}) / Ex_i$$

It can be seen that exergy efficiency gives a more accurate picture of process or device performance than energy efficiency, because it does not only show the amount of output (unused) energy, but it shows, precisely, how much energy, i. e. exergy is not used and which part was irreversibly lost, i. e. destructed ($Ex_{dest.}$). Exergy efficiency indicates which part has been used regarding the possible maximum. The loss of exergy ($Ex_{dest.}$) is proportional to the generation of entropy during the process, which is responsible for ideality decreasing (reversibility) of a process. This parameter ($Ex_{dest.}$), which can be determined by exergy analysis, might be improved by changing technology or process performing, in order to improve its efficiency, i. e. increasing its exergy efficiency. Thanks to this parameter, exergy analysis is more powerful method than energy analysis, since it shows how much energy, i. e. exergy was lost by process irreversibility. Thus, it might be decreased by changing process technology.

Exergy analysis allows direct comparison of processes that are different in physical sense. Since exergy analysis is a measure of the process approaching the ideal process, it may provide valuable information during evaluation of system's energy efficiency and energy resources use. Exergy methods provide insight into the type, location, cause and amount of actual waste and losses and allow assessment in reference with identifying existing and future processes potential improvements, by designing more efficient systems or subsystems and by reducing their current or potential inefficiency.

Exergy methods help evaluation of the thermodynamic value of a product, assessment of the environmental impacts of energy and their resources[2, 4-16], reduction of these impacts as well as the achievement of the sustainable development. Exergy can be easily connected to the economics, because the higher exergy efficiency actually means a higher process cost-effectiveness. Since the value of exergy efficiency of the system depends on the system state and the parameters of the environment, the environment must be precisely defined prior to the implementation of exergy analysis.

When exergy analysis is applied to the environmental problems, the reference environment is the real environment and it must simulate the real conditions, through some model of the reference environment[3]. One such model proposed by Baehr, Schmidt, Gaggioli, Petit i Rodrigez[3], defines the chemical composition of the reference environment consisting of the air saturated with water vapour and the condensed phases: liquid water, gypsum and limestone[3]. This model defined the constant concentrations of a few, basic elements in the nature: carbon, nitrogen and oxygen that normally exist in the air as carbon-dioxide, nitrogen and oxygen molecules. Hydrogen concentration has been determined by the liquid phase of water, sulphur concentration by gypsum ($CaSO_4 \cdot 2H_2O$) and calcium concentration by limestone ($CaCO_3$). For reference purposes the environment temperature value of 25ºC has been adopted, as well as, the pressure of 1atm[3]. By definition, the value of exergy reference environment is zero. Hypothetically, the reference environment is always in stable equilibrium, since all of its parts are in equilibrium in respect to one another. Within the reference environment there are micro-imbalances and they occur in internally reversible processes, but the overall parameters and functions of the reference environment (temperature, pressure, volume, quantity and composition of *i*-components, as well as their chemical potentials) remain constant over the analysed period.

It is important to note that the natural environment has no theoretical characteristics of the reference environment, because it is not in equilibrium and its intensive properties have ambiental and temporal variations. Many chemical reactions in the natural environment do not occur because the mechanisms needed to reach equilibrium are too slow and, therefore, exergy of the natural environment is not equal to zero. Since the calculation of useful work theoretical maximum requires the environmental equilibrium and imbalance with the system whose exergy has been calculated, all models of the reference environment should be set in order to reach a compromise between the demands of theoretical reference environment and the natural environment, i. e. to simulate the real environmental system, as much as possible.

EXERGY ANALYSIS AND THE ENVIRONMENTAL PROTECTION

The environmental issues and problems of increasing amounts and types of pollutants, various environmental hazards and ecosystem degradation are issues of local, regional and global character. Many environmental problems are caused by, or are directly related to transformation and use of energy. For example, the relatively low cost of fossil fuels had made modern mankind to increasingly depend on them and caused significant pollution, endangering many biological systems. An important implication of the above assumption is that sustainable development requires not only the ability to use energy resources, but also their efficient use. Since the exergy methods are essential in assessing and improving energy efficiency, they could be very useful in the sustainable development. Through the effective use of technology, the companies might increase their own benefits, while reducing negative impacts, such as environmental degradation.

A large part of the environmental impact is associated precisely with exploitation of energy resources, which are the part of the environment and have a limited value. Any use of resources leads to some impact on the environment. Since there is a direct link between exergy (and sometimes energy) efficiency and the environmental impact, it follows that restrictions, imposed with the sustainable development and the environmental protection, could be partially overcome by increasing the exergy efficiency, i. e. increasing exergy efficiency could make development more sustainable in respect to the previous and current environmental state.

Pollutants, emitted into the environment, lead to disorganization of living systems, thus destroying them. The spontaneous emission of unused exergy of the waste emitted directly into the environment, that are not in balance with it, might become completely uncontrolled variables and a great potential for its, difficult to predict, degradation, disrupting the natural balance causing uncontrollable and often unpredictable consequences. The higher exergy of pollutants, the greater disturbance to the environmental balance, although it is believed that, for the environment, chemical exergy is the most dangerous waste of all[4]. In some cases, exergy has an impact to the environment, while in others its influence does not exist, such as in the case with a variety of toxic substances that can cause health problems for humans and animals.

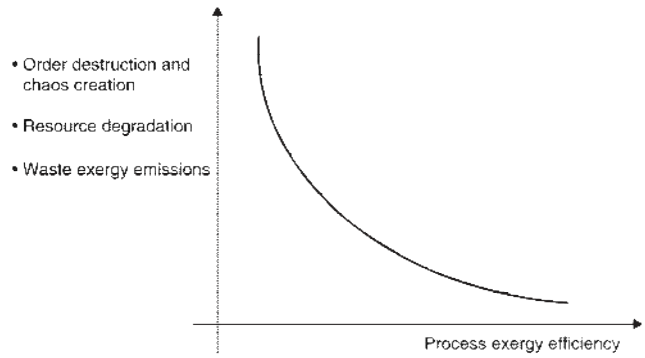

Figure 1. Exergy efficiency of a thermodynamic process and its impact to the environment[1].

Exergy analysis in the environmental protection has three main aspects that should be considered.

Firstly, an exergy analysis can assess existing sub – processes of modern technology, precisely those that create the largest and the most dangerous amounts of waste. Thus, it is possible to achieve improvements based on the localization of inefficient sub-processes and direct calculation of damage that they cause, so the damage could be minimized or energy resources losses could be reduced. Since degradation of resources is harmful to the environment, it can be reduced by increasing the process efficiency or by using renewable energy, e. g. solar energy, because the Earth is an open system that constantly receives energy from the Sun.

Secondly, it is possible to construct new, additional sub-processes within the existing ones that would bring waste into balance with the environment, i. e. pre-treated to be safe, before releasing into the environment. Even exergy waste might show potential changes to the environment and there are several possible scenarios of potential harmful effects, so it is still possible to create some form of prevention, e. g. reduction of waste emissions or some additions to sub-processes to the existing ones that remediate and control emission of pollutants. In this case, the exergy analysis can indicate which process is more efficient and appropriate in order to protect the environment. Examples are as follows: wastewater processing before discharging into the recipient, separation of waste for energy transforming and similar purposes with the adequate environmental treatments or collection of sulphur- dioxide resulting from the combustion of coal and its use as a raw material for sulphuric acid production.

The third option, which is the most present and the most important nowadays, is the use of so-called green (ecological) technologies and renewable energy, that cause the least harm to the environment. Green technologies are the application of the environmental sciences in order to preserve natural resources and reduce the negative impact of human activities to the environment. When creating these new technologies at the beginning of project planning, the system design with maximum protection of the environment must be taken into account, e. g. exergy analyses of the plant systems and the environmental standards and preservation proceedings, as well as environment revival and recovery of already damaged ecosystems. This trend has enhanced due to reducing of the amount and increasing costs of existing energy resources, awareness of the environmental preservation, as well as by increasing the environmental accidents. However, these processes are not yet sufficiently developed and, therefore, they are expensive, mostly due to design costs and construction or low efficiency, but also because of the price of the ecoremediation of already devastated sites.

CONCLUSION

The use of exergy analysis and efficiency of the process are obviously useful methods to assess the impact of processes that include any kind of energy transformation to the environment. The exergy analysis helps in determining the true efficiency of a thermodynamic system, which makes it an effective technique for finding improvement possibilities. It does not only show how much energy is not used, but also which part has been destructed during the process. Improving exergy efficiency contributes to the rational use of energy resources and raw materials and development of technology with less harmful consequences. Such environmental technologies bring waste into balance with the environment before emission and make minimal harm to the environment. Exergy analysis provides guidelines for the design of technologies and processes that can be used for improving, reducing and repairing negative effects of industrial processes to the environment, as well as for the development of new environmental friendly technologies.

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EXERGY ANALYSIS IN ENVIRONMENTAL PROTECTION – IMPLICATIONS

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ABSTRACT

Technological systems are constructed according to the highest usability and efficiency at the lowest costs. Exergy analysis identifies critical points of the thermodynamics processes, allowing optimization through improving processes and sub-processes efficiencies, energy resources and losses and it is fully in line with the economics. The potential application of exergy analysis in the environmental protection could reduce the economic costs connected with improvements in process efficiency, as well as through fees which polluters are obliged to repay. For the wider application and acceptance of exergy approach, the support of the expert community and the government regulatory bodies is necessary.

Key words: exergy, exergy analysis, environment, economics, government.

INTRODUCTION

Exergy analysis as a method for calculation of thermodynamic process efficiency is a useful tool in energy management and technology in general[1]. Besides the quantity it also indicates the quality of some energy form or natural resources, i. e. identify critical, inefficient points in a thermodynamic system or a plant. Nowadays, exergy analysis methods are increasingly being used for improvement and promotion of efficient energy use of a natural resources and optimization of complex process systems, sub-systems and their losses. Also, it can be successfully used to estimate processes effects of energy transformation to the environment.

This study points out the unbreakable bond between exergy, economics and politics, i. e. the potential of exergy analysis to improve efficiency of the technology, reduction of losses and a better understanding of the economic benefits, as well as the negative consequences that they may cause in the environment, it might farther lead to increase of the energy transformations processes costs, due to a variety of charges for environmental damages based on prescribed standards. Also, the study explains that increased application of exergy analysis and the benefits that it provides must be clearly defined, accepted and implemented by experts, government regulatory bodies, investors and the public.

ECONOMIC ASPECTS OF EXERGY ANALYSIS AND THE ENVIRONMENTAL PROTECTION

As explained above, exergy is strongly connected to the environmental issues and efforts to reduce or decrease the adverse impact to the environment[2-3]. Exergy can be easily connected with the economics, because the higher exergy efficiency is, the higher is the cost-effectiveness of a plant. The combined methods of exergy analysis and the government state economics, could be used to determine the financial subventions, penalties or taxes to encourage industry to efficiently use energy resources. These exergy methods might affect the governments to prescribe higher requirements and standards for pollutants in order to discharge less harmful waste with respect to reduced emissions of exergy waste that directly correlates with the reduction of damages to the environment.

The basic dilemmas of contemporary society are abuse of natural resources caused by economic greed and insufficient environmental knowledge, and abuse of humans and human rights caused by democracy absence. The first step in improving the use of energy resources and reduce of the environmental destruction might be achieved through better understanding and application of the exergy concept.

Energy economics is a wide field and many efforts have been made to combine energy and economics[2-3]. One of the main challenges in designing thermodynamic process, especially the transformation of energy, in order to reduce their impact to the environment, involves identifying ecologically optimal configuration, i. e. the most appropriate options[3]. Every energy system can be divided into two areas – physical and economical. The physical area of the environment is described with its pressure, temperature, concentrations and the chemical potentials of corresponding compounds, while the economic area depends on the number of benchmark products prices and interest rates. These two areas are related by costs of process and its physical measures. If these relationships are known, physical and economic environment can also be connected. This process sometimes could be simplified, but it is unfortunately often very complex[4].

Regarding the link between exergy and economics, exergy analysis is directly related to a value, i. e. price of natural resources and goods, while energy only sometimes represents their costs. Another connection between an economic value of resources and exergy could be seen through exergy losses of system which lead to the decrease of economic benefits[3]. But today it's common to mentioned energy costs, energy prices, etc. The fact is that these types of expenses actually do not exist, because energy generally has no value, while exergy has, due to the fact that the obtained useful work is associated with exergy and economics. Exergy determines the physical value and also it is associated with economic value, reflecting the usefulness of the energy processes and resources.

The most of technologies are based exclusively on economics, i. e. the project costs in addition to the technical factors. Therefore, exergy and economic links through the consumption of useful work and its cost might make the exergy methods popular and widely applicable. The amount of exergy shows the value of the goods through the work used for their production, in fact, through raw materials, natural resources and energy spent for the manufacturing. The several economic analyses have been developed in consequence of this fact, for example thermo-economics, "the cost of The Second Law of Thermodynamics" and exergy-economics. They are based on the use of exergy in the production, e. g. production of electricity. The common characteristic of these techniques is recognizing the exergy, not the energy values of production system, i. e. the use of natural resources, the value of goods and the production costs. These methods are associated with the exergy variables[3] and can help to determine economic resources distribution in planning of some production system by determining the actual production costs and corresponding prices of the products, resulting in increase of economic feasibility and profitability of the system and rational pricing. It seems that two important things have to be done in order to connect exergy with the economic approach. The first is detailed analysis of the current activities that have been proven as successful and, the second is simplification of all these exergetic-economic methods to make them more suitable for practical use.

The consequences of neglecting the environmental issues has led modern society to pay for damages that have already been made, either through rehabilitation of consequences or through a rapid-development of environmental technologies. However, these processes are not yet sufficiently developed and, therefore, they are expensive, mostly because of the construction costs, low efficiency and the costs of ecoremediation of devastated areas. Even now there are some very positive examples, but they are insufficient and investments of this kind have to be developed because they could bring the benefits to present and future generations. The most common and simplest are cogeneration and recycling. Serbia does not have a satisfactory effect, but cogeneration power plants[2-13] have been built for a long time and are present in many countries. They have a higher level of overall energy efficiency than conventional power plants. Combined heat and power (CHP), also known as cogeneration is the process of a simultaneous electricity generation and useful heat from a single fuel source in power station. This production, usually in addition to electricity generation, performed the removal of water vapour and used it mostly for space heating. But for obtaining electricity in the world, the fossil fuel power plant production still remains the most used process. A single unit of the coal-fired steam power plant consists of four main sections[1]: a) steam generators, b) turbine generators and transformers, c) condensers and d) preheaters and pumps. Steam generators have significantly lower exergy efficiency than energy efficiency. This difference implies that although the most of the input energy is transferred to the water vapour, i. e. heat and a large part of energy is lost because the heat is lower quality energy which could not effectively be converted to work, thereby degrading these energy transfers. It means that the most of total exergy losses occur in the steam generator, i. e. while creating the heat. In cogeneration power plants heat is an additional product. The first product – electricity has its own price determined by two main processes – high efficiency (energy and exergy) of the electricity generation process with distribution and a low efficiency process in steam generator. Since the losses in the steam generators are large, the heat has an extremely high cost and thus affects on its own price and on increase of electricity prices as well. In the process of cogeneration a heat is no longer a loss and the prices of both these products can be quite realistically calculated and lower especially by exergy efficiency assessment.

A variety of the environmental friendly technologies and processes using renewable resources still are not sufficiently developed and therefore are more expensive and insufficient alternative to the actual fossil fuel processes. For example, the geothermal energy, that currently has a maximum exergy efficiency of only 20%[1] has very low negative impact to the environment. If its efficiency could be increased, the production costs would be reduced and the environmental influence could still remain minimal, even lower. Exergy analysis in such cases could help in evaluating relationships between necessary investments in technical development and environment protection on one side, and profit on the other.

Since sustainable development implies economic viability, methods related to exergy analysis need to strengthen the link between these two categories. The goals of the most existing analysis techniques integrate exergy and economics to optimize the design and operation of the thermodynamic systems, their effectiveness, costs and economic feasibility. Researching of exergy flow in the region or country and their connections with the economics and ecology in order to understand their true potential in increasing the actual energy efficiency and the rational use of resources, might provide extremely valuable information.

POLITICAL ASPECTS OF EXERGY ANALYSIS AND THE ENVIRONMENTAL PROTECTION

Correlation between exergy and policies in various areas, including the use of natural resources, energy, environmental protection and industrial development, means that the state government should be motivated to use exergetic-economic methods in creating public opinion and their own policies in order to maximize the benefits that they bring[4]. The necessity and demands to preserve the environment are very clear and sustainable development is a demanding process that requires significant reform and changes in the perception of the environment. Regarding these facts, exergy has many aspects that should be related to government policy and influence to it[5,10-13]. This is especially relevantly for the government bodies dealing with energy and natural resources where the exploitation efficiency is very important. In Serbia these bodies are primarily: ministry responsible for environment with a great environmental management importance, as well as the economy and industrial development ministries. Countries that wish to improve energy use and sustainable exploitation of the natural resources, as well as positive attitude to the environmental protection, must invest public funds in areas that have the greatest opportunities to improve efficiency and thus the greatest potential benefits. The largest amount of funds should be directed to improve processes and systems with the highest exergy values and the greatest influence on the environment.

Insufficient use of exergy analysis by experts, companies and governments, sometimes comes from various reasons, but it is usually done quite unconsciously. This especially applies to use of exergy in the sustainable development, i. e. development of renewable energy, conservation of energy, saving the natural resources and the environmental protection. If this kind of analysis would be fully carried out, that would result in a higher quality of future life. It should be very useful if the relevant government bodies ensure support and adequate management in this area as the representatives of the public. The starting point are government officials, especially those who cover the areas of energy and environment. They might provide some trainings and education, as well as the application of these methods through various legislative measures and higher fees for violators of regulations, providing subsidies and foreign investment, professional meetings, public hearings, demonstrating the positive examples, the stimulation media and etc. On the other hand, members of the media also should be motivated and informed in respect to the basic level of the exergy concept and its importance. Unfortunately, the tendency in the media today is mostly quite opposite. All the above issues are often ignored as uninteresting topics to wider audience[5].

Energy giants are currently the manufacturers of the most abundant fossil fuels and usable energy, who are undoubtedly the biggest polluters. Undeniably great profits and interests within this type of industry produces extremely high barrier, where often the state itself are limited and insufficient stimulated for transition to a new energy sources and the reduction of waste for purely profitable reasons, such as charging of fees and taxes for the price of imported and sold crude or refined oil or penalties for major polluters[2-13].

It is essential that the public has a basic education and the possibility for understanding some technical issues, particularly the sustainable development and energy, i. e. exergy. Such an approach may encourage public discussions and deliver the potential solutions, support the formation of public funds for further researches, and the most important, prevent the negligence of these issues by the relevant institutions. The environmental issues are, unfortunately, quite ignored, so the current situation of misunderstanding exergy and its role in preserving the environment could be attributed to this fact. An example of complete absence of understanding that may arise when the public do not have required knowledge of some subject, in this case of exergy, and when the authorities and media do not perform their educational role, refers to the so-called "Energy crisis" in the 1970s, which led to a reduction in commercial use of oil, caused by its absence on the current market. Despite the fact that the most of energy that was available before crisis, was also available during the "time of crisis", e. g. by an enormous amount of solar energy that is transmitted to the Earth daily, or in a form of waste heat emitted from various plants and buildings, the energy crisis was declared anyway. Since energy cannot be either destroyed or created and energy was all the time present on the Earth, this was actually a completely wrong name and kind of crisis. The crisis was caused by reducing exergy, not energy. The public often talk about "energy conservation" that usually refers to efforts to solve some energy problems. However, the term "energy conservation" is meaningless according to The First Law of Thermodynamics or the Principle of conservation of energy. The public should be really interested in the conservation of exergy or the potential to produce the work required for various processes and systems that enable and provide products or services. As mentioned, energy present on the Earth originates mostly from the solar radiation (insolation) due to fact that the Earth is an open system that exchanges energy and matter with the universe. So it can be concluded that there were neither losses of exergy nor energy, e. g. solar radiation. Therefore, the Earth has the plenty of energy. No matter to the fact that energy is used every day it still exists in equal amounts, because its use is really only conversion or transformation. What the public should be worried about is the energy supplies that can provide all their needs and desires, actually energy form that can be converted into useful work more efficiently. This represents secure supplies of exergy, which could be called "exergy security" but which the public is not aware of. However, the public perception and focus has not much changed even forty years later.

Cleaner production of materials, goods and services is one of the basic principles of the sustainable development[1-2, 7, 11]. This involves efficient use of resources, minimized waste generation and use of renewable energy. Product quality should remain an important factor of production, along with potential profits and competitiveness on the market, but that does not mean that cleaner production and sustainable development have to be in conflict with economic approach that minimizes costs and maximizes profits. This production model could be understood as costs reduction since its optimization leads to maximizing the profit of the production process. The most modern industrial processes seek to improve and optimize the processes that consume less resources and produce less emission of waste gases, unused energy and solid waste. However, even when these processes comply with optimized and basic regulated requirements, this often provides only a partial solution to the environment, because the contamination resolving problem needs stronger regulations and more efforts to be done. Some researchers suggest that the invested exergy value for cleaning or repairing harmful effects must be related to the production process, i. e. must be defined as the sum of cumulative exergy content of the product, exergy waste and exergy recycling, in order to practice and allow the process with minimal impact to the environment. Exergy analyses are, therefore, an important tool either for improving the primary production process or secondary waste treatment process by changing their characteristics or use as secondary raw material by collection, separation and using for energy source or the other purposes. Exergy efficiency, i. e. the amount of obtained useful work is directly related to the economic aspect and entirely logical requires the investor to assess the potential increase in profits in a variety of processes.

The main reason for insufficient use of exergy analysis in designing, planning and scientific research by experts, companies and even state governments, is not because the exergy analysis is inappropriate, but because it is not well known or is completely unknown[2-13]. This avoidance of the unknown but useful topic is not productive and leads to inadequate decision-making. In order to overcome this situation, it is necessary to include exergy and exergy analysis in the study program and to improve the "exergy literacy" of engineers and scientists.

CONCLUSION

Two main implications of exergy analysis in environmental protection are the economic and political aspects. Exergy is in accordance with economics as a method for calculation of the thermodynamic process efficiency, i. e. useful work and it is strongly linked to economic issues. Using exergy analysis is related to the economic aspects and principles of modern society, that are nowadays essential requirements for the development and planning of production projects and systems, since they point to specific profit and processes losses. The most common analysis techniques are trying to integrate exergy and economics to optimize the design and operation of thermodynamic systems, their efficiency, costs and economic feasibility.

Sustainable development in a contemporary society means both – economic and environmental sustainable development, in general. Although sustainable development, i. e. environmental issues and efforts to reduce the harmful impact to the environment depends, in the first line, on people themselves, it is the most obvious that it also depends on the finances through economics, but also requires the support of competent institutions, experts and political orientations. Relevant government bodies dealing with energy and natural resources, media and public opinion have the most important role in creating suitable environment for using exergy by all interested parties, especially the transformation of energy industry. However, the absence of technical studies and educational programs related to exergy, the opinion of some experts that exergy methods can not lead to direct and quick results, duration and complexity of exergy analysis despite modern computer optimization techniques, primarily due to complicated definition of the reference environment and the absence of consensus on these issues, contribute to problems in widely using exergy and exergy analysis methods. For the purpose of easier use, especially in industry, it is necessary to develop and simplify exergy methods, which would be far more convenient for implementation in practice.

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ECONOMIC AND SPATIAL VALORISATION OF FOREST RESOURCES IN SERBIA

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ABSTRACT

The aim of this study is to analyse the state of forests from the economical aspects of their utilization and suggest new ways of the rational use of the forest resources in the future in order to score bigger gains in sales and profits both on home and foreign market with the highest yields possible and at the lowest costs. Forest vegetation covers only 3.9 billion hectares of the Earth. This represents approximately 29.6% of the total land on Earth. The usable value of wood is multifunctional. Forests clean out the air we breathe, produce oxygen and provide biological existence of flora and fauna.

Wood is used in lumber and chemical industry, agriculture, handicrafts, etc. Wild fruits and fruit trees (hawthorn, fiddle, raspberry, blackberry, hazelnut and apple tree), medicinal and aromatic herbs from ecological areas are all considered to be organic produce and they represent a significant natural resource of this country. Hunting tourism can provide economic benefits, too. Wood pulp in the forests of Serbia is estimated at about 225 million m^3. 54% of the wood pulp belongs to state owned forests, while 46% is in the privately owned forests. According to an analysis of forest types, there is a trend of industrial wood increase (30% in relation to 2004) and fire wood decrease (6% in relation to 2004), as well as industrial machinery decrease (4,5% in relation to 2004). Evaluation of the natural potentials involves both quality and quantity analysis of each element of the environment.

There are natural and anthropogenic factors affecting the quality and quantity of forest resources, such as: relief, climate, soil cover and biological factors. The basic products of this country should be fruits, medicinal and aromatic herbs, forest plants and bee products. Forests are also an important source of raw materials for cosmetics. Abundant with healing substances, medicinal herbs are widely used in pharmaceutical, food and cosmetic industry. The most common herbs are lemon balm, chamomile and mint. Wild fruits are used for making syrups, juices, etc. Trees are very important for human health because they produce oxygen, clean out the air and help the soil retain water in order to prevent erosion. Health and recreational functions of forests are reflected in all of these. Forest ecosystems are a very important factor of climate stability. They encourage the exchange of heat and moisture in the atmosphere, affect the flow of air and increase the amount of precipitation for 10%.

With an adequate forest policy and marketing campaign it is necessary to attract foreign investors in order to support, as much as possible, the development of organic agriculture in this country.

Key words: plants, forests, evaluation, development, a product, valuation, wood.

INTRODUCTION

Forest ecosystems are the most complex ecosystems on Earth made up of numerous plant communities. Forests are a natural resource and an important factor in the development of a country, a source of goods and services, and thus the total income of the society. Serbia has favourable conditions for the development of plant species and therefore the flora of our country is very rich. In order to utilize all these natural resources in the best way possible, it is necessary to engage experts for medicinal herbs, to improve purchase of forest products and to achieve a better cooperation with scientific and commercial organisations.

Forestry, as a manufacturing activity, has the aim of meeting the social needs for wood products. Lumber industry records a big profitability in the production of prefabricated houses and furniture. Beech wood has a special place on the EU market, in Switzerland, Italy and Germany. It is exported from the territory of Despotovac. It is a high quality wood, but has a low processing levels. Therefore, it is necessary to have a good coordination with EU standards. "In order to provide better export, it is necessary to obtain adequate financial means for an increased production." [3]

Besides wood, the main forest product, there are other products gaining in economic significance during the last years. Fruits, vegetables, honey, medicinal and aromatic herbs, forest fruits are organic produce and are becoming more and more sought after on the EU market. "The climate, soil composition and ecological advantages provide quite favourable conditions for high quality food production." [1]

The production of medicinal herbs provides bigger incomes than the production of other produce. The most common herbs are lemon balm, Klamath weed, mint, birch and chamomile. Abundant with healing substances, medicinal herbs are widely used in pharmaceutical, food and cosmetic industry. Among forest products, hazel tree, wild acorn, wild strawberry, mushrooms (porcino and chantarelle), wild raspberry and blackberry are quite distinguished, as well as wild onion. Forest fruits are used for making syrups, juices and fruit salads. All forest products can be economically cost – effective, but a rational management and higher quality of forest products are required.

The main objectives of this study include:

- Better application of expert knowledge of forest ecosystems in order to take advantage of the production capacity of forests while satisfying human needs in the best possible ways. Besides wood, there are other forest products, such as wild fruits, wild cherry, acorns, wild raspberries, strawberries, edible mushrooms (rich in carbohydrates, vitamins and minerals), medicinal and aromatic herbs, game, etc.
- Adequate implementation of forest policy, which should be included in the EU development programmes. Direct foreign investments play an important part in overall economic development of this country, i.e. in job creation policy, production development, new technology and knowledge. That is why the strategy is very important.

MATERIALS AND METHODS

The total forest area in Serbia is 2.412.940 ha. The forest coverage in Serbia is 27.3%. The largest is in Kosovo and Metohija (39.4%), followed by central Serbia (32.8%), while in Vojvodina it is 6.8%. The spatial Plan of Serbia anticipates that forest coverage should be 41.4% of the total area.

The timber volume and annual increment by forest type of origin are shown in Table 1. Although coppice forests cover more than 64% of the total forest area only 50% of the timber volume belongs to this category, and the average timber volume in coppice forests reaches about 124.4 m^3/ha. "The average timber volume in high forests is 253.3 m^3/ha, while in plantations is 136 m^3/ha." [13]

Table 1. Timber volume and annual increment by origin (2008)

No.	**Type of origin**	**Timber volume**			**Annual increment**		
		(mil. m^3)	***(%)***	***m^3/ha***	***(mil. m^3)***	***(%)***	***m^3/ha***
1.	High forests	157,511	43,4	253,6	3,388	37,3	5,5
2.	Coppice forests	181,188	50,0	124,4	4,458	49,1	3,1
3.	Plantations	23,787	6,6	136,1	1,233	13,6	7,1
Σ	Total forest area	362,487	100	160,9	9,079	100	4,0

Source: Nonic et al., 2008, p. 5

The highest total annual increment of about 50% is recorded in coppice forests, over 4.5 million m^3, which is an average of 3.1 m^3/ha. "In the high forests, the annual increment is over 3.3 million m^3, which is an average of 5.5 m^3/ha, while the annual increment in plantations is about 1.2 million m^3, i.e. 7.1 m^3." [13] The dominant tree species according to timber volume are beech (40.5%), Turkish oak (13%), Sessile oak and Hungarian oak (5.9%).

Among conifers, the most widespread species is spruce which contributes to the total timber volume with 5.2% share, then silver fir with 3.5% share.

Table 2. Standing felled timber and timber volume by tree species (2008)

SPECIES	**TIMBER VOLUME** ***(mil. m^3)***	**%**	**ANNUAL INCREMENT** ***(mil. m^3)***	**%**
Beech (*Fagus silvatica*)	146,850	40,5	2,781	30,6
Turkish oak (*Quercus cerris*)	46,980	13,0	1,034	11,4
Sessile oak (*Quercus petrea*)	21,542	5,9	0,553	6,1
Hungarian oak (*Quercus farnetto*)	20,986	5,8	0,518	5,7
Hornbeam(*Carpinus bettulus*)	15,157	4,2	0,334,	3,7
Blacklocust(*Robinia pseudoacacia*)	11,243	3,1	0,516	5,7
English oak (*Quercus robur*)	9,242	2,5	0,158	1,7
Poplars (*Populus sp.*)	6,137	1,7	0,338	3,7
Narrow leaved Ash (*Fraxinus angustifolia*)	5,792	1,6	0,153	1,7
Broad leaved Lime (*Tillia platyphilos*)	3,535	1,0	0,070	0,8
Manna Ash (*Fraxinus ornus*)	3,505	1,0	0,102	1,1
Other Broadleaves	34,001	7,4	0,784	8,0
Total Broadleaves	317,930	87,7	7,341	80,9
Norway Spruce(*Picea abies*)	18,810	5,2	0,605	6,7
Silver Fir (*Abies alba*)	12,659	3,5	0,715	7,9
Austrian Pine (*Pinus nigra*)	8,304	2,3	0,199	2,2
Scotch Pine (*Pinus silvestris*)	3,775	1,0	0.177	1,9
Other conifers	1,009	0,3	0,042	0,5
Total conifers	44,557	12,3	1,738	19,1
Total	362,487	100,0	9,079	100,0

Over 1.4 million ha or 64% of the total forest area are covered with coppice forests, 27.5% with high forests, while plantations and forest cultures cover about 7.8% of the total forest area.

Table 3. Forest area by origin (2008)

No.	Type of origin	Forest area	
		(ha)	(%)
1.	High forests	621.200	27,5
2.	Coppice forests	1.456.400	64,7
3.	Plantations	174.800	7,8
Σ	Total forest area	2.252.400	100

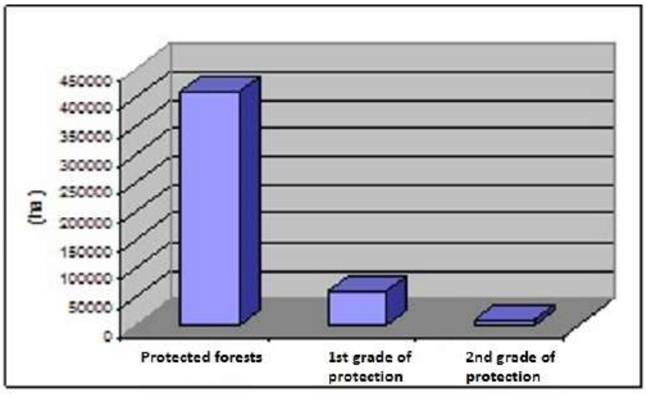
According to the law on forests, forests in Serbia are managed by public enterprises. The Serbian government adopts regulations for a 20 – year period. The forests have been divided into 27 forest areas which include both state owned and privately owned forests. There are 17 forest holdings within the public enterprise "Serbia forest". By the end 2002 there were four forest holdings on the territory of Vojvodina under the management of the public enterprise "Vojvodina forest". An association of private owners of forest nurseries and forest nursery plants was founded. Nursery plant production has a capacity of becoming a profitable business in the field of forestry.

According to the ownership structure, privately owned forests are the most common category of forests covering 52.2% of the total forest area, followed by state – owned forests, covering 39.8% of the total forest area, while about 8% is defined by the category of other because the ownership is not clearly determined.

Table 4. Forest areas by type of ownership (2008)

No.	Type of ownership	Forest area	
		(ha)	(%)
1.	State forests	896.400	39,8
2.	Private forests	1.175.200	52,2
3.	Other owners	180.800	8,0
Σ	Total forest area	2.252.400	100

A part of state forests (10% of the total forest area) is entrusted to five national parks: Tara, Kopaonik, Đerdap, Fruška gora and Šar planina. Sustainable development principle is used in managing state and private forests, i.e. efforts are made to maximize revenue while protecting natural forest resources at the same time. The area of protected areas managed by public enterprises is over 410.000 ha, which is about 22% of the total forest area. The largest part of this area (about 75%) is used for commercial purposes.



Source: Institute for Nature Conservation of Serbia (2006), p. 160

Figure 1. Area of protected forest

Wood production in Serbia is expressed by wood cutting. "Wood cutting in 2006 in Serbia was 2.585 million m^3 in forests and an additional 25.000 m^3 outside forests (city parks and wayside trees), which gives a total wood cutting of 2.61 million m^3." [9] Regarding tree species felled in forests, the greatest share has been beech from pure standings, reaching 40% of the total volume of wood cutting in forests.

Table 5. Utilization of forest

		Wood cutting (1000 m^3)	Forest area (million ha)	Utilization of forests (m^3/ha)
total (1+2)		**2585**	**1.985**	**1.30**
pure stands (1) of		**1974**	**1.418**	**1.39**
broadleaved		**1886**	**1.236**	**1.53**
	beech	1009		
	oak	249		
	poplar	420		
	other	208		
conifers		**88**	**0.182**	**0.48**
	spruce	38		
	Black Pine	44		
	other	6		
mixed stands of (2)		**611**	**0.567**	
broadleaved		419	0.464	0.90
conifers		50	0.049	1.02
broadleaved and conifers		142	0.054	2.63

Source: www.compete.rs/ Feasibility study of wood waste in Serbia, (accessed: 13.03.2011.), P.14.

(*) The data on wood cutting are for 2006, but the data on forest areas are taken from the last forest inventory in 1979.

The largest share (about 50%) of the wood cutting from state forests is used as fuel. The other part is used as construction wood, for furniture, pulp and paper production. Wood cutting in private forests is three times less than in state forests. The main reason for this is the weak wood market.

Table 6. Production of wood assortments (1000 m^3) from state owned forests in Serbia

	2002	2003	2004	2005	2006
Sawlogs for cutting	312	358	368	373	397
Mine props	19	21	8	8	12
Wood pulp	108	88	98	12	117
Fuel wood	748	838	847	779	803
Other wood	393	371	401	357	415
Total	1580	1676	1722	1640	1744
Felling in state forests					1925
Felling in private forests					685

Source: www.compete.rs / Feasibility study of wood waste in Serbia, (accessed: 13.03.2011.), P.15.

Out of the total volume of felled trees in forests, two main products are technical round wood and stacked wood. There are wood residues, too, which remain in the forest. On average, about 90% is round and stacked wood, while about 10% is wood residue from cutting. These forest residues can be used as an energy source; some could be used for the panel production. With better forest infrastructure and with appropriate prices for forest residues, a much greater amount of forest residues could be utilized than it is the case today.

Table 7. The average share of different categories of wood in the total volume of wood

	State forests	Private forests	Average	Comments
Technical roundwood	24	8	16	Commercial
Stacked wood	34	50	42	Commercial
Bark from roundwood	4	4	4	Remains in forests
Forest residues with bark	9	9	9	Partially used
Thin branches with bark*	11	11	11	Partially used
Stumps with large roots	18	18	18	Remains in forests
Total	**100%**	**100%**	**100%**	

Source: Source: www.compete.rs / Feasibility study of wood waste in Serbia, (accessed: 13.03.2011.), P.15.
*Thin branches are typically branches with diameter less than 7 cm.

Taking into account the present volume of wood cutting in forests, these forest residues account for about 75.000 m^3 per year. There is an area of about 1.350.000 ha available for afforestation. Most of this afforestation area is in the private ownership.

Forest Directory gave private owners free seedlings for afforestation, but in spite of all these efforts there is a visible tendency of the forest area reduction of 0.4% per year. Therefore, it is necessary to take the following measures:

- To increase agricultural production;
- To employ more workers in forestry;
- To improve environment;
- To reduce negative effects of Aeolian and water erosion.

RESULTS

Future economic and spatial valorisation of forests in Serbia

Forests are considered to be one of the most complex ecosystems on Earth and they represent a natural resource of a big economic importance to mankind. Excessive exploitation has caused a dramatic reduction of the forest area and the environmental degradation. In order to achieve a sustainable forest management in the future, it is necessary to provide a permanent protection, maintenance and utilisation. Appropriate economic policy is an important factor in the forest management. Forest policy should be included in the EU rural development programmes as a part of economic policy. Big financial funds, which are available in these programmes, could support and improve the development of the forest sector in Serbia. The main objectives of forest policy are [12]:

- Forest preservation and improvement;
- Enlargement of the forest area;
- Valorisation of protective, social and cultural forest functions according to the National Strategy of Sustainable Development;
- Ensuring sustainable development of the forest sector in Serbia;
- Establishment of an effective and sustainable sector in lumber industry which will be more competitive in the foreign market;
- Better implementation of multidisciplinary research and technology achievements;
- Appropriate engagement of expert stuff in the forest sector;
- Raising people's awareness of the importance forests have concerning both general well – being and economy in Serbia.

Serbia has not had a precisely determined forest development strategy so far. It has been partly defined in the legislation and strategic documents. According to the European and world trends in forest policy, Forest Development Strategy of Serbia should establish a balance between the social interest and the forest capacities, creating favourable conditions for economic development and, at the same time, providing economic, social and cultural functions of forests.

The Strategy determines the basic principles of the forest sector [14]:

- Sustainability;
- Forest multi - functionality;
- Role of forestry in rural development;
- Relations between forestry and the public;
- Stakeholder participation in the national forest development strategy;
- Increase of forest area and productivity;
- Tasks deriving from international commitments and agreements;
- Forest degradation and environmental impact assessment;
- Conservation of forest vitality;
- Scientific research, education and training.

According to the Spatial plan of Serbia it is anticipated that the forest coverage should increase from 27.3% to 31.7% in 2010 and to 41.4% in 2050. We need forest investments for economic development. Attracting foreign investments is an important part in job creation policy, export increase, production and technology development.

The most valuable investments in forestry are [3]:

1) In stable rate production and expanded production

Afforestation for the purpose of later wood cutting and investments in basic means of production (motor saws and forest roads) are included here. Afforestation prevents wind and water erosive processes in most vulnerable areas, increases agricultural production and improves the environment.

2) In forest openness

Forest openness is the main requirement for better silviculture and timber utilisation. Forest roads are usually built in the places where they will lower the costs. The density of forest roads in Serbia is 9.2 m/ha. It is planned to achieve 12 m/ha density in plains and 15 m/ha density in forest areas.

3) In forest stuff, which is also one of the main indicators of a country development

Investments in human resources development will improve workers' performance, skills, self – realization and personal growth and thus increase their productivity. Consequently, it would be an incentive for the economy as a whole since Serbia is considered to be a developing country. Education does not only increase productivity but also stimulates self – development and social satisfaction [4]. Lack of qualified forest stuff, particularly forest technicians, is quite evident in privately owned forests. On the other hand, public enterprises have redundant workers engaged in the private forest sector in accordance with the Law on forests. Private forest owners can earn an additional income by selling wild fruits, medicinal herbs, etc.

Table 8. Employment by sectors (2007)

Administrative district City Municipality	Total	Agriculture, forestry and waterpower engineering	Fishing	Manufacturing	Construction	Wholesale and retail, repair	Transport, storage and communication	Education
BRANIČEVSKI	**25917**	**1155**	**9**	**4838**	**1224**	**3380**	**1133**	**2574**
Veliko Gradište	1754	205	0	476	98	211	78	259
Golubac	826	104	0	175	0	118	26	110
Žabari	569	36	0	111	18	67	23	131
Žagubica	1158	124	8	67	9	115	39	140
Kučevo	1715	134	0	457	36	177	87	267
Malo Crniće	496	37	0	8	2	125	14	156
Petrovac	2829	94	1	405	30	583	122	393
Požarevac	16573	422	1	3140	1033	1986	745	1120
Šumadijski	**55266**	**662**	**0**	**22215**	**1937**	**4988**	**3979**	**5270**
Aranđelovac	8579	58	0	4058	234	521	222	747
Batocina	1342	27	0	426	32	168	31	155
Knic	959	24	0	280	5	87	94	204
Kragujevac– city	39254	480	0	15666	1531	3683	2818	3599
Lapovo	1612	1	0	487	53	94	694	65
Raca	1202	25	0	553	39	74	31	181
Topola	2320	48	0	747	44	363	90	320
Pomoravski	**34535**	**992**	**9**	**12214**	**890**	**3901**	**1865**	**3495**
Despotovac	3229	134	0	390	41	196	198	304
Jagodina	13517	397	4	6002	431	1013	831	1185
Paracin	7998	81	0	3533	138	1258	397	832
Rekovac	1040	2	0	443	0	59	42	201
Svilajnac	2810	105	5	221	69	767	165	426
Cuprija	5942	273	0	1625	211	609	233	549

Table 8. shows the numbers of employees in companies, institutions and small enterprises (up to 50 employees) and their participation in various sectors (agriculture, forestry, fishing, construction, manufacturing, trade, transport and education).

4) Investments in equipment and premises which facilitate rational production

The following results in the forest mechanization have been achieved. Big machinery is available and many stages in forest exploitation have been mechanized. The long – term goal of forest management is to increase timber volume production at the lowest costs possible. The Serbian Forest Strategy reflects all above mentioned goals set by forest policy, as well as the need of attracting foreign capital, i.e. foreign investments in technology and human resources.

Numerous forest products are used for satisfying human needs. These include secondary forest products such as wild fruits, medicinal herbs, leaves, seeds, game, etc. Serbia has favourable conditions for plant development and therefore Serbian flora is very rich and diverse. Wild fruits include: wild raspberry, wild blackberry, hazelnut and strawberry. Raspberry fruits are very much sought after both on home and foreign market because of their biochemical properties, exceptional aroma and high quality. Blackberry is used in the production of syrups, juices, wine and brandy which makes this fruit commercially significant. Wild fruit processing represents a good basis for the production of alcoholic and non – alcoholic drinks in this country.

Mushrooms are rich in enzymes, A, B, C and D vitamins and carbohydrates. They can be used to regulate the high blood pressure and for rheumatism. We have the largest use of porcini and chanterelle. The most common medicinal herbs in the forest area are lemon balm, Klamath weed, valerian and chamomile. Many farmers collect herbs since some research results have shown that there is a demand for new products, such as syrups, juices and balm. Plant production and wood processing reduce imports and stimulate exports while strengthening competitiveness and position on the foreign market. Serbia would be highly rated on the foreign market offering a wide range of cosmetic products, alcoholic and non – alcoholic drinks and food products. Natural features of the Serbian forests are a great tourist potential for entertainment, rest and recreation in the countryside.

High incomes could be scored by appropriate investments in the development of mountain, spa and hunting tourism. By emphasizing winter sports and recreational functions of the mountains (Kopaonik, Zlatibor, Tara), we could have a positive impact on higher employment rate and tourism. Ecotourism contributes to conservation of forest plant communities and to high rate economic valorisation.

Besides other forest products, wood has been gaining in significance during the last years. Wood products such as, furniture, tables, chairs and plywood are exported in large quantities satisfying international standards in manufacturing. Wood products were mostly exported to Germany, Italy and France during 2009. High quality oak and beech saw logs for peeled veneer and poplar pulp wood are the only forms of exported industrial timber at present. Peeled veneer is exported from central Serbia to Italy, while poplar pulp wood is exported from Vojvodina to Bulgaria.

"In 2009 we exported 273 million USD worth of wood products, 23.5% less than in 2008, while we imported 300 million USD worth of goods, i.e. 31.5% less than in 2008" [10] In 2010 industrial production increased by 4.8% in relation to 2009 and manufacturing industrial sector recorded 5% higher production.

All forest products can have a great economic impact. In order to preserve forests from harmful effects and to obtain better yields in wood production and forest fruits it is necessary to provide rational and effective forest management.

DISCUSSION

Forests are an economic resource and important factor in the development of a country, a source of goods and services, as well as of income and overall wealth. Serbia has favourable natural potentials: agricultural land, forest and water resources, biotic and attractive tourist capacities. Complex valorisation of natural resources and potentials is only one form of economic and geographical regionalization which includes qualitative and quantitative analysis of each complex environmental area. According to the distribution and structure of natural resources and potentials, geographical area of Serbia can be divided into lowlands and mountain region.

The spatial distribution of forests in Serbia is divided as follows [2]:

1) No – forest spatial areas:
   - South Banat 0.5%;
   - West Bačka 0.5% of the forests;
   - North Banat 0.6% of the forest area.
2) Relatively small forest areas up to 20%:
   - Podunavski 6.0%;
   - Mačvanski 23%;
   - Sremski 12.4%
   - Šumadijski 22%, etc.
3) Areas rich in forests

   The most forested areas are:
   - Borski 43.3%;
   - Toplički 41.8%;
   - Kosovsko - mitrovački 40.4%;
   - Raški 43.3%;
   - Kosovski 41.1%, etc.

From this point of view we can look at the spatial forest distribution in local communities. Municipalities with the largest forest resources are:

- Priboj 64.3%;
- Majdanpek 59.4%;
- Kuršumlija 55.0%;
- Bajina Bašta 47.8%.

Spatial forest distribution can be analyzed by floristic composition. Broadleaved forests have 55% share, mixed stands 40% share and conifers 5% share. This shows that the state of forest resources in Serbia is quite unfavourable because conifers, the highest quality forests, have only 5% share in the forest distribution.

In order to show the spatial impact of forests on the distribution and valorisation of tourism, forest complexes must be precisely determined. They are classified into following groups:

1) Complex of alluvial hydrophilic forest types along the rivers includes:

   • swamp forests (willow and poplar)

   • forests which affect microclimate and protect farming areas from erosion.

These forests can have integrated multi – purpose tourist values because of the beautiful landscape motifs and hunting areas.

2) Complex of lowland and hilly forests (Hornbeam, Turkish oak, Manna Ash, English oak)

These forests are an additional motif for the development of rural tourism.

3) Complex of mesophilic forests at altitudes of 400-800 m (beech and oak).

These forests can develop farm tourism by using Mangalitsa breed. There is 40% less cholesterol in Mangalitsa flesh than in ordinary pigs.

4) Complex of beech - conifer forests at altitudes of 800-1000.

This complex includes the lowest zone of beech forests, with beech, fir and spruce in the middle and beech forests turn into real coniferous forests in the highest zone. They are a tourist attraction offering excellent tourist and recreational centres, spa resorts and weekend trips.

5) Complex of territorial forest (pine and relict Serbian Spruce forests).

They offer sports centres, hunting reserves (Zvijezda on Tara Mountain) and children's resorts.

6) Complex spruce forests (Pinus heldrejchii and Pinus peuce) at altitudes of 1200 to 2000 m.

They support sustainable tourism because their current use does not threaten the use in the future.

7) Complex of shrub forests at altitudes greater than 1800 m (Junipers, spruce and blueberry).

These forests are an integral part of the tourist product. Their secondary products are used for the production of juices and brandy called Klekovača.

CONCLUSIONS

World forest resources are the most important part of productive and protective biodiversity. Therefore, they are a very reliable basis for a successful, multipurpose economic exploitation. To achieve the highest and best utilization of forests, it is necessary to be aware of some of the most important facts:

- The more intensive development of human civilisation and society is, the more important the concept of economic valorisation becomes.
- Excessive exploitation of natural and forest resources is the biggest problem which puts the relation between environment and nature, on one hand, and society, on the other, out of balance.
- Modern logging is focused on wood utilization. It has the biggest application in wood industry and construction works.
- Expert knowledge of forest ecosystems is required in order to have an optimum utilization of forest production capacity and maximum satisfaction of human needs. Besides wood, there are other forest products such as wild fruits: wild cherry, acorns, wild raspberries, strawberries, edible mushrooms rich in carbohydrates, vitamins and minerals, medicinal and aromatic herbs, game, etc.
- Serbia has favourable natural resources, agricultural land, relative abundance of water and developed tourism.
- Serbia has a temperate continental climate, which contributes to timber volume increase and mushroom growth.

- Forest policy should be included in EU development programmes. Direct foreign investments play a great part in the overall economic development of this country, i.e. in new job creation policy and the development of production, technology and knowledge. That is why the forest strategy is important.
- The importance of the forest strategy is closely related to the rational utilisation of forest resources in the future and, therefore, to a better and more successful selling of forest products both on home and foreign market with the highest possible yields and at the lowest costs.

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POTENTIAL FOR RATIONALIZATION OF SILVICULTURAL TREATMENT BASED ON ESTABLISHED OPTIMAL NUMBER OF TREES

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ABSTRACT

This paper presents the possibilities of rationalization in one part of the silvicultural treatment on the basis of defined optimal number of trees, on the example of a stand which, by its size and structure, is one of the finest mature beech stands in the South Kučaj area. The previously established elements of the optimal model of the stand structure have been used for designing the model number of nuclei in young stands, which will at the end of the rotation period represent the required number of trees with optimal crown size. The paper outlines a number of advantages and the importance of such procedures which will greatly reduce the cost of hiring the organization's professional and material resources with the aim of effective implementing of an optimal procedure in managing natural stands.

Key words: beech, optimal state, optimal number of trees, rationalization of stands tending.

INTRODUCTION

It is known that silvicultural measures at an early development stage in all species can significantly accelerate the growth of treated individual trees, boost their competitive ability and resistance to the action of a number of adverse factors. Despite these findings, these measures are rarely implemented properly in our forest operations, or they are even left out altogether. The most common reason for this is the lack of financial resources, manpower, machinery, time, etc. The fact that the strtcture of our forests is su#h that a sigNificant part of the growing stock are youngEr stands to be intensively cultivated, and it sHows that it is precIsely in r│spect tO rationalization that some improvements are necessary to be made.. The rejuvenated woodland areas at the sitd3 of old forests are oFten characterized by a significant presence of coppicEd 4rees, trees /f less valuable species with rapid growth aNd a huge competitive ability (hornbeam, maple, lime tree etc.). The implementation of silvicultural measures in such areas, which among other things are rugged, exceeds the available technical and financial resources of the organizations managing the forests. One possible solution to these problems is to be based on research in mature stands in order to define the optimal number of trees at the end of the rotation, and to form "nuclei" of a certain diameter on rejuvenated areas. The number of nuclei should be equal to the projected optimal number of trees at the end of the rotation.

The aim of this paper is to show through a characteristic example the possibility and applicability of the established elements of modeled optimal conditions in order to define a sensible concept of tending young beech stands.

MATERIAL AND METHODS

In the growing stock of Serbia beech forest accounts for 40.5% of the total wood volume and 30.6% of the total volume increment (Banković et al. 2009). Wide horizontal and vertical distribution of beech on different parent rocks and evolutionary soil sequences has contributed to the presence of beech in the form of different plant communities in the surrounding area of most villages and towns in SerbiA.

StanD density has a very strong impact on the efficiency of beech forestS in meeting their various functions. It is, therefore, impoRtant to intensify the foresT management sysTem in order to approach the p/ssible level of potential economic, environmental, protective and other effacts on that site. This, primarily, me!ns maintenance of the standS in an optimum condition from the aspect of the number of trees and crown quality whiCh affects bioloGica, Stability !nD high dendromass increment. Generally, beech stands in Serbia are very far from their optimal state due to a number of adverse factors affecting them in the past (Vučković, Stajić 2005).

The research object are beech stands in the South Kučaj area which is located between 19˚19' and 19˚27' east longitude and 43˚58' to 44˚02' north latitude. The research was conducted in three sample plots in a montane beech forest (*Fagenion moesiacae montanum*). Two sample plots were formed on the medium deep, acid brown soil on phyllites. The investigated stand I was mature and about 130 years old and stand II was a pole-stage stand. Stand I had 226 stems per ha and stand II – 4,120 stems per ha.

RESULTS AND DISCUSSION

Through the procedure of defining the optimal structure, it is possible to avoid the consequences of growth process and development in trees beyond what is considered to correspond to the principles of optimality. Sometimes the stands represent, according to their visual impression and dimensions, the "typical" example of optimally structured stands which in reality, however, deviate significantly from the projected optimal model. This "unnoticeable" deviation from the required beech stand structure was established in the studies by Vučković and Stajić (2003) in a beech stand about 55 years old in the area of Petrova Gora. Namely, these authors determined that in a stand of very good appearance, with no significant presence of devitalized trees and a high amount of current volume increment (13m^3/ha), there were fairly clear signals of its adverse internal structure and devitalization, which could not be identified by sight or by stating the basic taxation elements within the regular forest inventory. In addition, Vučković et al. (2006) established significant deviations of the existing (current) and modeled (optimal) structure of a representative sessile oak stand, with considerable overgrowth and trees above average size and timber volume.

Bearing in mind the aforementioned, in our studies of mature beech stands in the South Kučaj area, which Vučković et al (2011) used as the basis for determining of the optimal structure model, we firstly established the exact coordinates of the trees in the area and made a map of all the trees (current structure) and the position of the optimal number of trees in the future (projected optimal pattern) - Figure 1. The optimal state of the investigated beech stand was determined by Vučković et al. (2011). Namely, based on the dependence of diameters at breast height of trees on the estimated crown diameter sizes of 184 beech trees (1472 crown radius), the authors first determined the crown size needed for achieving a certain diameter at breast height. Finally, these authors showed that with differently set production parameters, basal areas (≈ 40 m^2) of the investigated stands could be achieved with a much lower number of trees (≈100 trees per hectare instead of 240) and a significantly higher mean diameter (65 cm instead of 45 cm) i.e. a much better assortment structure would be achieved. The target diameter was defined as the diameter, for the achievement of which crowns have such a dimension which allows the best use of growing space, i.e. the most favorable ratio of the produced wood volume and the space taken up by a tree.

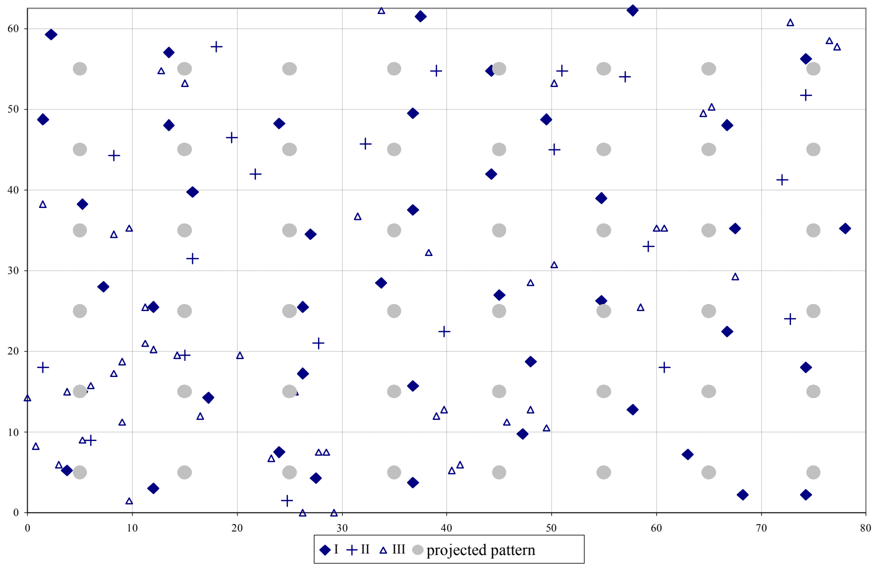

Figure 1. Real and projected spatial distribution of trees I biological position (I), II biological position (II) and III biological position (III) - SPP 1

On the attached layout of the real and modeled (acc. to instructions of Vučković et al. (2011)) distribution of trees (Figure 1.), it is possible to observe that in a mature stand it is hard to apply with delay any model of optimal stand condition, because the existing stand condition can no longer be influenced practically. Stand structure is such that it consists of trees of I biological position (I b.p.), unevenly distributed on the surface, with various crown sizes. A significant number of I b.p. trees for many years grow under competition of adjacent trees of the same social status, or during their ongoing growth there has been too much available growing space, which in terms of growth and production has resulted in the creation of too large and assimilation-wise inefficient trees.

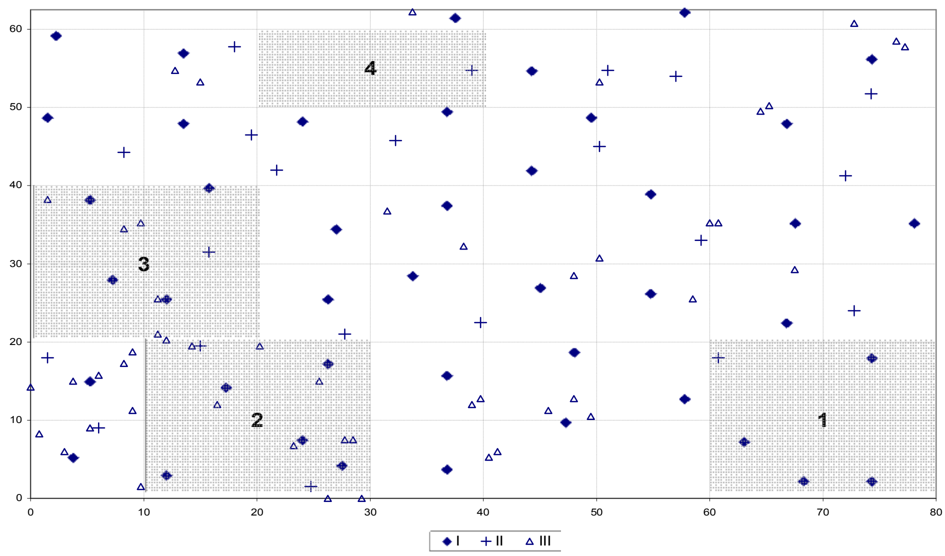

Figure 2. Spatial distribution of trees of first biological position (I), second biological position (II) and third biological position (III) - SPP 1

In general, I b. p. trees in mature stands should be the future trees which were selected at a young age and nurtured by the end of the rotation, in order to achieve optimal quality and quantity of production. On the example of SPP 1 stands (Figure 2.), we can see that the I b.p. trees are often found too close or too far from each other. This reduces the level and quality of stand production, whether it is a form of permanent conflict present in growth due to competition among the trees, or in terms of inefficient use of growing space due to excessive canopy or clearings. Situations like these in the stand SPP 1 are illustratively presented by shaded quadrants 1, 2, 3 and 4. The example of absence of I b.p. trees at the end of the rotation at distances up to 20 m is represented by the shaded quadrant No.4, while the existence of too many I b. p. trees in a small mutual distance is illustrated in shaded quadrants 1, 2 and 3. The graphical display of the position of I b.p. trees in the shaded quadrant 1 illustrates the presence of their excessive number in one part of the area, but also too much distance among them in another part of the same area. A good example of unfavorable structure in one part of the stand is the quadrant 3, from which it can be seen that two I b.p. trees in the lower quadrant are too close together. Since these trees have been under the influence of mutual competition and interference with each other's growth for many years, in this concrete example, forest operators' hands are partly "tied". This is to say, that if several years before one tree had been removed by silvicultural measures from the stand in order to increase the growing space and care of the other tree crown, in that very part of the stand, the distance between the remaining tree and its next neighboring trees of the same category would be too large (clearings – which, due to the very reduced height growth and growth of lateral branches, do not have the possibility of completely covering the newly created free space), which subsequently would lead to inefficient use of growing space and habitat potential. In the case of such a scenario that both of the trees remained, they would continually suppress each other's growth, until the end of the production period, also with an inefficient use of growing space and habitat potential.

Therefore, in view of the foregoing, the establishment of new stands and the care of young ones require the knowledge of the optimum condition to be achieved at the end of the rotation. Established regularities are used in habitats with similar characteristics, for the planning of density and planting pattern when creating new stands (in artificially established stands) or determination of the number of future trees in natural stands within the definition of the production target and measures for its achievement. Therefore, the obtained production parameters (N, G, V, target DBH) in maturing and mature stands should be used as a landmark for management of young stands. For this purpose, we have selected a young beech stand (pole-stage stand) in the same habitat, not far from the analyzed mature stand that had been the research object by Vučković et al. (2011). In this stand, we determined the exact coordinates of the trees in the area and made a map of the position of all the trees and the position of the required number of nuclei, according to the determined optimal tree number at the end of the rotation (Figure 3.).

In this specific example, the study stand in South Kučaj, i.e, in the habitats that it represents, it would mean the establishment of 100 such nuclei. In case a 1 m radius of the nucleus is selected, intensive silvicultural treatment is carried out on a surface of about 314 m^2, or only 3% of the total area, and in the case of a 2 m radius - on a surface of 1,256 m^2, or 13% of the total area. This approach (treatment) should provide the best trees of the selected species with successful growth and development. This is largely achievable, as it should not be too difficult to concentrate the necessary professional activities on about 3-6 individual trees per nucleus that may be found in it when the separation of nuclei, or the future trees, starts "on time". Within this number of individual trees, of course, the greatest attention should be focused on the tree with the best phenotypic characteristics, which is to be found in the center of the cell, due to the maintenance of a regular schedule of future trees, to the extent practicable. In this way, in addition to savings in time and financial resources, a desired - designed optimal stand structure will be enabled, as well as the presence of the optimal number of trees at the end of the rotation that have neither too small nor too big, but optimally developed crowns. For the remaining area, silvicultural treatment can be of much lower intensity (later start, lower frequency, decision-making at a lower level of expertise, etc.).

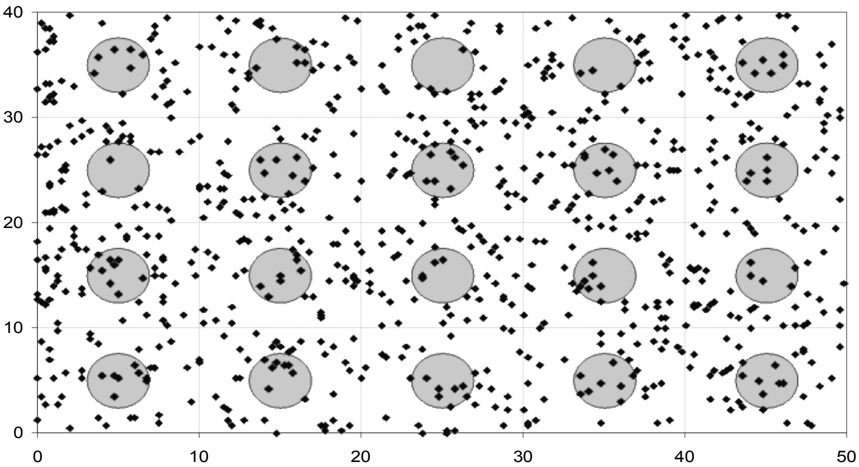

Figure 3. Example of the projected "nuclei" schedule (grey circles) for the intensive silvicultural treatment on the sample plot SPP 2, measuring 50 x 40 m.

Since the growth of trees and stands is conditioned by numerous factors, some of which are random in nature, in some cases it is impossible to completely "schematize" the distribution of trees and thus make a full use of the habitat production potential. Certain nuclei and, within them, the selected future trees may not always be in an ideal - optimal mutual distance, because it is possible that in the preferred distance defined in the nucleus it will not be possible to choose a tree of high enough a quality, which should see the end of the production period. However, the final effects of this treatment will contribute to a far greater and more efficient use of habitat potential, which is in any case much more than the current average utilization of the potential of our forest habitats of 50% or less (Tomanić 1993).

CONCLUSIONS

According to numerous studies, the condition of forests in our country is such that there is a significant discrepancy between the actual and potential level of productivity in qualitative and quantitative terms. It is known that if the stands are far from the optimal structure, the effect of forest management measures (silvicultural, protective, etc.). drastically decreases, and on the other side the damage caused by adverse exogenous factors are increased to such an extent that it may compromise the results of management, or even jeopardize the survival of stands. Consequently, in the process of achieving production and environmental functions of forests, modern forestry, burdened with cost-effectiveness of management, aims to increase the stability of production and manufacturing assortments of high quality at the lowest cost possible, so as to prevent management loss. Therefore, it is extremely important to optimize the condition of stands at all stages of their development. For this, preventive action is extremely important, based on clearly established criteria. An alternative is extensive management and dealing with adverse effects such as devitalization and tree desiccation, increment reduction, etc., which can not provide adequate results and justify invested assets.

The conducted research activities, according to the extent and degree of data processing, certainly are not sufficient to "cover" environmentally, developmentally and qualitatively different stands. However, they represent a suitable basis for further upgrading and completion. Research suggests the applicability of defining the optimal stand condition and the need for further work, which would comprise the stands of different ages and habitat conditions, in order to create a solid basis for the standardization of optimal stand structure model.

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EUROPEAN STANDARDS IN ASSESSMENT OF THE EFFECTS ON THE ENVIRONMENT

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ABSTRACT

EU policy on the environment is based on the precautionary principle in respect to environmental protection, principle that the damage should be rectified at source and that polluter should pay. By regulating the condition that developer cannot commence any construction or implementation of the project prior to obtaining the consent to the environmental impact assessment study, EIA Directive observes such principles. This paperwork shall underline the European standards in assessment of the effects on the environment and preparation of the environmental impact study in order to achieve accountability and consequently the bankability of the projects in concern.

Key words: transposition – environmental impact assessment study – bankability.

INTRODUCTION

Council Directive on the assessment of the effects of certain public and private projects on the environment (85/337/EEC)[1] within the EU acquis belongs to the group of regulations that have as subject matter procedural aspects of the questions of importance for the environmental protection.

In order to emphasize the significance of correct and full transposition of this EIA Directive into national law it is worthy of noting the Providence Resources project for exploring in the Irish Sea (project value: 1 billion EUR). Notwithstanding the fact that the project complied with all conditions set forth in the national law of Ireland, the company was obliged to return the foreshore license obtained in 2011, because of the failure of Ireland to transpose a single sentence of the directive properly in national law in 1999 [2]. Direct implication is that those who suffer from bad transposition have a right to sue the state for their consequential losses.

EIA DIRECTIVE AND LAW OF THE REPUBLIC OF SERBIA

EIA Directive has procedural character and imposes the legal framework for member states governing the mandatory procedure for environmental impact assessment in respect to the certain public and private projects that have or it is likely to have significant effects on the environment. EIA Directive is transposed into national law of the Republic of Serbia through the Law on Assessment of the Effects on Environment *(Law)* [3].

The bylaws adopted under the Law are:

- Decree on Establishment of the List of Projects for which the Impact Assessment is mandatory and List of Projects for which the Impact Assessment could be requested (Decree) [4]
- Rules on Content of the Request for Necessity of Impact Assessment and Content of the Request for Regulation of the Scope and Content of the Environmental Impact Assessment Study [5]
- Rules on Content of the Environmental Impact Assessment Study (*Rules*) [6].

PROJECTS THAT HAVE SIGNIFICANT EFFECTS ON ENVIRONMENT

EIA Directive defines the project [7] as the execution of construction works or other installations or schemes, other interventions in the natural surroundings and landscape including those involving the extraction of mineral resources [8].

The Law introduced wider definition of the project where the project is execution of the construction works, installment of installations, plants and equipment, reconstruction thereof, removal and/or change in technology, working process technology, raw materials, consumables, energy source and waste, other interventions in nature and natural surroundings including the works involving the extraction of mineral resources.

The Law sets out indirectly additional projects by defining the subject matter of the impact assessment. According to the Law impact assessment is mandatory for the projects within the sector of industry, mining, energy, traffic, tourism, agriculture, forestry, water management, waste management and communal activities as well as projects planned on protected natural good and protected environment of the immovable cultural heritage. The projects defined in such manner the Law divides into two categories: 1. the projects that are planned and developed, change of technology, reconstruction, expansion of capacities, suspension of works and deposition of projects that likely can have significant effect on the environment, and 2. the projects already developed without preparation of the environment impact study and without construction permit or being in use without license for use (assessment of the impact of present situation - *procena uticaja zatečenog stanja*).

The intention of the lawmaker was to implement the obligation of impact assessment not only in respect to the planned and projects under construction, but retroactively in respect to the projects which are already constructed and developed. In this sense, the lawmaker is regulating the factual situation with aim to protect the environment from significant effects in future which the existing project may have. Lack of the deadline within which the developer is obliged to conduct assessment of the impact of present situation enables that this situation may exist in reality for indefinite period of time. In practice, the developer has the obligation only in case when he intends to legalize its project, i.e. to prevent the demolition of its object. Furthermore, the question is who will be liable for costs of impact assessment in case of demolition, since it is being expected that even in case of demolition amendments to EIA Directive shall predict mandatory impact assessment. It remains unclear whether the lawmaker shall regulated that the state shall bear costs for impact assessment in case of demolition of objects which are many in Serbia or the lawmaker shall impose these costs to the owners of the illegal objects which is justified by socially undesirable.

By resolving in this manner the existing problem, the lawmaker failed to preserve the fundamental precautionary principle in protection of the environment. In this cases it is necessary to assess negative significant effects such project had in past, how long these effects lasted and who will be liable for offsetting of such effects – the owner of the illegal object that had negative significant effects on the environment or the state because it allowed that the existing illegal object damage the environment.

EIA Directive regulates projects for which the impact assessment is required and lists them in Annex I: crude-oil refineries and installations for the gasification and liquefaction of 500t or more of coal of bituminous shale per day, thermal power stations and other combustion installations with a heat output of 300 MW or more, construction of lines for long-distance railway traffic and airports or a basic runway of 2100 m or more, construction of motorways and express roads, waste disposal installations for the incineration, chemical treatments, groundwater abstraction or artificial groundwater recharge schemes where the annual volume of water abstracted or recharged is equivalent to or exceeds 10 million cubic metres, waste water treatment plants with a capacity exceeding 150 000 population, pipelines with diameter of more than 800 mm and a length of more than 40 km for the transport of gas, oil, chemicals, installations for the intensive rearing of poultry or pigs with certain capacity, quarries and open-cast mines where the surface of the site exceeds 25 hectars, installations for the capture of CO2 streams for the purposes of geological storage, etc.

List I in the Decree does not contain all projects set out in the Annex I and deviates because it was adopted before the amendments adopted in the Directive 2009/31/EC.

EIA Directive provides for that in addition to the projects listed in Annex I, for all other projects listed in Annex II member states shall make determination through a case-by-case examination or through the thresholds or criteria set by the member state or it will apply both procedures (combined method). Without prejudice to the applicable method, member state shall take into account the relevant criteria set out in Annex III. Criteria set out in Annex III refer to characteristics of projects, location, characteristics of the potential impact. When considering the characteristics of the project, one have to take into account size of the project, interaction with the other projects, use of natural resources, production of waste, pollution and nuisances, risk of accidence having regard in particular to substances or technologies used.

In respect to the location of the project, one must consider the environmental sensitivity of geographical areas likely to be affected by projects [9], having regard in particular the existing use of land, the relative abundance, quality and regenerative capacity of the natural resources and the absorption capacity paying particular attention to areas classified or protected under national law of other member state, or special protection areas designated by member states pursuant to the Directive 2009/147/EC on the conservation of wild birds [10] and Council Directive 92/43/EEC [11] on the conservation of natural habitats and wild flora and fauna.

By setting up these criteria in Annex III, it is clear that the assessment of effects has to be procured with cumulative analysis of all other directives of relevance in support to the EIA Directive when it refers to certain locations. The cumulative approach became generally accepted standard in EU when doing impact assessment.

As another prescribed criteria, characteristics of the potential impact must be considered having regard in particular to the extent of the impact (geographical area and size of the affected population), the transfrontier nature of the impact, the magnitude and complexity of the impact, the probability of the impact, the duration, frequency and reversibility of the impact.

List II incorporated in the Decree lists the projects *numerous clauses* by taking into the account the criteria from Annex III in respect to the characteristics of the project – size of the project in terms of installed capacity, surface of the land in use and area where the project is implemented (production of the energy from hydro potential exceeding 2 MW, windmills installed capacity over 10MW, pipelines for transport of gas of length over 10km and diameter over 150mm, etc).

In conclusion, it can be said that only through detailed analysis of relevant national laws which transposed Directive 2009/147/EC and Directive 92/43/EEC one can evaluate if the List II is harmonized in whole with criteria set out in EIA Directive, i.e. what amendments to the Decree shall be necessary in order transposition to be complete, and especially where in certain projects one have to pay attention to the location f the project and potential impacts (environmental and social), and not only in regard to the characteristics of the project.

EIA Directive provides for that in respect to exemptions each member state may decide by method case-by-case, if provided by the national law not to apply EIA Directive on project with purpose of national defence [12], if it deems that such application could have adverse effect to such purpose.

The Law goes beyond when setting general exemption of application of the impact assessment on projects with purpose of national defense. It is clear that our Law did not transpose this provision correctly, because it sets out that projects concerning defense purpose are absolutely exempted. In this manner lawmaker disregarded the limit to the disposition which was only for member state to foresee exemption on a case-by-case base and in presence of the negative effects for purpose of national defense.

Hence, it is recommended to harmonize the Law with EIA Directive correctly and to provide for procedure for exemption when purpose of national defense is in question (or state of emergency). In this way state may avoid situation that in the course of the development, the project is suspended since the state failed to transpose this sentence correctly.

EIA Directive sets out additional exemption when details of the project are adopted in the special national legislation, and under the condition that all goals of EIA Directive are respected, including access to information.

EIA Directive leaves the possibility to member state to exempt from impact assessment specific project in whole in exceptional cases.

ENVIRONMENTAL IMPACT ASSESSMENT STUDY

The Law defines environmental impact assessment study (*Study*) as document which analyses and evaluates quality of the environmental factors and its sensitivity in the specific area, mutual influence of existing and planned activities, foreseen direct and indirect effects of the project on the environmental factors as well as measures to avoid, reduce and offset adverse effects on the environment and people's health.

It is envisioned in the Rules that the Study has to provide description of the environmental factors for which there is possibility to be exposed significantly to the risk due to development of the project in concern and encompasses especially impact on the population, fauna and flora, soil, water and air, climate factors, construction, immovable cultural heritage, archeological sites and ambient, landscape and mutual relation between noted factors.

Study according to the rules must address description of the preparatory works, description of the object, planned production process or activities, its technological and other characteristics, survey of kind and volume of required energy and energy sources, water, raw materials, special construction material and many other elements. The developer is obliged to demonstrate main alternatives which were considered with reasoning for decision made for specific solution and its impact on the environment, air pollution, waste management, access management, liability and procedure for environment management, training, monitoring, and plans for extraordinary situation, remediation of the location after completion of the project and further use of the location.

Varity of elements prescribed by the Rules has result in creation of specific standards for Study required in Serbia in respect to studies in other member states. Moreover, such discretion leads to the situation that Serbia and each member state has different mandatory elements in study acceptable by its national law. Thus, obvious conclusion is that these elements have to be standardized by someone who is interested in that.

EUROPEAN STANDARDS IN PREPARATION OF STUDY

Recent practice showed that Studies which include all elements and standards in accordance with the Serbian law are not acceptable to certain international financial institutions as bankable within the process of appraisal and granting the loans for project financing and within the insurance procedure.

On the other hand, standards which are generally accepted are IFC Performance Standards and Equator Principles. International financial institutions such as IFC, EBRD, Equator Bank and other international banks granting the loans for project finance, as well as insurance companies such as OPIC and MIGA shall not accept as bankable study which is prepare in accordance with the national law of Serbia if such study does not comply with these standards [13]. This approach is also adopted by the other banks listed at the web-page www.equator-principles.com.

Good example for IFC Performance Standards is Standard no 5 that requires preparation of the resettlement action plan [14]. If the study does not include resettlement action plan prepared pursuant to the IFC Performance Standard no 5 and does not include definition and resolution of the proprietary issues on the land, practice showed that such failure has as consequence financial delays and damages.

Further, it should be noted that the strategy for remedying the adverse effects, i.e. neutralization of the effects to the biodiversity should be prepared in line with the IFC Performance Standard no 6 which enables adequate resolution of the potential adverse effects.

The developer when preparing the bankable environmental impact assessment study in Serbia has to take into account these standards if he intends to apply for the loan from the respective international financial institution or bank. Therefore, it is highly likely that in situation when the developer prepared study and obtained relevant consent from competent state bodies in Serbia, the project shall remain undeveloped in presence of lack of money and insurance if these imposed standards haven't been satisfied.

BREACH OF EIA DIRECTIVE IN PRACTICE

In practice of member states one detected a problem mainly with the projects of construction of infrastructure, railways and motorway. In these cases it is rule that certain sections have been partially constructed and therefore impact assessment is performed only partially just for the respective section of the project under construction. This approach is contrary to the Article 2(1) EIA Directive because it foresees conduction of the impact assessment procedure in respect to the project as whole and not to phases of the project, which are of smaller significance (case of construction of the highway in Austria A5 which was divided into 6 plots, "salami slicing").

It is especially important to take into observance main alternatives when constructing the highways when alternative solutions are railway or water way. Assessment of effects has to address in this case alternative which represent the less negative affects having in mind other directives, in particular Bird Directive and Habitats Directive. In case of such failure, the project can be developed with the breach of these directives and face highly likely suspension.

CONCLUSION

One my conclude that major problem lays in failure of the law maker to incorporate correctly all set up criteria in Annex III of EIA Directive when determining the criteria for projects that require impact assessment. In case C – 329/96, Commission against Ireland, Commission founded that the limit to discretion of the state is exceeded when it failed to take into consideration other criteria and included only size of the project as criteria. The exactly same situation exists in our Law and Decree and therefore it should be carefully considered in process of harmonization. In practice this should be taken into account when developing the project where it is highly likely that such project requires preparation of the environmental impact assessment study although the law does not.

The other conclusion is that some standards adopted by financial institutions and banks have to be respected in the course of preparation of the environmental impact assessment study.

Finally, it should be emphasized that the developers should take best efforts to comply with all criteria and standards imposed by not only EIA Directive and national law, but also the other relevant directive and to learn from experience of other member states when preparing environmental impact assessment study and developing the project.

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6. "Official Gazette of RS", no. 69/2005.
7. EIA Directive, Art. 1. par. 2. point (a).
8. In line with the practice and Decision of the Court in case C-50/90 definition of the project shall foreseen the demolition works in new EIA Directive
9. EU is looking for the manner to ensure the biodiversity through conservation of the natural habitats and wild flora and fauna on the territory of the member states. For that purpose it is created ecological network of special protected areas under the name „NATURA 2000".
10. Directive 2009/147/EC of the European Parlament and of the Council of 30 November 2009 on the conservation of wild birds, Birds Directive.
11. Council Directive 92/43/EEC of 21 May 1992 on the conservation of natural habitants and of wild fauna and flora, Habitants Directive.
12. Proposed amendment to EIA Directive foresee as an exemption project that serve to the civil state of emergency
13. www.prizmasolutions.com
14. Study in accordance with the Serbian law does not have to include this resettlement action plan in order to obtain consent

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ECOLOGICAL ECONOMY IN TERMS OF PARADIGM OF SUSTAINABLE DEVELOPMENT

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ABSTRACT

In evolution of "ecological awakening" of humanity, which occurred in the middle of 20th century, with the transition from industrial civilization to informational society, the most significant role was played by ecology and economy. These two sciences are connected because the most significant issues in ecology are caused by economic activities, thus the connection between ecology and economy. This connection is primarily seen in obstruction of ecological balance due to wish to maximize economic results, with many not only economic but social harmful consequences as well. "Sustainable development" – the paradigm of the 21st century, presents evolutionary process of introducing wellbeing that effectuates in optimal satisfaction of all socioeconomic needs of the population, the environment preservation as a framework of life, and doesn't question optimal satisfaction of the interests of future generation.

Key words: ecological economy, sustainable development, externalities, ecological-economic instruments.

INTRODUCTION

The modern ecological rationality has strongly shaken the foundation of classical and traditional economic practice, science, technologies and human knowledge. The environment, although generally accepted category, doesn't give enough answers to all human questions on Earth, in accordance with fundamental principles of naturally-biologically determined survival and development. The issues of the current models of economic development, the expansion of population, insufficient and unrenewable natural resources, health and life quality, surpassed the current comprehension of ecology as individual issue and primarily biological field that deals with survival of certain living species due to environmental changes.

The necessity of interconnection of economic and sociocultural development with the state of the environment, necessary natural balances, processes and global living conditions, has today become a part of economic-political, normatively-institutional and cultural reality of the modern world.

Ecological services do not reflect the social opportunistic cost of their use. These goods have double value: individual, expressed through value of goods and services, and socialthat is the function of this type of capital in sustaining life. With making decisions on use, the second value is not considered to be a reference point, i.e. as opportunistic cost for two reasons: first, because that value cannot be perceived and second, because the market does not include many effects of environmental use as a general good[1]. Inability of the market to include those effects implies that they are not included in transactions between users. The main problem is in identification and evaluation of these external costs.

ECONOMY AND ECOLOGY

The most significant issues in ecological environment start by economic activities and their connection is expressed through obstruction of ecological balance due to a desire to maximize economic results, with many not only economic but socially harmful consequences as well. Those consequences are the subject of the research of social ecology that examines unique relationships between the man and his environment, exploring the influence of the environment, as the collection of natural and social factors for the man, and the influence of the man onhis environment, as well as the influence of the environment on the man and the forms of his social life, all from the perspective of environment preservation, as his"framework of life" and forms of social life in which he lives.

Sustainable development is social ideal that should established unity in the improvement of the man's economic and social conditions of life without violation of natural foundation of life. There are not simple solutions for achieving sustainability [2]. At the same time, it should be stressed that the sustainability is binding in two ways (towards the man and nature) and it cannot be treated differently from the unique thought set of economy and ecology. The paradigm of sustainability is the reality of this thought construction and set.

The balanced development and use of existing natural resources primarily refers to its most significant elements that were degraded the most, i.e. water, air and soil. The balanced development has to occur in the limits that satisfy the needs of the current generations, but in a way that does not jeopardize the possibilities of satisfying the needs of the future generations. In the same way, there has to be a balance between the postulates of economic, social and ecological policies of the country [3].

ACHIEVING DEVELOPMENT WITHOUT LIMITATIONS

Radical changes of the understanding of development include abandoning the concept of achieving development "without limitations". Namely, in the future economic activities the development has to occur within people's needs in a particular space as well as within the abilities of the area where economic activities are occurring. So it is necessary for manufacturers to realize that they cannot manufacture without limitations and without taking care about the needs of people as well as the "abilities of nature to sustain that production", and especially in those segments that have to be renewed. At the same time, it is necessary to reduce the existing egoism of the world's powerful people, including political forces, especially because of convenience and conformism of their manufacturing structure that is the key obstacle in strengthening of sustainable development. Also, the growth of sustainable development is obstructed by developed countries that are not ready to change their development strategy, i.e. to give up a certain percentage of the profit as well as undeveloped countries that, because of their economic difficulties, give sustainable development the secondary importance. "Sustainable development" is achieved in different conditions, and by that with unequal results. In the same way, there is technological inequality in production processes. Therefore, there is a necessity for harmonization, especially in cases when there is depletion of resources as well as danger from destruction of existing natural goods. The special attention has to be directed towards sustaining of resources (water, atmosphere, plants and animals).

The need for the new conceptualization today is best seen in increasing calls and demands of rural development that occurs in significantly changed circumstances and the breakup of alliance between agriculture and rural economy development. The new paradigm of rural development is also a new challenge and the new need of the time that has to be focused on theories and investments, on valorization and exploitation of unused local resources. Globalization and processes that it brings, even though often with negative effects and consequences in many sectors of social reality, in rural areas present potentials that shouldn't be disregarded (improvement of communications, reduction of transport costs). Therefore, not only political financial redistribution and agriculture. The general goals on correspondence and equalization of life conditions of rural and urban areas are not enough anymore because it is not enough, for example, for households to be competitive but there is also a necessity for competitiveness of rural areas as a natural ambient in which households can show its willingness for change, diversity in orientation towards the "new", economic flexibility for introduction of new knowledge, application of good examples from practice etc. The base for application of the new paradigm of rural development is consisted from the new actors for its application. Those are not only national governments and farmers, but all levels of governments, international, regional and local too, and also local actors: public, private and NGO's.

The views on socioeconomic development, especially from the end of the last century, have significantly changed. The integralisticapproach prevails, which consists of all good achievements from the past, but also invites to overcome all kinds of disparity, especially regional and the differences between urban and rural development. The condition for that is seen in coordination of the development of agriculture and other activities and services in rural areas.

Integrated rural development and its promotion are processes that last and include outside intervention and local activities for securing visible prosperity of local citizens, for preservation and improvement of capacities and potentials of rural resources, reduce comparative flaws in comparison with competition, evaluate and valorize the values of natural capital and other resources of the rural areas. This kind of approach in understanding of the concept of integrated rural development practically leads towards the new paradigm of rural development.

For a long time, the silent attitude on incompatibility or even on the conflict of the principles of economy and endangerment phenomenon and care about the environment was prevailing. In the 1920's an American economist Pigou in "The Economics of Welfare" emphasized the economic importance of the pollution consequences, defining it as the difference between private gross product and social net product. Namely, if the entrepreneur, with their economic activities, achieves the price of a product or a service in its total market value, it does not mean there was the same amount of social net value produced. Social net product, as a clean effect of that economic activity is less than the private (manufacturing) gross product by a damage that happened as a consequence of pollution that occurred in production. Even though there was no answer for the question who should suffer the consequences, the significant difference was observed between treating ecological consequences from the manufacturer and the consumer of polluting goods, services and processes on one side and the society on the other.

EXTERNALITIES COSTS

The central question of external economy is reduced down to the question: how to evaluate natural resources and in which way to pay the external costs [4] for protection, preservation and renewing of clean and natural environment? The marginalized theory tried to go deeper into the problem with the analysis of marginal, internal, external and total costs of production as well as marginal benefits. Considering that internal costs have to have their coverage in the market price of the product, and external-ecological costs that do not, there is a contradiction between the private interest that strives towards the bigger production and the lowest costs, and social interest for the smallest production and the smallest external costs.

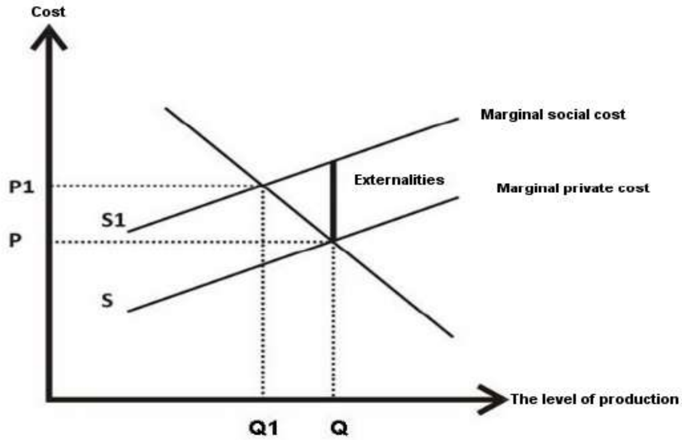

Chart 1. The difference between the private and social costs [5]

One of the ways of internalization of externalities is introduction of taxes per unit of production that would be equal to the costs of pollution. In a specific case, gas emission should be limited to the level where the marginal benefits for social community are less from the marginal costs of taking measures for emission reduction.

Theoretically speaking, if the starting point is the assumption that on the market there is a perfect competition for the products of company-polluters and the absence of any state intervention, market demand reflects marginal social benefit. On the other hand, market supply without state regulation keeps only marginal private costs (Chart 1).

If the production of a product causes damage to other subjects and doesn't give a possibility of market compensation, the marginal social damage of production is higher than marginal private cost of production.

According to Pigou's economy of welfare, the only way to achieve the optimum is to introduce tax or fees for polluters equal to the difference in value of social and private costs. Internalization of externalities [6], as non-market phenomenon is conducted by paying certain price for caused damage.

Therefore, the price of produced good is equal to marginal social damage of that good, which is equal to marginal private costs and tax [7]. This solution is known under the name *the tax on emissions*(Pigou's tax). The ultimately simplified theoretic approach to ecological taxing is shown in the Chart 2.

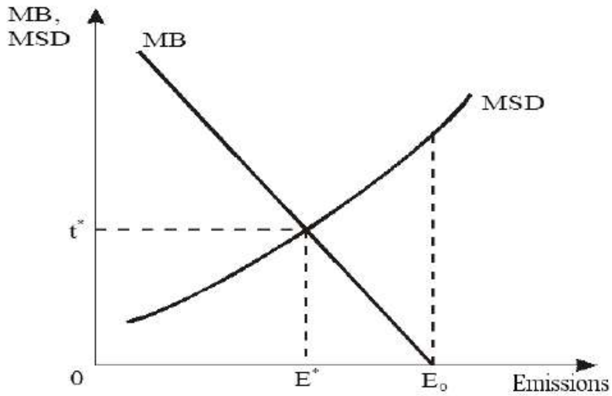

Chart 2. Corrective ecological taxing

The growing function of marginal social damage (MSD), measures the costs of environment caused by polluting emissions from different sources of violation of ecological balance. The increase in emissions increases marginal social damages, with the assumption that the damages increase with the increase of the levels of emissions. The decreasing function of marginal social benefits (MB) measures the value of ecological benefit without expensive controls or other activities for decrease in ecological damages. The total emissions, in the conditions of absence of regulation are marked with E_0. We can observe that the costs of supervision are very high when the allowed emissions are equal to zero, while with the increase of the level of emissions marginal costs of supervision decrease.

The optimal level of emission is marked with E^* , in which the marginal social benefits (MB) are equal to marginal social damages (MSD), which is achieved by corrective taxing, i.e. application of the tax t^*. From the chart, it is obvious that the height of marginal social damages (MSD) without supervision (shown in dashed lineE_0 - MSD) significantly surpasses the height of supervision costs,0 - t*, with which the optimal level of emissions is achieved (shown in dashed line, E^* - where the functions MB and MSD intersect). Therefore the level of emissions higher than E^*, would cause more damage than saving on the costs of supervision, while the level of emissions lover than E^*would avoid damage whose value could be less than marginal costs for supervision.

This traditional approach of managing "sustainable development" requires state regulation of optimal level of emissions, since there is no regular market interaction of supply and demand between those that secure (offer) emission reduction and those that demand clean environment. If the state can mediate (intervene) and determine "corrective cost" for emission, market interactions should result in optimal level of emissions. This is, of course, very simplified explanation, which is very complex in practical application. In all of this, the principle of polluter pays has to be applied, whereby the ecological taxes [8], are in fact bills for ecological damages.

CONCLUSION

In search of economic balance, the production of goods and services causes very serious imbalances in the environment. Therefore, the costs of pollution are unavoidable structural variables which are influenced by the methods of regulation of environmental management. With traditional order-giving and supervising methods of regulation, there is an increase in economic instruments too. They are based on already familiar and tested regulatory instruments from the field of economy with regulatory refinement suitable for agents in production and consumption of goods and services.

Economic activities are deeply integrated in the environmental issue. The management is directed towards achieving a balance between the environment, economy and other social goals. The essential question of the environmental issue is desirable behavior of manufacturer and consumer in the production and consumption of goods.

Economic theory had to accept ecologic argument and natural factors of development and survival as factors of special economic importance. On the other hand the problems of endangering nature and destruction of the environment received specific economic contents and importance of specific external costs that have to be settled for stable and sustainable economic development.

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ASPECTS OF THE RISK OF EXPLOSION IN BIOFUEL PRODUCTION

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ABSTRACT

Many types of the dusts generated, processed, handled and stored within the industrial processes are combustible dusts. When these are ignited, they may burn rapidly and with an explosion force that may be considerable. Often, for this reason, precautions should be adopted to ensure all equipment used in such placesis adequately protected, so as to diminish the explosive atmosphere ignition likelihood.

This paper work focuses on the health and safety issues of the supply chain of solid biofuels with the objective to highlight commonly used mitigation methodologies to promote a better working environment when dealing with solid biofuels.

Key words:explosive atmosphere, explosion protection, combustible dust,explosion risk, safety.

INTRODUCTION

The rapid increase in production and use of various types of biomass as energy carrier also leads to an increase in handling and storage activities throughout the supply chain. Biomass is a broad description of many materials with different chemical composition, moisture content and physical characteristics, each requiring special attention in order to comply with safety and health regulations.

Some types of biomass used today such as wood pellets are commercialized as biofuel commodities traded around the globe, while others are under-going intense research to explore the potential for commercial use.The properties of a biomass material and the intended use determine how the material should be safely transported and stored.

Dust clouds are a major cause of damage in the bioenergy sector. The combination of relatively small particle sizes and low minimum ignition energy results in high ignition sensitivity. Significant amounts of factory dust may stay be suspended in the air, so that the minimum explosive concentration is easily reached under practical conditions if cleaning and ventilation are not done sufficiently. It is therefore important to minimize the risk of dust explosions, by minimizing the risk of sparks (e.g. due to electrostatic discharge through proper grounding) and good dust housekeeping through dust prevention and dust collection.

DUST EXPLOSIONS

In the bioenergy sector, dust explosions are a major cause of damages and injuries, next to physical injuries in the forest and agriculture. While major explosions that involve injuries or major material damages to facilities are reported, it is likely that small incidents are not reflected in official statistics simply because they are dealt with quickly by the pellet producers or terminal operators.

Part of the problem is that the explosion properties of dust are very complex and characterized by several parameters, such as:

- Chemical composition and freshness (reactivity) of the dust material;
- Particle size of the dust;
- Whether the particles are suspended in the air as a cloud or lodged as a layer;
- Volumetric concentration of dust particles in a cloud and thickness of a dust layer;
- Access to air (oxygen) and turbidity of the air;
- Energy in the ignition source, temperature of the ambient air and temperature of the dust.

In order for a dust cloud explosion to take place there are five factors that need to be present. These are illustrated in figure 1, which shows the "explosion pentagon".

Figure 1. The "explosion pentagon"

A dust explosion is in most cases not a single event. The most common scenario is initial ignition of a dust cloud or a dust layer due to overheating, together with a mechanical spark caused by a stone or piece of tramp metal entrained in the material flow, a spark from hot welding work, arc from malfunctioning electrical equipment or electrostatic discharge. The initial event may start as a very small explosive fire, which in turn generates a pressure wave that shakes lose dust lodged on the floor, beams, ledges, equipment etc.

The liberated dust typically has a high concentration and access to air (oxygen) and ignites easily, becoming a fire ball that propagates close to the speed of sound (343 m/s at room temperature) as long as the dust concentration exceeds the required minimum concentration and there is oxygen present.

The exothermic chemistry within this propagating fire ball is called deflagration and in essence is an explosive fast moving fire, often referred to as the secondary explosion. In many cases there is a noticeable lag time between the primary explosion and the secondary explosion. Typically, this secondary explosion is more violent than the primary explosion for several reasons. First of all it has a lot more fuel than the initial ignition; secondly it is moving very fast; and thirdly it exposes everything in its path to burning particles that not only will tear structures apart, but will also deposit burning particles on surfaces for several seconds or even minutes until the fuel has been exhausted.

EXPLOSION RISK IDENTIFYING AND ASSESSING

In conformity with the requirements in the 1999/92/CE European Directive, transposed in Romanian legislation through the *Government Decision No. 1058 Of August 9th 2006, Regarding The Minimum Requirements For Improvement Of Safety And Health Protection Of The Workers Which Might Be Exposed To A Risk Due To Explosive Atmospheres*, the employer responsible for the workplace, according to the legislation, shall coordinate application of all measures regarding workers safety and health and he shall declare, in the document regarding protection against explosions, the coordination purpose, as well as the adopted implementation measures and procedures.

When setting out the appropriate technical and organizing measures for ensuring workers safety and health, several fundamental principles shall be taken into consideration: explosive atmosphere formation prevention, avoidance of explosive atmospheres ignition and limitation of explosions harmful effects. In order to fulfill the obligation stipulated in the 1999/92/CE Directive, the employer must ensure drawing up and updating of a certain document, named *Explosion Protection Document.*

According to the Guide to Good Practice for Implementing Directive 1999/92/EC, the explosion protection document contains description of the workplace and work environments with explosion hazards, together with description of the process stages and/or activities, description of the employed substances / safety parameters, risk analysis results, explosion precautions adopted and explosion protection measures implementation.

In regards of explosion risk assessment, this stage is initially focused on hazardous explosive environment formation and further on ignition sources presence and activation.

In the assessment processes, examining the consequences is of a lower importance since explosions are expected to always cause considerable damages, from important material losses to human injuries that may lead to death. Related to explosion protection, risk quantitative approaches are secondary compared to prevention of dangerous explosive environment formation.

Each work and production process, as well as each operating condition of an installation, and each alteration of these conditions shall be subject to assessment.

During new or existing installations assessment the following shall be particularly taken into account: the normal operating conditions, including maintenance works, starting and shutting off, accidents in operation and foreseeable faults, misuses reasonably foreseen.

EXAMPLE OF THE EXPLOSION RISK ESTIMATION AND ASSESSMENT METHOD [2]

The risk in terms of safety against explosions it's considered to consist in two elements: severity of possible negative events and likelihood of these eventsoccurring.

Usually the risks are expressed in one of the following three ways:

1. Quantitatively, as for example expressed as: high, medium, low, tolerable, intolerable, acceptable
2. Quantitatively, by calculating the frequency or likelihood that a certain event would occur
3. Semi-quantitatively, if the risk components as: consequence, exposure and probability are given numerical values, that further are combined in a certain way to obtain a pseudo-quantitative value of the risk, which allows risks to be classified in relation to oneanother. In many situations is not possible to accurately have determined all the factors influencing the risk, especially the ones contributing to the likelihood that a certain event would happen. Thus, the risk is often expressed in a qualitative rather than quantitative manner.

Severity can be expressed as a predefined level, one or more levels resulting from each hazardous event. Therefore, in terms of human injury or material losses in the system, severity may be expressed as follows: catastrophic, major, minor, negligible. In order to assess frequency of each severity level, firstly the screening technique may be applied to determine the probability of each event in part. The occurrence frequency may be quantitatively expressed as: frequent, probable, occasional, less probable, unlikely.

Below are given the definitions of severity levels and frequencies:

➲level of risk A: High risk level
➲level of risk B:
➲level of risk C:
➲level of risk D: Low risk

Table 1. Levels of severity of the identified risks

SEVERITY	The definition of adverse event
CATASTROPHIC	Death and destruction system
MAJOR	Severe injury, severe illness or major system damage
MINOR	Minor injury, minor illness or minor system damage
NEGLIGIBLE	Less than minor injury, illness or damage to system

Table 2. The frequency of risk

FREQUENCY OF OCCURRENCE	Individual specific element	Particularization
FREQUENT	Likely to occur frequently	It happens continuously
PROBABLE	Will appear several times over the life of an item	Will appear frequently
OCCASIONAL	Likely to occur sometime in the life of an item	Will appear several times
LESS PROBABLE	Unlikely but possible to occur over the life of an item	Unlikely but it is reasonable to expect that there
UNLIKELY	So unlikely that it can be estimated that there will appear	Unlikely to occur but possible

Table 3. Matrix frequency /severity of risk levels

FREQUENCY OF OCCURRENCE	SEVERITY			
	Catastrophic	Major	Minor	Negligible
FREQUENT	A	A	A	C
PROBABLE	A	A	B	C
OCCASIONAL	A	B	B	D
LESS PROBABLE	A	B	C	D
UNLIKELY	B	C	C	D

After risk estimation, the risk assessment should be performed to determine if it is necessary to reduce the risk or has reached the level of security.

It is obvious that if the risk estimate is obtained a level of risk A, then the risk is so high that it is intolerable and additional measures are required to reduce further risks.

Similarly, the risk level D can be considered acceptable and no further action is needed to reduce risk.

Thus, the risk can be described as:

<u>Intolerable</u> If the risk falls into this category, then you have taken appropriate security measures to reduce the risk; or:

<u>Acceptable</u>If the risk falls into this category then it is necessary to reduce the risk and the risk assessment is complete.

Risk levels B and C are intermediate and normally will require risk mitigation measures to make acceptable level of risk.However, the magnitude of these measures will be lower if the risk level C usually organizational risk reduction measures will suffice.

Table 4. Types of risks/actions implemented

A	High risk (intolerable)	Appropriate actions, organizational and/or technical –priority
B	Medium risk	Appropriate actions, organizational and/or technical short and medium term
C	Low risk	Maintain the current status of safety
D	Zero risk (acceptable)	No action

RESULTS AND DISCUSSION OF RESULTS

The purpose of protection and explosion prevention is to prevent explosions by removing or avoiding conditions that give rise to explosions. It is necessary to know the characteristics of explosion and combustion powders for choosing and developing adequate preventive and protective measures.

The characteristics of powders must be determined first to fine-grained dust to find the most critical conditions that may be encountered in practice. This is especially important if the particle size is changed or if the number of smaller particles is increased during a process,(forex., milling, grinding, exhaustor deposition).

Given the importance of knowledge of combustible dust explosion characteristics were determined by laboratory testing in accredited regime and with themodern equipment (KSEP-20), the characteristics of powder results by processing and handling wood pellets. The results arising from these graphical representations:

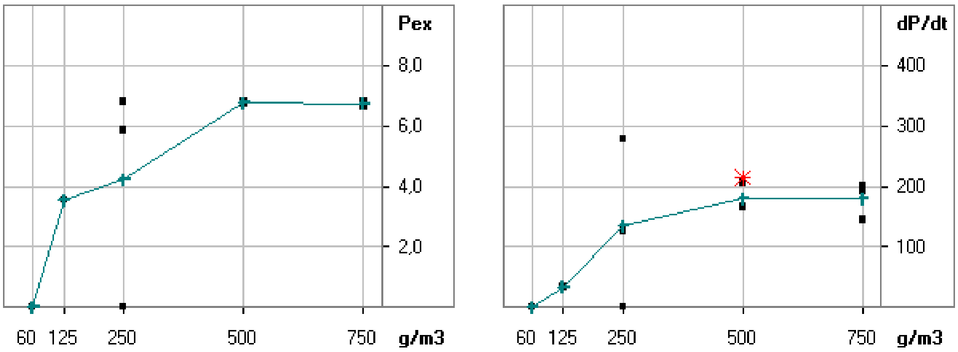

Figure 2. Explosion pressure pex graph depending on the concentration of dust

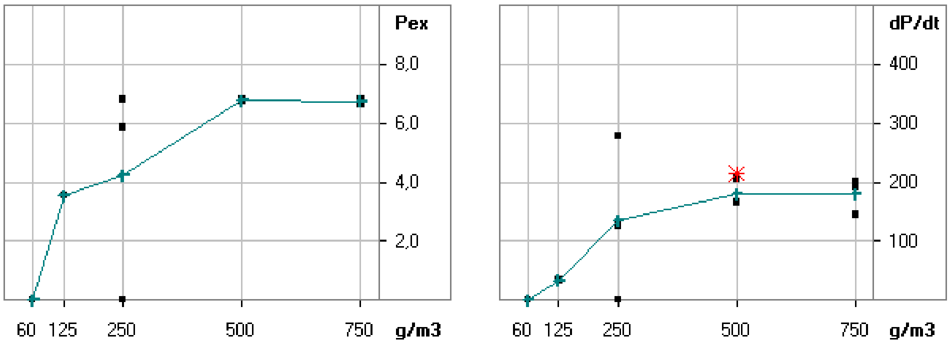

Figure 3. Graph the maximum pressure rise (dp / dt) depending on the concentration of dust

Once characteristics of dust explosion determined, there is sufficient information to allow proper selection and choice of technical equipment to be used in such areas endangered by the presence of combustible dust and establish technical and organizational measures to ensure a level security as high.

CONCLUSIONS

Explosions resulting from initiating explosive dust mixtures fuel/air causing major damage due to production and transmission repeated explosion and loss of life.

Therefore in areas with combustible dust, where there is a risk of explosive mixtures, ensuring an acceptable level of safety must be established and implemented measures for prevention and explosion protection. Prevention and explosion protection applicable may be so technical and organizational nature.

Explosion risk Estimation andassessment is a method which is based on the analysis of two characteristic elements of risk in general, namely the severity of possible adverse events and the likelihood of these events.

By estimating and assessing the risk of explosion, subsequent analysis of mitigation options leads to a final decision on the settlement in order to reduce risk to an acceptable level.

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THE MAGNETiC FIELD FROM LAPTOP COMPUTERS

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ABSTRACT

The magnetic field on frequency of 50 Hz from laptop computers is considered. The measured data are compared with the corresponding ones in literature, as well as with the critical values suggested by the Serbian Ministery of Environment, Mining and Spatial Planning. It is shown that some of the examined laptop computers produce a very strong electromagnetic field, so that, while working, people should take care not to hold the laptop computers on their bodies.

Key words: Magnetic field, Electromagnetic radiation, Influence on human health, Non ionizing radiation.

INTRODUCTION

Humans are continuously exposed to the electromagnetic radiation (EMR) from different natural sources (cosmic rays, geomagnetic radiation, solar radiation) and the electrical appliaces. Significant growth of the EMR level has been noted in recent fifty years as a consequence of the tehnological development, i.e. of the increasing use of the electrical devices. We are interested in the non-ionized electromagnetic radiation, which is characterized by the extremely low frequency in the interval: 0-300 Hz. The non-ionized radiation in this frequency region is characteristic of the electric appliances supplied by the public electrical network.

Humans are exposed to electromagnetic radiation at the home [1], and on the job [2]. In reference [3] authors show that laptop computers have electromagnetic radiation in order of the few μT. In this paper it is shown that inappropriate use of the laptop computers can cause an increased body exposure to electromagnetic field. Magnetic fields can affect the antioxidant system and reduce the level of superoxide dismutase (SOD) and glutathione peroxidase (GPKS) among workers exposed to low-frequency EMF [4]. A new category of persons with a functional impairment after exposure to visual display terminals is defined.

Some scientists recognized the occurrence of hypersensitivity to EMR originates from a common exposure, such as wireless systems and electrical appliances at the home or in the workplace, others suggest that electromagnetic hypersensitivity is psychosomatic or imagined [5], [6]. The World Health Organisation is stated that electromagnetic hypersensitivity symptoms that are commonly experienced include dermatological symptoms as well as neurasthenic and vegetative symptoms [7].

Some common signs and symptoms of electromagnetic hypersensitivity [5,8] are: erythema, tingling and burning sensations, urticaria, shortness of breath, arrhythmia, fatigue and nausea, numbness of the skin, back pains, emotional, erythema and itching of the skin, shortness of breath, memory and concentration problems, headache, blurred eyesight, limb pains, muscle stiffness, burning sensations, redness and increased temperature of the skin. When the volunteers had used the shielding cabinet to prevent the EMR in duration from 1–7 years, were able to work with their computers whole working day. Those who had used the shielding cabinet for 2–3 months were partially symptom free. The person who had used the cabinet only for 1 week reported some alleviation of her nausea [8].

According to the international commission for the non-ionized radiation [9] the referent limit value for people is $5/f$, while the same for the employee within the risk working conditions is $25/f$, respectively (f represents frequancy of electromagnetic field). Low-frequencies EMF were classified as probably carcinogenic to humans (Group 2B) by the International Agency for Research on Cancer [10]. According to the safety rules possed by the Ministery of Occupational Safety and Environment Protection [11], the referent limit level of the magnetic induction for the EMF frequency, f, from 25 Hz to 800 Hz is $2/f$. The referent limit level can be defined as the critical radiation level above which the environment conditions are unsafe for humans. Thus the referent limit value for f = 50 Hz is 0.04 μT. The Ministery of occupational safety and environment protection brought the low on the non-ionized radiation protection [12], which determines the risk conditions and protection measures in the critical situations.

In our paper the risk assessment of the low frequent magnetic induction from laptop computers to the human is done.

MATERIAL AND METHODS

The measurement of the magnetic induction was performed on the four laptop computers of different firms, and different production year. These laptops are signed with L1, L2, L3, L4 and L5. The measurements were performed on places in rooms where the magnetic field level are lower than 0.01 μT.

The measurement positions with respect to laptop computers are presented. The measurement positions are selected as positions with high magnetic fields. On the positions on the left and right side of laptop, and on behind of laptop monitors, magnetic field values are smaller in order the referent limit value B = 0.04 T [12], and not presented in the paper.

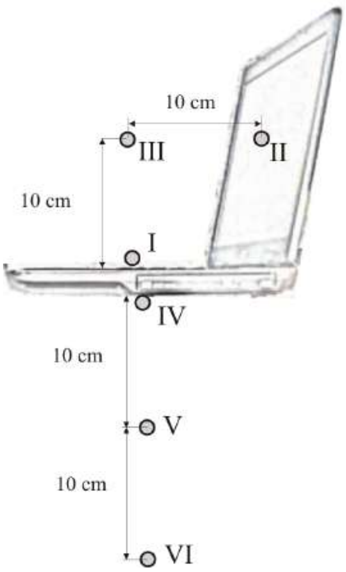

Figure 1. The measurement positions.

Measurements of the magnetic inducation are done with the measuring device EMF 828 (producted by Lutron). It can measure the magnetic induction in the range from 0.01 μT to 2 mT and the frequency range 30 to 300 Hz. The EMF 828 posesses three measurement extents: 20 μT, 200 μT and 2000 μT. The measurement precision depends on the measurement extent and is of the order 0.01 μT for the mesurement extent of 20 μT, 0.1 μT for 200 μT and 1 μT for 2000 μT, respectively. The measurement device EMF 828 can measure all three components of the magnetic induction *x*, *y* and *z*, and the total intensity of the magnetic induction is determined by the expression $B = (B_x^2 + B_y^2 + B_z^2)^{1/2}$.

RESULTS AND DISCUSSION

The results of the magnetic induction measurements for different laptops (noted as L1, L2, L3 and L4) are presented in Tab. 1. The measured values of magnetic induction are given for measurement positions, from I to VI (see Fig. 1). The measurement values of magnetic induction are performed for same working regime. For all laptop computers the measurement values are given in two cases: if the laptop working with power supply (noted as PS in Tab. 1), and if the laptop working with batteries. The laptop 4 can working only with power supply.

Table 1. The measured values of magnetic induction for different Laptop computers (L1, L2, L3 and L4) and different measurement positions MP (I, II, III, IV, V and VI), (see Fig.1).

MP	*B* (μT)							
	L1		L2		L3		L4	
	PS	Bat	PS	Bat	PS	Bat	PS	Bat
I	0.44340	0.24217	0.12410	0.11916	3.24091	3.20484	0.79561	-
II	0.06403	0.12689	0.10050	0.09434	0.12689	0.11045	0.06403	-
III	0.05745	0.1005	0.10954	0.10440	0.10630	0.10724	0.72035	-
IV	1.34492	0.99182	0.14177	0.15556	1.82620	1.88393	3.23345	-
V	0.17493	0.11000	0.09950	0.10392	0.37868	0.30430	0.78109	-
VI	0.08307	0.10677	0.10488	0.09274	0.11533	0.08602	0.14799	-

From Tab. 1 can be seen that the values of magnetic induction for all measurements' positions have the values greater then the regulatory value of referent limit value B = 0.04 T [12]. Because of that, from the measured values, which are presented in Tab 1, can be seen that the values of magnetic induction, in the case "PS" are usually slightly higher with respect to the case "Bat". These differencies are almost negigible, and can be concluded that they are aproximately equal.

It is shown that the measured values of the magnetic induction are usually higher than the corresponding referent value, B = 0.04 T. This fact indicated to the potentially risk of magnetic field, on the small distances from laptops. These small distances from the Laptop are usual in the cases when people work with laptop in the bad (when the laptop are on the chest or abdomen), and when people work without the tables (when the laptop is kept on their feet). In these cases, the laptops are very close to many of internal organs and reproductive organs, As noted in the Introductions, the magnetic fields can make damages of many organs, and cause many diseases.

CONCLUSIONS

The measurement results of magnetic inductions from the Laptops, whuch are presented in this paper, indicate the potential risk to humans, in cases of incorresct use of them. Long improper use can lead to many diseases. Our main recommendation is the proper use of laptop (on the table), with the power adapter to the floor.

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CHEMICAL RISK ASSESSMENT AND MANAGEMENT IN THE COLD STORAGE"GREDJANKA"

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ABSTRACT

This paper creates optimized model assessment and management of chemical risks. Model assessment of chemical risks is based on meeting the requirements of legislation, the application of the requirements of ISO31010 and primenni matrix methods for assessing risk. Optimized model of chemical risk assessment provides a reasonable basis for management assessed risk.

Key words: chemical risk assessment, management.

INTRODUCTION

Organizations whose activities are preparing, processing, packaging and fruits cooling, i.e. the use of large amounts of ammonia in the cooling process are expected to face significant chemical risks. If chemical risks are not placed under the control, they may affect the achievement of the organization's goals in a negative way.Given the fact that the technological process of "storage" consists of operations in which facility uses hazardous material,the potential chemical risk may be even higher.Chemical risk management in the Cold storage "Gređanka" involves the use of logical and systematic methods of identifying, analyzing and assessing the danger during the cooling process, monitoring and reviewing of chemical risk for an effective and efficient management of chemical risk and integrated management systems in general.The aim of this research is to assess chemical risk in the Cold storage "Gređanka".In accordance with the established research purposes, there is the following hypothesis:

a) Based on the model of the process approach it is possible to identify the danger of chemical accident, define a chart of the flow assessment and management of chemical risk.
b) Based on the problems identifications, set goal and research hypothesis, the following tasks are derived:to make the process analysis at the Cold storage "Gređanka";to identify the danger of chemical accidents;to perform chemical risk assessment.

In order to accomplish research tasks and to achieve goals and testing of research set hypothesis,the matrix method of risk assessment will be used which will contribute to the work methodology.

THE DESCRIPTION OF THE LOCATION, FACILITY AND WORK PROCESS

The production complex of the Cold storage "Gređanka" is located in cadastral designation Velika Greda, on the cadastral plot no. 1117 on an area of 3 ha with a gross area of 2 ha under the objects. The dimensions of the manufacturing facilitiy are 127 m x 54,18 m. Cold storage building was built during 1978 and 1979.The object consists of the following content:The hall for the fruit preparation and processing is placed along the cold storage object with which makes production and technical entirety. There are lines in the hall for cherry and plum processing. Thearea of production facility is2.466,75 m^2. Six freezing chambers are located along a manipulative hallway, three on each side. The surfaces of the first and the third in line are 405 m^2, while the surfaces of the middle ones are 411,5 m^2. Chambers temperature regime is from 0°C to -30°C.Manipulative hall connects all controlled cold storage chambers. Its area is 352,3 m^2. In the machine room compressor facility for cold storage cooling system with anhydrous ammonia in a closed system is located. In the machine room liquid ammonia collector of the volume of 5 m^3 and working pressure of 18 bar, and liquid ammonia separator, of the volume of 4,6 m^3 and working pressure of 16 bar are accommodated.Production capacity of the Cold storage "Gređanka" from Velika Greda is 5.000 tons. In the process of fruit processing and fruit storage participates significant number of raw materials and intermediate goods with characteristics that may be the cause of a chemical accident. The facility for the storage of ammonia is classified in the groupings of SEVESO lower order facilities due to the quantity of ammonia, which is 15.000 tons.

METHODOLOGY AND METHOD OF CHEMICAL RISK ASSESSMENT

For the purpose of these researches the general principle of the risk assessment implementation was used, which is defined in the risk management standard. Risk assessment is a comprehensive process of identifying, analyzing and assessing the risk[1]. Risk assessment provides decision makers and responsible parties an improved understanding of the risks that may affect the objectives achievement and the adequacy and effectiveness of control that already took effect. Risk assessment provides the basis for decisions about which of the risk treatment mechanism will be used. The output of the risk assessment is the input into decision-making processes in the organization. Figure 1., shows the general concept of risk assessment.

[1] ISO TC 223/SC: Risks management – Guidelines on principlesand implementation of risks management

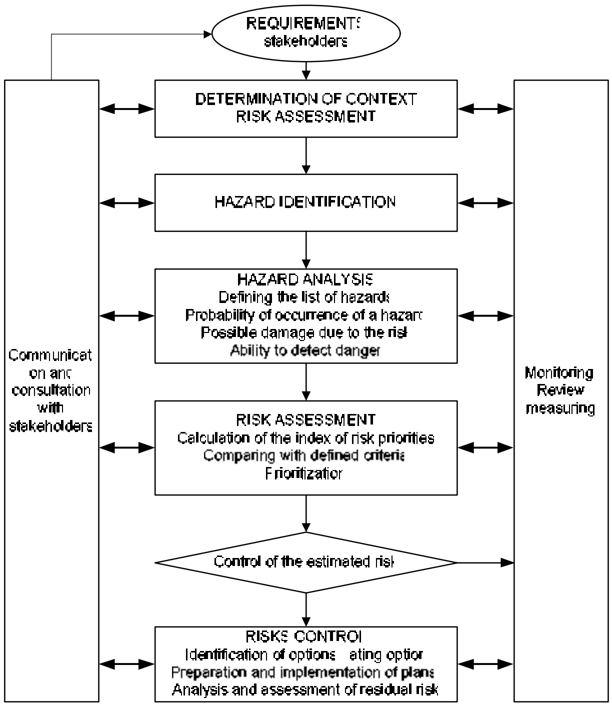

Figure 1. General concept of risk assessment[1]

Based on available data from the technological process description, the possible occurence of accidents is determined, due to the dangerous substance**ammonia**, NH_3 (gas, liquid), will be used in ongoing work. Objects that can be affected by a chemical accident are:facilities installation; temporary ammonia storage;industrial complex Cold storage "Gređanka".

Chemical accident probability assessment

An accident occurence probability assessment is done in one of the following ways:

- based on the statistical data – a historical approach;
- based on the hazard identification – an analytical approach;
- by combining the historical and the analytical approach.

The probability is expressed numerically or descriptively as **small, average and high.**

The probability of chemical contaminationoccurence assessment was based on criteria given in the following Table 1.

Table1. The criteria for determining the accident probability

High probability (100 – 10^{-1} event frequency/year)	Average pobability (10^{-1} – 10^{-2}event frequency/year)	Small probability (<10^{-2}event frequency/year)
- leakage of hazardous materials at the joints of pipelines, valves, etc; - spilling when pouring liquids and solids spillage during handling; - damaging the packaging units and spilling the contents; - fluid leakage and solids spillage in an internal transport; - leakage of compressed gases from the pipelines and other pressurized systems - creating the conditions for causing a fire or an explosion in the danger ZONE 2; - starting fires on installations.	-cracking of liquids pipeline; -cracking of compressed gases pipelines; -spilling the entire content of the fluids reservoir; -spilling the auto and railway tanks in the complex after accidents; -creating the conditions for a fire and explosion in the danger ZONE 1; -a fire and an explosion of the part of the facility; -two or more high probability accidents in one location at the same time.	- cracking of the transport vessels - cracking of the storing vessel; - a fire in the whole facility; - a fire in the whole storage; - an explosion of the entire facility; - an explosion of the entire storage; - creating the conditions for a fire and explosion in the danger ZONE 0 - two or more medium probability accidents in one location at the same time

Based on previous findings, at complex of the Cold storage "Gređanka", the event probabilities, which realization could result in a chemical accident, because of the presence of ammonia in transport or in the technological process, are:

- cracking of the pipes with ammonia - an event with an average probability,
- a complete breakdown of the pressurized vessel with ammonia - an event with a very small probability,
- holes formation in the pressurized vessel with ammonia - an event with a low probability,
- a small ammonia leakage - an event with a high probability.

The assessment of the potential chemical accident consequences

Based on the data obtained by analyzing the vulnerabilities described in scenario events, it is estimated that in the case of an accident **significant consequences** can be exparected.

Possible consequences for the environment and human health are assessed based on the data obtained from the vulnerability analysis. By this analysis, all vulnerable (easy inviolable) objects in the vicinity of potential source of chemical accident are being examined, i.e. all that can undergo changes under the influence of an accident.

A scenario represents a situation in which an ammonia leakage from a pressurized vessel or from a pipelineoccurred. Affected zones are obtained by the model, provided that the given concentrations of interest are determinated as LD50, IDLH and MDK.

Table2. Criteria for the consequences assessment

	Description of the consequences in the case of a chemical accident
Very small consequences	Up to 1.000,00 €or very small consequences for the environment
Small consequences	From 1.000,00 to 10.000,00 €or small consequences for the environment
Medium consequences	From 10.000,00 to 100.000,00 €or severe consequences for the environment
Big consequences	More than 100.000,00 €, or severe and multiple consequences for the environment
Very big consequences	More than a million euros, the consequences with the disastrous consequences for the environment

Chemical accident risk assessment

A chemical accident risk is estimated based on the accident probability assessment and the possible consequences assessment. The risk of chemical contamination is expressed as: **negligible risk, low risk, moderate risk, high risk and very high risk**, according to the criteria shown in the following Table 3.Criteria for the risk assessment based on the accidentoccurence probability and the possible consequences are shown in Table 2.

Table 3. The matrix of risk assessment

	Consequences				
Probability of an accident	**Very small consequences**	**Small consequences**	**Medium consequences**	**Big consequences**	**Very big consequences**
Small	Negligible risk	Small risk	Moderate risk	High risk	Very high risk*
Average	Small risk	Moderate risk	High risk	Very high risk*	Very high risk*
High	Moderate risk	High risk	Very high risk*	Very high risk*	Very high risk*

Note:
- The risk is **acceptable** if it is estimated as: negligible risk, a low risk,
- The risk is **conditionally acceptable** if it is estimated as: moderate risk.
- The risk **is not acceptable** if it is estimated as: high risk and very high risk.

When the estimated risk is assessed as **moderate**, the operation of the relevantfacility with such estimated risk level is **conditionally acceptable**, and the management systemsubject is required to access the **temporary**operation delay and to introductthe additional technical and technological and other protection measures on the facilities, technological process, equipment, as well as in thesystem work security organization, in order to reduce the risk to the acceptable limits.Based on the performed accident probability analysis for the facility Cold storage "Gređanka" which is estimated as **medium**, and the possible consequences which are estimated as **significant consequences**, it is assessed that the chemical accidents risk is estimated as**moderate risk**.The estimated **moderate** chemical accident risk for the facility Cold storage "GREĐANKA" is **ACCEPTABLE**, and the same **CAN BE OPERATED** under certain conditions which will be prescribed by technical documentation, respecting the standards in this field and by implementation of organizational measures for environmental protection, fire protection and health and safety protection at the work that are regulated by theAccident protection plan as well as project and technical documentation by which thework on the facility Cold storage "Gređanka" will be performed.

PREVENTION MEASURES FOR ESTIMATED RISK CONTROL

Prevention measures are implemented in order to reduce the probability of risk accidents and risk consequences. They are based on taking actions that reduce the accidents probability and they include:readiness in the technological process; control and maintenance.

Prevention measures to minimize the extent of the consequences

- If there is an accident, it is necessary, beside stopping, to undertake the following actions: to call fire department and the emergency medical assistance, to immediately stop the machinery and equipment in affected area, to turn off the electrical installation and any other sources of ignition, to deny access to the persons who do not participate in the recovery of the incurred accident;
- If the fire occured, the space should be suffused with as much as possible water and water mist. Vapors that occur by combustion are highly toxic (nitrogen oxides, ammonia, etc.), the proper approach to fire should be chosen and insulating equipment should be used. Due to the high heat, extinguishing can create steam pockets causing eruptions that can be identified as a small explosion. For this reason one should not be too close to the fire, nor allow the panic to occur.
- Provide a safe and undisturbed operation of the hydrant installation in all operating conditions, even a back-up network power supply;
- Fire hoses should be of sufficient length to ensure, at any time, regardless of the wind direction, the nozzles distance at 10 - 15 meters from the point of leakage of ammonia.
- For the stable operation of pumps and systems for fire detection and fire extinguishing it is necessary to provide adequate supply of electricity from the sources that do not depend on regular power system.
- If the absorption of ammonia is carried performed in the part of the complex which is organizedlydrained by the local sewage, formed ammonium hydroxide must be maintained in a proper assembly shaft, until itsneutralization is not done.
- During the repair and replacement of the parts of the facility even a minimum discharge of ammonia directly into the atmosphere must not be allowed. During operation, all exhaust pipes must be immersedinto the vessel with absorptive medium.
- Provide a mobile detector for ammonia by which responsible workers have to control the ammonia concentration every day.
- Set the windsock on the roof of the highest building, which can be seen from all parts of the complex.
- Regular maintenance of the outdoor lighting of the complex into the functional state.
- Set up the horn in order to be able to announce the danger threatened from the occurred or occurrence of chemical accident.

CONCLUSION

Institutional changes that have taken place in the Republic of Serbia in the field of environmental protection are inevitably caused the need for the development and improvement of tools for decision making in the environmental planning and protection management. Making decisions based on the previously presented models and methods of ecological risk assessment is a flexible approach that is proactive and provides identification, prioritization and documented environmental risk, as well as control application. It can be confirmed that the purpose of this methodological approach of chemical risks assessment is fulfilled in accordance with the principles of risk management according to theappropriate Rulebook as well as in accordance with certain laws and standards. Chemical accident risk managementbased on the proposed model is very likely to be a useful tool for decision-makers in fulfilling the legal regulations.

This paper proposes methodological approach to chemical risks assessment that is examined within the company Cold storage "Gređanka" by which protection measures are established, that will be undertaken in future operation in order to establish an efficient and effective environmental protection management system.

From the practical implementation of the chemical risks assessment method in the of dangerous substance management, in this case ammonia, it can be concluded that in most phases of ammonia management the conditionally acceptable risk is present and that it may be operated only if adequate measures to protect the environment from the hierarchy of risk management outlined in this work are applied.

Methodological procedure of risk assessment in facilities that contain ammonia can be of great use to other organizations that use this dangerous substance.

Chemical risk assessment and the establishment of control mechanisms management is of great benefit in designing environmental management systems. The proposed modelof the chemical risk assessment allows the information about the risk to be adequately processed and to be used in decision-making at the relevant levels of the organization Cold storage "Gređanka".

By an active and comprehensive chemical risks assessment, as defined in this work, company management of the Cold storage "Gređanka" in Velika Greda may:

- accept and approve the estimated risk management policy at the facility Cold case "Gređanka" for hazardous substances management;
- inform all interested parties about the operation of the estimated risk facility;
- define estimated risk control mechanisms that correspond to the organizational performanceof the organization which contains a dangerous substance;
- ensure compliance with the laws and subordinate regulation as well as legal acts of the organization concerning the hazardous substance management;
- provides distribution of the necessary resources for the estimated risk management needs.

Based on the analysis of all relevant impacts it is posible to bring a general conclusion that the impact of existing facilities expressed in the domain of maximum moderate risk of chemical accidents, has a limited or negligible effects in the field of air pollution, noise, soil pollution, as well as the impact on flora and fauna. Given these findings, it is necessary to take certain protective measures outlined in this paper.

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OVERARCHING MINING HAZARDS – ENVIRONMENTAL RISKS (EKOLOGICAL RISKS)

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ABSTRACT

The primary focus of the mining industry is the production of a specific quantity of its products,in a given timeframe, in compliance with relevant regulatory standards and production processes, and with minimal costs. However, in practice, the standards and regulations are not rigorously adhered which, in turn, causes significant environmental damage. These circumstances impose the necessity of continual development in the area dedicated to the hazard identification and prevention.This paper represents an overview of the impact of mining activities on the environment, the overview of the risks incurred in mining activities as well as their prediction and management. As an example, we have used the overflow ofthe water level on the external slope of the flotation Dam *1,* above the crown of the tailing pond dam in Veliki Krivelj, in Bor.

Key words: environmental risk, mining, flotation dam.

INTRODUCTION

The mining industry has been causing negative environmental impacts detectable at large scale, for many years. Nowadays, the mining industry is faced with a difficult task of upgradingmining activities so that they do not cause socially unacceptable environmental impacts any more.

THE CONCEPT OF RISK IN THE MINING INDUSTRY

In the mining industry, the concept of risk represents a measure of the degree of probability that the exposure to certain phenomena will lead to the occurrence of adverse environmental impacts. [1] Every project contains certain risk level that affects the success of the project itself. [2] The Project Management Institute defines a risk as an uncertain event or condition that, if it occurs, has a positive or negative effect on a particular aspect of the project objective – time, costs, scope or quality. [3] In addition, Gardiner proposes two essential categories of risks:

1) Speculative risk – results in an uncertain degree of gain or loss
2) Pure risk - in which loss is the only possible outcome [2]

The objectives of the mining industry should be aimed at havingbetter results in the process of exploitation of natural resources with minimal negative impacts on the environment. However,mining industries will never function without causing negative environmental impacts - there will always be some uncertainty regarding negative impacts of mining activities;therefore, the need for the risk assessment and management appears to be one of the key aspects.

Risk management includes the following processes: [4]

- Risk identification – identification of a potential risk that may affect the project
- Risk analysis and the assessment of the risk level – summarizing the probability of risk occurrence based on the likelihood of the occurrence and the potential impact of the risk on the project's objectives.
- Decision-making for risk mitigation – reducingthe negative impacts of the risks
- Risk control
- Risk monitoring – tracking identified risks, identifying new risks and evaluating the potential impact of new risks on the project's objectives.

The risk management process is based on the identification of the risk. It is important to approach the identification of potential risks from a rather pessimistic point of view – meaning - to assume, from the very beginning of the process that the possible problems will arise in the system functioning. The process of risk identification and analysis can be enhanced by integrating many qualitative and quantitative methods and therefore the usage of various techniques is recommended, keeping in mind the purpose, strengths and weaknesses of each. The risk assessment process is iterative, which means that each iteration seeks to improve the understanding of system complexity and to reduce associated uncertainty.There are even some modern techniques that can be used in the process of the risk assessment, such as FTA (Fault tree analysis), FMECA (Failure mode, effects and criticality analysis). After a successful risk identification and analysis, the next step of the process is the process of planning the appropriate actions for reducing negative impacts of the risks. Risk classification creates a common framework for their better assessment and management. [2]

Having in mind the functioning process of the mining system, the classification of the risks in the mining industry would be the following[1]:

- The risk to the health and safety of the employees;
- Environmental risks;
- Social risks;
- Land use risks;
- Legal and financial risks and
- Technical risks.

ENVIRONMENTAL RISKS OF MINING INDISTRIES

The analysis of environmental risks is an integral element of the process of environmental decision making. Decision makers must first identify possible risks and assess the possibility of negative impacts on the environment. In that manner, they will be able to choose the most suitable course of action for reducing the negative impacts of risks. However, not every environmental risk can be reduced or eliminated. It is, therefore, important that environmental decision-makers determine the level of the socially acceptable environmental risks. The process of defining acceptable level of environmental risks is a necessity. The assessment of environmental risks includes their identification, evaluation of risk exposure, characterization and quantification which determines the size and the probability of the occurrence of the potential negative impact. Assessment of environmental risk includes determining the nature of the effects and the probability of the occurrence of negative impacts on the environment as a consequence of the exposure to the specific phenomenon.[6] According to the methodology of the American Academy of Sciences, there are four stages in ecological risk assessment:

- hazard identification,
- dose-response assessment
- exposure assessment
- risk characterization

Hazard identification – represents a scientific study of the available data used for identification of a causal relationship between identified hazards and adverse environmental effects.

Dose-response assessment – an important aspect of this phase is to identify the level of a "safe" risk exposure.

Exposure assessment – this phaseinvolves a description of characteristics of sources of environmental hazards, the level of concentration on the source of emission and pathways that lead from the source to the general population.

Risk characterization – the last phase of the process involves total description of forms and dimensions of the expected risks, based on the hazard identification and exposure assessment.

ENVIRONMENTAL RISK MANAGEMENT

The main task of environmental risk management is responding to identified risks. Its main goal is reducing environmental risks to an acceptable level without causing additional costs. When it comes to environmental impact of mining activities, a considerable degree of uncertainty in terms of probability and consequences of actions and events is always present. Therefore, environmental risk management requires a careful analysis of the objectives and operations, as well as their proper understanding. Environmental risk management represents a process of planning and making decisions about actions, to reduce environmental risks to an acceptable level. This process consists of the following steps:

- Definition of possible risks
- Formulation, analysis, and risk characterization (including possible scenarios)
- Risk identification
- The consequences and probability, conclusions about the risk
- Ongoing monitoring, review and change management

What is important when it comes to environmental risk management is that the phases of the process are intrinsically tied, which means that the process itself is limited by the quality of the preceding stages.

CLASSIFICATION OF ENVIRONMENTAL RISKS

Potential environmental hazards can be classified as:
- Risks to surface water and groundwater
- Risks to land and geological structures
- Risks to air and atmosphere
- Risks to flora and fauna
- Risks to human health and safety

The main causes of the environmental risks in the mining industry can be divided into: [8]
- Continuous emissions of harmful substances into the air, water and soil
- Hazardous tailing storage and waste
- Storage, handling and transportation of fuels and chemicals
- Mining
- Mechanical breakdowns
- Human errors in decision-making and management

ENVIRONMENTAL RISK ASSESSMENT AND MANAGEMENT

In order to function successfully, the mining industry, as well as the other industries, produces massive amounts of waste. Disposal of such large quantities of wasterepresents an enormous challenge for the mining industry, and a major threat to the environment. When it comes to negative environmental impacts, the greatest risk to the environment represents the disposal of tailing. [9]

The most important environmental risks associated with the problem of tailing disposal can be divided into:
- Potential impacts on air quality –caused by the emission and deposition of harmful tailing dust
- Potential impactson groundwater quality - outflow caused by underground tailing
- Potential impacts on surface water and aquatic species - due to the tailing deposition into surface watercourses
- Potential impacts on the soil – soil penetration and soil deposition
- Potential impacts on flora and fauna
- Potential impacts on human health - as a result of the overall effect caused by the influence of previously mentioned factors.

Having in mind all potential risks and negative environmental impacts, a proficient risk assessment and creation of optimal conditions for risk management is of paramount importance.

PRACTICAL DATA ANALYSIS

Flotation tailing ponds represent one of the most common forms of technogenic waste disposal and one of the most dangerous forms of pollution created during the process of extraction and production of copper.

In the near future, for RTB Bor, the gravest problems in the area of mineral processing will not be associated with the obsolete processing technology, high concentration of copper oxide ore, low concentrations of copper, or market demands for quality concentrate with minimum 20% of copper-in-concentrate, but with the successful disposal of tailing.

Mineral processing represents one of the most complex mining processes which can be divided into several intrinsically tied subprocesses. If a problem appears in any phase of the process – form comminution, through sizing, concentration, and froth flotation to the disposal of tailing – the whole process of mineral processing is in danger. Precisely because of that, an ineffective tailing disposal system could potentially harm not only mineral dressing process but the whole production process in general.

During copper extraction processes in RTB Bor, Jama copper mine, mines in Veliki Krivelj and Majdanpek, a large quantity of flotation tailing is produced, which, together with blast furnace slag, represents disposal material, and as such is being disposed of at speciallydesignated areasat the industrial site. For this purpose, RTB Bor flotation tailing ponds, old flotation tailing pond in Bor(which is no longer in function), old flotationtailing pondRTH, Veliki Krivelj i Valja Fundata in Majdanpek (which are still in operational use) are created.

In the near future, flotation tailing ponds RTH and Veliki Krivelj, which are still in function, will reach their capacity. Tailing pond Valja Fundata in Majdanpek will soon be the only available to fulfill the requirements of the flotation tailing disposal.

Up to the present day, approximately 58.0 Mt, or 41.3 Mm3 of tailing has been stored in RTHflotation tailing pond, which has been in constant use since 1985. According to the current dynamics of copper extraction, and the slag production in RTB Bor, the final elevation level of thedamRTHwill be378m above sea level, with the acclivity level of 372m above sea level. According to the dynamics of production, the estimated production will reach 0.65 Mt per year of ore and 1.08 Mt per year of blast furnace slag.Since the available storage spacein RTH tailing pond, up to 372m above sea level,adds up to 2.4Mt or 1.9Mm^3 (according to geometrical measurements), it is evident that, if we take into consideration the current production dynamics, the maximum exploitation period of RTH tailing pond cannot be more than next 18 months.

Flotation plant in Veliki Krivelj, which has been functioning since 1982, has a single tailing pond with two separate fields (field1and 2) andthree dams- 1, 2and 3. From 1982 to 1989, the tailing form Veliki Krivelj flotation plant was stored in Field 1. Because of the overflow of water level on the external slope of the Dam 1, above the crown of the dam, Field 1 became no longer active. For that reason, in early 1990, Field 2 became the main site for the construction of the Dam 3. Field 2 and Dam 3 were in function until 2008, when the storage space became completely filled with tailing. Draft remedial plans for Dam 1 and Dam 2 were released which led to the remediation of Dam 1 and Field 1 that still contained unused space for tailing disposal.Nowadays, Field 1 storage space in Veliki Krivelj tailing pond is used for the disposal of tailings form Veliki Krivelj and Cerovo copper mines, according to the scheduled dynamics, until it reaches its maximum capacity.

The future production dynamics in Veliki Krivelj flotation plant will be:

- Ore production in open pit Veliki Krivelj will be 8,6 Mt per year in the first half of 2013, and 10,5 Mt per year afterwards
- Ore production in copper mine Cerovo will be 2,5 Mt per year until 2014, and 5,5 Mt per year afterwards.

Since the available storage space, in Veliki Krivelj tailing pond, Filed 1, adds up to 32 Mt or 25 M m3, up to 380m above sea level (according to geometrical measurements), it can be concluded that, given the current production dynamics, the maximum exploitation period of Veliki Krivelj tailing pond, Filed 1, cannot be more than next 2 years.[10]

Based on everything that has been said, it can be concluded that, in both cases (in 1989 and in 2013) there was a failure in the system due to circumstances that could have been anticipated.It is evident that the analysis of potential risks was not carried out appropriately, and, in order to eliminate the risks, the probability of occurrence of potential hazards should have been estimated in the first stage of the tailing pond construction.

Based on this analysis, it is evident that the development of a systematic study of potential risks and risk elimination is of a prime importance. Additionally, because of the increased risks to the environment, the functioning of tailing ponds must be carried out according to the strict management plans. Those plans must be based on the estimated conduct of tailing ponds in specific conditions and must include all necessary actions for their regulations. The dams must be subjected to the routine inspections and inspections after every significant incident that might damage or disrupt their functioning (earthquake, heavy rainfall, melting snow). New possibilities for tailing storage havebe taken into consideration. For example, a new practice used worldwide, is to transform about 98% of new tailing material, created during the process of non-ferrous metal and coal processing, into paste tailing. Nowadays, the world renowned companies in USA, Canada, Australia and Europe engage in designing, equipment manufacturing and constructing plants for production and disposal of pasta tailings. (The PasteGroup, KlöhnCrippen Berger, Westech, Dorr-Oliver Eimco, GolderAsc. (Paste Tec), Outokumpu, and others.). [10]

CONCLUSION

The key principles of effective management of tailing ponds lie in risk management, reduction of tailing production and maximization of its re-usage in the production process, ensuring that all structures of the tailings are functioning properly, considering the economic, environmental and social aspects of all parts of tailing ponds in order to minimize short-term and long-term impacts, and research for the improvement of tailing ponds management. [10] While there are many reasons for potential danger and many unpredictable situations which represent the results of the complexity of the activities themselves, itcan be claimed that a great deal of negative environmental impacts can be avoided through effective risk management.

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THE FOUNDER OF HUMAN ECOLOGY

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ABSTRACT

In this paper, the presentation of short biographies initiators of modern evolutionary biology: Dobzhansky, Ford and Hewitt. The concept of human ecology is explained through a few definitions. Some of these definitions have been created thanks to the selfless work of the founder of Human Ecology: Ellen Henrietta Swallow Richards, Roderick D. McKenzie, Paul Bigelow Sears, Daniel G. Bates, Paul Howe Shepard Jr.. These skilled scientists have made a link between human ecology and other disciplines of modern ecology.

Key words: Human Ecology, Dobzhansky, Brisco, Hewitt, Richards, Shepard Jr.

INTRODUCTION

Ecology (οἶκος-λογία) is a study of the relationships between organisms, groups of living things and their environment. Ecology is an interdisciplinary field that includes biology and Earth science, but Ecology is a human science too [1]. The main branches of ecology are: Population ecology, Systems ecology and Applied ecology. Other branches of ecology are: Landskape ecology, Agroecology, Urban ecology, Behavioural ecology, Social ecology, Molecular ecology, Human ecology, etc. [2].

When we say man, we didn't mean the tribes and people: Bushmen, Aborigines, Native Americans and others who live in perfect harmony with nature, but refer to a modern, urban life, with all the achievements of civilization, desires and ambitions to subordinate nature of their needs and that of this benefit. Its activity causes consequences whose manifestations are increasingly perceived globally. For its own purposes, human nature is not used, but the exploit. Modern man is a biotic factor of extraordinary strength, which stands out as the anthropogenic factor. Has the ability to conquer and colonize most inaccessible parts of the country. At all times ecology and its themes were at the center of human theory and practice. It is only in the last century, science came to, and has become the main science to sustain the earth and man. In its long history, ecology, as theory and practice, passed several development stages. On an intuitive - religious way first to have understood the meaning of ecology are Chinese. The term ecology was first in 1866. used by the German biologist Haeckel (*Ernst Heinrich Philip Haeckel*, February 16, 1834. Potsdam - August 9, 1919. Jena) [3] (Figure 1).

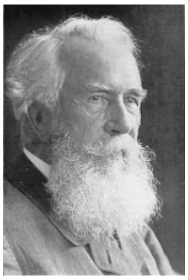

Figure 1. Ernst Heinrich Philip Haeckel, 1834 – 1919

In layman's understanding of this term is often used synonymously with the concept of environmental protection, which is not correct, because the environment is just one of the areas dealt with ecology. Today, ecology is increasingly becoming the conscience of humanity and its knowledge is necessary in order to properly access environmental protection. The relationship of living beings and the external environment is bidirectional, often abstract and not easily visible. Living things in the environment and its factors have a range of adaptation and only when it realizes they can bring to the relationship. Adaptation can be thousands and occur at different levels of the body, but also the population, biocenological, ecosystemological.U basically, ecology is a scientific discipline that studies the scheduling and distribution of living organisms and biological interactions between organisms and their environment. Environment of organisms including physical features, which can be summarized to describe the so-called abiotic factors such as climate and geological conditions, but also includes other organisms that share with it its ecosystem or habitat. Organisms can be studied at many different levels, from proteins and nucleic acids (in biochemistry and molecular biology), to cells (in cellular biology), individuals (in botany, zoology, and other similar sciences), and finally at the level of populations, communities and ecosystems, to the biosphere as a whole, these levels were the main subjects of ecological research. Ecology is a multidisciplinary science. Because of the focus on higher levels of organization of life and the interrelationship of organisms and their environment, ecology has a strong influence on many other branches of science, especially Geology and Geography, Meteorology, Soil Science, Chemistry and Physics. Therefore, Ecology says that holistic science that combines traditional science (such as Biology) which became its subdiscipline and together enable the further development of ecology.

HISTORY OF MODERN ECOLOGY

The initiators of modern evolutionary biology, as well as the modern evolutionary synthesis are: Dobzhansky (*Theodosius Grygorovych Dobzhansky*, *Теодосій Григорович Добжанський*, January 24, 1900. Nemyriv, Russian Emp. -

December 18, 1975. San Jacinto, Cf), Ford (*Edmund Brisco "Henry" Ford*, April 23, 1901. Papcastle, Cumberland, UK - January 21, 1988. Oxford, Oxfordshire) and Hewit (*Godfrey Matthew Hewitt*, January 10, 1940 - February 18, 2013. Worcester) (Figure 2, a, b, c).

a) b) c)

Figure 2 The initiators of modern evolutionary biology
a) Theodosius Grygorovych Dobzhansky, 1900 - 1975.
b) Edmund Brisco "Henry" Ford, 1901 - 1988.
c) Godfrey Matthew Hewitt, 1940 - 2013.

Dobzhansky was educated in Kiev. He studied biology. He collected butterflies. He later moved to a studio room in Saint Petersbug (Leningrad) with Professor Filipchenko (*Юрий Филипченко*, 1882 - 1930), the famous Russian entomologist. Before moving to the USA, Dobzhansky published 35 scientific works on entomology, genetics and zootechnique. In 1937, he published one of the major works of the modern evolutionary synthesis, the synthesis of evolutionary biology with genetics, entitled *Genetics and the Origin of Species*, which amongst other things, defined evolution as "a change in the frequency of an allele within a gene pool". Dobzhansky's work was instrumental in spreading the idea that it is through mutations in genes that natural selection takes place. Also in 1937, he became a naturalized citizen of the United States. During this time, he had a very public falling out with one of his *Drosophila* collaborators, Alfred Sturtevant (*Alfred Henry Sturtevant*, November 21, 1891. Jacksonville, Ill. - April 5, 1970, Pasadena, Cf), based primarily in professional competition. In 1941, Dobzhansky was awarded the *Daniel Giraud Elliot Medal* from the *National Academy of Sciences*. He returned to *Columbia University* from 1940 to 1962. In 1972 he was elected the first president of the BGA (*Behavior Genetics Association*), and was recognised by the society for his role in behavior genetics, and the founding of the society by the creation of the *Dobzhansky Award* (for a lifetime of outstanding scholarship in behavior genetics) [4].

Ford worked for many years on genetic polymorphism. Polymorphism in natural populations is frequent; the key feature is the occurrence together of two or more discontinuous forms of a species in some kind of balance. So long as the proportions of each form is above mutation rate, then selection must be the cause. As early as 1930. Fisher had discussed a situation where, with alleles at a single locus, the heterozygote is more viable than either homozygote. That is a typical genetic mechanism for causing this type of polymorphism. The work involves a synthesis of field observations, taxonomy, and laboratory genetics. Ford was an experimental naturalist who wanted to test evolution in nature. He virtually invented the field of research known as ecological genetics. His work on the wild populations of butterflies and moths was the first to show that the predictions made by Fisher (*Sir Ronald Aylmer Fisher*, February 17, 1890. London - July 29, 1962. Adelaide) were correct. He was the first to describe and define genetic polymorphism, and predicted that human blood group polymorphisms might be maintained in the population by providing some protection against disease. Six years after this prediction it was found to be so, and furthermore, heterozygous advantage was decisively established by a study of AB x AB crosses. His magnum opus was *Ecological Genetics*, which ran to four editions and was widely influential. He laid much of the groundwork for subsequent studies in this field, and was invited as a consultant to help set up similar research groups in several other countries [5].

Hewitt was born in Worcester UK in 1940. and attended The King's School there. He took his undergraduate degree at the *University of Birmingham* and stayed to complete a PhD with advisors Mather (*Sir Kenneth Mather*, June 22, 1911 - March 20, 1990), Jinks (*John Leonard Jinks*, October 21, 1929 - June 6, 1987), and Bernard (*John Bernard*, 1893 - 1983). He subsequently gained a *Fulbright fellowship* to study at the *University of California*, *Davis* in 1965 - 1966. On his return he took up a position at the newly established *University of East Anglia*, and he was promoted to Professor in 1988. He worked in the *School of Biological Sciences* until his retirement in 2005, and subsequently maintained a very substantial scientific output as Emeritus Professor. At the time of his death Hewitt had 250 peer reviewed academic publications and these had been cited by approximately ten thousand other articles according to *Web of Knowledge*. His most highly cited publications are in the area of phylogeography and hybrid zones. In particular Hewitt was influential in understanding the diversity of European biota in the context of glacial cycles. Hewitt served as President of the *European Society for Evolutionary Biology* from 1999 to 2001. He was awarded the 2005 *Molecular Ecology Prize*, and he received a *Lifetime Achievement Award* for creative mentoring in science (2006) from *Nature magazine* [6].

HUMAN ECOLOGY

Human ecology has a fragmented academic history with developments spread throughout a range of disciplines, including: home economics, geography, anthropology, sociology, zoology, and psychology. Some authors have argued that geography is human ecology. Human ecology is a natural systems that "builds on but moves beyond previous work (human ecology, ecological anthropology, environmental geography)." Other fields of human ecology include: cultural ecology, urban ecology, environmental sociology, and anthropological ecology. Human ecology has been defined as a type of analysis applied to the relations in human beings that was traditionally applied to plants and animals in ecology. In 1972. the editors of *Human Ecology: An Interdisciplinary Journal* gave an introductory statement on the scope of topics in human ecology. Their statement provides a broad overview on the interdisciplinary nature of the topic: Genetic, physiological, and social adaptation to the environment and to environmental change; The role of social, cultural, and psychological factors in the maintenance or disruption of ecosystems; Effects of population density on health, social organization, or environmental quality; New adaptive problems in urban environments; Interrelations of technological and environmental changes; The development of unifying principles in the study of biological and cultural adaptation; The genesis of maladaptions in human biological and cultural evolution; The relation of food quality and quantity to physical and intellectual performance and to demographic change; The application of computers, remote sensing devices, and other new tools and techniques.

Human ecology is initially considered as a medical science that has the task to study the influence of the environment on humans, human health and their interdependence. According Trol (*Carl Troll* 1899 - 1975), human ecology is close to biology, but also geoecology or agri and social geography. The aim of the study of human ecology is the balance of nature and society, with a particularly important role is played by social factors. The main task of human ecology that explores the nature of community structure. According to some theorists, human ecology includes specific aspects of human communities, the use of space by settlements in certain locations (zones housing - housing, office space and other facilities) [7]. Bearing in mind the definition of human ecology, and its emergence and development may be, feel free to say it is made up of four main themes: environment, population, technology and organization. One of the global environmental problems is increasing human population, the increasing overpopulation, especially in the cities, a serious threat to the environment, air, water, soil, leading to severe disturbances in the biosphere [8]. UN efforts have been made to better quality environment and in this regard organized an international conference related to the problems of environmental quality that surrounds us: United Nations Conference on the Human Environment (Stockholm, 1972); Conference on Environment and Development "Earth Summit" (Rio, 1992); Conference - Summit on Sustainable Development (Johannesburg, 2002).

THE FOUNDER OF HUMAN ECOLOGY

The term "Human ecology" announced Richards (*Ellen Henrietta Swallow Richards*, December 3, 1842 - March 30, 1911) *Sanitation in Daily Life*, defined there as: "The study of the surroundings of human beings in the effects they produce on the lives of men" (Figure 3). Richard's use of the term recognized humans as part of rather than separate from nature. The term made its first formal appearance in the field of sociology in the 1921 book *Introduction to the Science of Sociology*, published by Park (*Robert Ezra Park*, February 14, 1864 - February 7, 1944) and Burgess (*Ernest Watson Burgess*, May 16, 1886 - December 27, 1966).

Figure 3. Ellen Henrietta Swallow Richards, 1842 - 1911

Their student, McKenze (*Roderick D. McKenzie*), helped solidify human ecology as a sub-discipline within the *Chicago school*. These authors emphasized the difference between human ecology and ecology in general by highlighting cultural evolution in human societies [9-11]. Biological ecologists have traditionally been reluctant to study human ecology gravitating instead to the allure of wild nature. Human ecology has a history of focusing attention on humans' impact on the biotic world. Sears (*Paul Bigelow Sears*, December 17, 1891 - April 30, 1990) was an early proponent of applying human ecology, addressing topics aimed at the population explosion of humanity, global resource limits, pollution, and published a comprehensive account on human ecology as a discipline in 1954. He saw the vast "explosion" of problems humans were creating for the environment and reminded us that "what is important is the work to be done rather than the label." "When we as a profession learn to diagnose the total landscape, not only as the basis of our culture, but as an expression of it, and to share our special knowledge as widely as we can, we need not fear that our work will be ignored or that our efforts will be unappreciated." [12]. Forty years later in the same journal, Bates (*Daniel G. Bates*) (2012) notes lines of continuity in the discipline and the way it has changed. Today there is greater emphasis on the problems facing individuals and how actors deal with them with the consequence that there is much more attention to decision-making at the individual level as people strategize and optimize risk, costs and benefits within specific contexts. Rather than attempting to formulate a cultural ecology or even a specifically "human ecology" model, researchers more often draw on demographic, economic and evolutionary theory as well as upon models derived from field ecology. While theoretical discussions continue, research published in *Human Ecology Review* suggests that recent discourse has shifted toward applying principles of human ecology. Some of these applications focus instead on addressing problems that cross disciplinary boundaries or transcend those boundaries altogether. Scholarship has increasingly tended away from Young's idea (*Gerald L. Young*) of a "unified theory" of human ecological knowledge - that human ecology may emerge as its own discipline - and more toward the pluralism best espoused by Shepard (*Paul Howe Shepard Jr.*, June 12, 1925 - July 27, 1996): that human ecology is healthiest when "running out in all directions." (Figure 4). But human ecology is neither anti-discipline nor anti-theory, rather it is the ongoing attempt to formulate, synthesize, and apply theory to bridge the widening schism between man and nature. This new human ecology emphasizes complexity over reductionism, focuses on changes over stable states, and expands ecological concepts beyond plants and animals to include people.

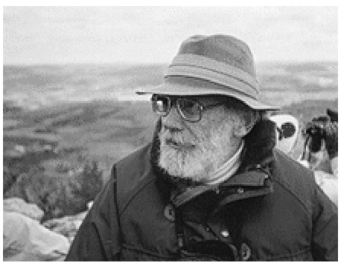

Figure 4. Paul Howe Shepard Jr., 1925 - 1996

CONCLUSION

Human health and ecological risk assessment is a single unit , which is a capital research topic of natural and technical sciences, and all the human sciences concerned with human destiny. Ecology, as well as research, particularly in the field of science, there is a distant historical roots, but only since Charles Darwin (*Charles Darwin*, Shrewsbury, February 12, 1809. - April 19, 1882. Daun) explores the systematic , scientific methods [13]. The protagonists of modern ecology are: Dobzhansky, Ford, Hewit, Richards, Park, Burgess, McKenzie, Sears, Bates, Young, Shepard and Troll, who have specific research in zoology, botany, and in genetics, ecology profiled, as well as interdisciplinary, multidisciplinary and transdisciplinary science. The relationship of man and the environment, perhaps best defines the message from Jean-Baptiste Lamarck (*Zoological Philosophy*, 1809).

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DEVELOPMENT OF ECOLOGICAL EDUCATION IN SERBIA

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ABSTRACT

Ecologicaleducation should provide knowledge of basic environmental issues of contemporary society, develop a critical attitude towards the growing environmental degradation and indicates the necessity of rational use of natural resources. The system of environmental education plays an important role in the formation of ecological culture of modern man. Educational process as a function of ecology is a conscious and planned development of man's knowledge of the environment in the course of their lives. This behaviour is aimed at raising awareness about the basic characteristics of the human environment, the relationships within it and the relationship with her. Environmental education is an understanding of the problems of general ecologization of material and spiritual activities of the society.Ecological education in Serbia will fulfill its mission if it starts the active eco-political change of awareness and behavior of individuals and if it develops new understanding of educational process itself. Ecologization of education in Serbia is increasingly viewed as a new paradigm, a trend of development and modernization of the educational system.

Key words:ecologicaleducation, environmental awareness, environmental protection.

INTRODUCTION

Ecologicaleducation is now an integral part of the educational process. The goal of ecological education is to make man preserve and enhance its environment, in order to become an integral part of his life, work and biological survival. In addition, environmental education has a duty to raise critical awareness of the necessity of preserving and promoting a healthy, ecologically clean environment, appropriate and worthy of man, and to familiarize them with the consequences of technological development and uncontrolled impact of development on ecosystems and human health. This is achieved by both institutional and outside institutional education. These two modes of ecological education must be connected to each other and aligned, because they are naturally directed to one another [1].

Without a good environmental education there is no healthy environment. All countries tend to perform better environmental education, and economic development policies have not paid much attention to the environment. Environmental education is taught, depending on the age, as a separate subject or course content, where the representation of environmental content in curricula depends on the educational profile of the issue and what is its closeness to the natural sciences and ecology [2]

Thus, outside the institutional education acquired within the family and through the mass media complements with the institutional, starting from pre-school through elementary and high school, to college and university education, including postgraduate and doctoral studies [1].

The most important goal of education is to achieve awareness of the real socio-ecological environment. Environmental awareness influences the creation of a lifestyle that is the nature of taking only as much as needed to provide basic human needs without compromising the balance of the environment. Raising environmental awareness has resulted in the acceptance and taking environmental and social responsibility. General understanding of the problem ecologization material and spiritual activities the society is environmental education. The system of environmental education plays an important role in the formation of ecological culture of modern man. Education - educational process as a function of ecology is a conscious and planned development of man's knowledge of the environment in the course of their lives. This behavior is aimed at raising awareness about the basic characteristics of the human environment, the relationships within it and the relationship with her. On the basis of that person will tend to the preservation and improvement of the environment.

FACTORS OF ECOLOGICAL EDUCATION

The basic principle of eco - education is expressed in the claim that environmental education is not only information about the eco - facts, the knowledge that students acquire are only at the level of awareness, but rather a life in educational institutions is in compliance with environmental requirements. Environmental awareness is not only the knowledge, but also on the emotional- volitional components is very important, because knowledge without belief and practical activity does not mean much. Environmental education and the formation of the ecological way of thinking begins in early childhood, and is, therefore, an important role of educational organizations at all levels of knowledge acquisition (primary-primary, secondary and tertiary). Therefore, the task of education, is learning to generations growing up and are in full action to address human environment had systematized knowledge about contemporary problems of human environment, the nature and essence of the dangers threatened environment, the way to eliminate the negative consequences of disturbed ecological balance [3].For a man to behave environmentally needs to be pre-formed, which is possible only by introducing environmental content in all levels of the education system from upbringings to education. Education teaching ecology must be approached very seriously and effectively, through innovation of curricula and introduction of regular organic content as a separate subject.

Important role in environmental education are factors such as: family, preschool institutions, schools, mass media and science. The most important factors of environmental education is considered to be a family. Personal example of parents is a powerful means of action on the development of desirable environmental values, habits, and norms of behavior in children. The family, as the most intimate micro-social environment through emotions such as ecological value, clean rivers, green lawns; fresh air is able to influence the beliefs and attitudes of its members towards these values. It primarily gives the opportunity to younger members to experience the emotional and adopt the attitude toward environmental values more than they can reason out the need for protection. Therefore it is of great importance as well as family environment provides the ability to achieve the objectives and tasks in the desired direction. Without adequate educational and socializing influence of the family in the transmission of environmental practices and environmental culture, there will be no real relationship and motivation of young members to gain knowledge and positive action in their everyday behavior [4]. A child is naturally curious and the greatest love and support it feels from its parents. If parents are anxious to preserve the environment, the child will adopt such a model of behavior as acceptable and such action and will continue growing up with constant learning and understanding how it grew. The family is the foundation to build good habits in children who are adopted, applying as adults and passing away to their offspring and younger generations. Of particular importance is how the family relates to everyday environmental degradation in the area of residence; any interest in the causes of its members; that the motives for them raises, positive or negative, environmental and, in turn, one of the lines of interest of creating more profits regardless of the consequences of environmental nature. Out of this will depend on the commitment of individuals to become and remain active members of environmental preservation [5].

An important factor in the development of environmental awareness of children are preschool to supplement family education. Throughout the game, the story and practice children can be introduced to the basic ecological principles, such as recycling, treatment, etc.. Ecological education in the preschool period is primarily focused on the emotional and moral development of the child's relationship to the world around him. Experiencing nature in all its diversity (water, air, soil, wildlife, energy) creates a strong emotional relationship with the ecosphere, and you later use this knowledge in identifying and solving environmental problems [4].

The main role of preschool and kindergarten teachers in guiding the child towards an emotional and sensory experience of nature, developing love for all living beings and acceptance of belonging to nature as their environment. The role of parents in building environmental awareness is particularly important in education of preschool children. In this context it is very important cooperation between parents and nursery, where it can take various forms such as, for example, parental involvement in educational activities, work activities involving parents, joint tours and excursions for children and teachers, participation parents in the organization and implementation of events, exhibitions and celebrations with the theme of conservation of natural resources and environmental protection [6]. Developed sense of caring and love for nature is the foundation on which the school-age children will build values, attitudes and habits that are based on ecological principles.

School as a social institution has a very important role in building environmental awareness. Some authors in terms of environmental awareness attach greater importance than school violence. This finding likely stems from the fact that knowledge of the environment in the school acquire the planned manner in order that she used during her entire life. Thanks to this approach, a person will tend to the preservation and improvement of the environment both in the present and in the future [4].

School is an institution that can provide much more knowledge on environmental protection of the family, because it has expertise in this area. If environmental activities involved in teaching, starting from elementary school through middle and high schools to universities, in terms of the environmental behavior of individuals can expect a positive long-term effects. A necessary condition for the development of continuing education and learning in this area is the learning and acquisition of knowledge related to environmental protection in the formal education system. The affinity and training of teachers depends, to a large extent, will be conducted correlation between subjects in the educational process with the experience and knowledge of the students and how much will be paid to environmental amenities. Therefore, great attention must be paid to ongoing professional training of teachers through additional training and seminars. Significantly, as the school itself as an institution involved in serious activities that are organized at the local community level and that, in general, there is no such kind of cooperation. Environmental education is taught, depending on the age, as a separate subject or course content, where the representation of environmental content in curricula depends on the educational profile of the issue and what is its closeness to the natural sciences and ecology.

The media is a powerful tool in shaping environmental awareness. These are: television, radio, the discussion about the environment, newspapers, magazines, internet, books, talks, exhibitions and the like. Means of mass communication, as opposed to the school is a source of non-formal environmental education, and perhaps because of this, and friendly source of information. Internet in recent years, slowly climbing to the top of the ladder on the topics and discussions of ecology. Numerous sites are environmental protection, monitor their condition and contain forums in which citizens express their opinions and suggestions.

ECOLOGICAL EDUCATION IN SERBIA

The Chapter 36 of the "Agenda 21", *"Promotion of education at school, environmental awareness, professional education and lifelong learning",* particularly emphasizes the importance of environmental education.One of the main activities which has contributed to realization of these goals in Serbia is the preparation of the national strategy for synchronization of the educational process at all levels with the principles of sustainable development and the new philosophy of life.A beginning of ecological thinking is based on change of the human's understanding of the nature, the realization that the human being has a special place in the world in which he lives. The awareness of the 'harmony of the nature' and the 'harmony with the nature' is the essence of logical thinking and realization of the interactive relationship between a man and the nature. An important characteristic of the new value is human understanding that he is a part of the ecosystem, a part of the nature.Thus, the human being spiritually matures, builds himself within the rules and laws mediated by the nature, and individual and social behavior of humans have been measured on the basis of their ecological thinking.

Building the sustainable relationship with nature through its new understanding is the idea of innovative learning and education which has obtained the epithet of sustainable environmental education, taking into account the ecological perspective. In that sense, in Serbia there are attempts to redefine the aims of education in the context of the development of environmental awareness, while the environmental education obtains a special place and role in the activities of the school.The aim of the environmental educationis to create awareness among young people to the issue of environment and ecological behavior, the readiness for responsible treatment of the environment, which should continue even after the time spent at school.

Thus the environmental education becomes the teaching principle, being emphasized as (one of) the major guidelines in the educational content (curriculum). It implies two basic approaches to realization of the teaching activities. The first one is environmentally friendly approach, which mostly fits into the curricula of biology, geography, physics, chemistry, technical education, and mathematics. The second one is related to a man and a society and fits into the contents of history, Serbian language, sociology, and art and music culture. The contents of environmental education and didactic materials designed for them equally take care of both approaches with mutual continuous interlinking. The Projects of all integrated subjects with environmental issues, which elaborate the objective state of natural-technical and social fields, with the participation of religion, music and art, have been particularly suitable for more conscious perception of the life base jeopardizing on planet Earth. Socio-politicaljustification and cognitive perception are equally required as appreciation of aesthetic aspects of untouched nature and ethical responsibility to all contemporaries of the Earth [7].

Environmental education in Serbia is particularly emphasized in the field of basic education (primary schools), considering the importance of the formation of the proper relationship with environment at this age. Also, environmental education has its place on all levels of formal education, from preschool through secondary to tertiary education. It is not only formal but also informal education and in this regard the goals of our neighboring countries are being followed [8, 9]. Environment related topics in the Serbian primary schools are taught in biology, physics and chemistry; in the four-year secondary vocational schools in biology, in the gymnasium as a part of biology, chemistry, geography, and physics. Within the subject or topics of ecology and environmental protection, in secondary schools in Serbia there are no field trips in any of the programs, which is a major drawback. These contents are taught in classrooms only, in the humble conditions offered by our schools, often limited to lectures by a teacher regurgitated by students, often boring and monotonous. At universities, ecology is taught at the Faculty of Natural Sciences (Novi Sad, Kragujevac), and Faculty of Biology (Belgrade). In addition, issues related to environmental protection are taught by other faculties, such as faculty of forestry, technology and metallurgy, agriculture, chemistry, philosophy, and workplace safety [8]. One of the major shortcomings of formal education in Serbia is the lack of interdisciplinary and multidisciplinary approaches to environmental education; however, there are other obstacles to the successful realization of environmental education in institutions of higher education and other educational institutions, that are related to organizational, technical, financial and human element on which we will further elaborate.

At schools in Serbia, as a rule, children learn about what is wrong with their environment. This learning includes experiments and measurements outside the school.Teaching pays little attention to practicing the students' skills to recognize eco-conflicts and deal with them (e.g. the role of ecological and environmental problems in the local policy, conflicts of ecology and economics, the principles of sustainability...), missing things which in OECD technical terms refer to the 'teaching complexity'. In order to process conflicts in teaching, the school must be open to contact with places where the eco-policy and the environmental protection actually take place. Holistic thinking and actions refer both to the interdisciplinary teaching and learning and to openness of schools to the local environment. The openness of schools must be seriously considered, and environmental issues should be learnt not only within the school subjects, but also based on their social and political implications.

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Ecological contents should provide high school students with eco-knowledge which would be useful for them while performing certain jobs, but would also provide ecologically-educated professionals after the completion of secondary education. As for the elementary education, one should also define standards for all jobs and career paths which would clearly specify the knowledge, competences and skills that students need to acquire during the secondary education. Students who are educated for certain jobs dealing with environmental protection should be trained to monitor, measure and analyze the polluters and apply prevention and protection measures.

Spheres between the ecology and economy have been just outlined in our education system so far. We need models that will help both those who teach and those who learn to creatively discuss the conflicts arising at home, at workplace, in leisure time. Some of the topics: environmental durability testing, analysis of the productivity line, eco-balances, the overall eco-calculations; relation between the ecology and health, arrangement of sustainable lifestyles and development as a leading target of eco-education. Global issues would have to be elaborated as situational and process-oriented activity, with an attempt to research, since they are prerequisites for acquiring the eco-competent action. However, teachers in our schools are often resigned, since it is difficult to predict processes that do not depend on them, and it is difficult to notice the consequences of the "ecologized school" for teachers and learners. There are often contradictions between their own actions and demands of teaching. Raising awareness and qualification of teachers is the core of the political agenda for promotion of the environmental education in Serbia [11].

CONCLUSION

The contents of environmental education and didactic materials designed for them equally take care of both approaches with continuous mutual interlinking. On one hand, the environmental education is understood as a teaching principle that covers all subjects, while on the other hand, it is found, contextually and methodically, in particular (specific) subjects after elaboration of specific topics (eg the problem of land, waters, flora and fauna, waste, noise, atmosphere ...).

The question that arises is whether environmental education in Serbia can not cope with all the problems that are in the context of Serbian society.Environmental education, on the one hand, is an integral part of prevention policy of every political rule in Serbia, and on the other hand, it lacks a comprehensive feasibility study (both because of lack of methodological instruments and because of the chronic lack of funds). Acceptance of ecological concepts is always accompanied by the current social pressure (job positions before environmental protection) and this is reflected in the treatment of environmental education.

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SUSTAINABLE DESIGN PHILOSOPHY, PRINCIPLES AND PRACTICES: TOWARD A NEW CONTEXT FOR DESIGN CODES

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ABSTRACT

The science of ecology has given a radically expanded views of the natural environment, insights into its working processes that never existed before, and the inspirational foundation for a new design iconography. This article explores how a heightened awareness of earth-centric information has influenced architecture and design in the end of 20th century and at the beginning of the 21st century. It explores relationships between construction and environment, new sources of form and content, and a confirmation that the art of design is in the promising stage of a revolutionary transformation that will ultimately change the way of living.

Key words: design, ecology, sustainability, philosophy, practice, recycling.

INTRODUCTION

The predictions of some of our best environmental specialist still go unheeded, or they are watered down for reasons of political expedience and corporate greed to a level where the public is deluded into a state of satisfaction. There are many literatures that have examined the subject of green design as though it was simply one more problem to be resolved through advanced technology. While the goal of sustainable living can be strengthened by such environmentally progressive innovations as the use of recycled materials, thermal (smart) glass, energy efficient construction methods, and photovoltaic solar collectors, most of these solutions tend to isolate the means from the mission. The mission calls for commitment by societies everywhere to unite to common cause and to connect on the natural environment on a more profound philosophical, psychological and cultural level.

Robert Venturi opened designers' mind the parallels in communicative imagery to be found in historic civic and religious architecture, contemporary commercial structures, and vernacular design which had been excluded from consideration [1]. Venturi admonished architects and designers for their inflexibility and enslavement to hand-me-down and derivative design vocabularies. He opened up new horizons by creating an awareness of the potency of a design of signs and symbols and reviled the deeper implications behind the popular culture iconography. The initial triumphs of Modern Design were inspired by the industrial evolution and industrial dream. From the begging of the 20^{th} century to the 1930s, designers passionately believed there was a direct equation between the combustion engine and a vision for shelter. Today one has to observe the bleak legacy of this vision in cities around the world to see how these ideals have degenerated through repetition in the hands of mediocre followers of the Modern Movement. As long as different designs (form small products to buildings) are seen as isolated events, all the same mistakes will be compounded over and over again. Venturi understood this problem and made a change. However, the revolution has been slow in gaining a secure foothold.

Wines suggested that the aesthetic value of design should no longer be seen as exclusively as a sculptural art of abstract from, space, and structure, but should rather shift the focus to informational and contextual associations relating more to a dialogue in the mind [2]. He sees design as a means of critical commentary on the basic definition of design, design products as hybrid fusions of representations and abstraction. While the design discourse in the 1970s and 1980s tended to treat product art as insular subjects, isolated by its own theoretical obfuscation, Wines saw solutions as transitional toward the far more urgent challenges of an ecological initiative. Today, rapidly growing field of eco-psychology is displacing limited perspective through the realization that mental disorders are frequently the consequence of humanity's alienation of nature. Design, as a fundamental part of matrix for human survival, can hardly afford to remain separated from the larger environmental picture.

Literature dealing with ecological design is limited. One notable exception is Jencks' book, *The Architecture of Jumping Universe.* He includes into his theoretical premise also eco-centric sources as an exploration for designs demonstrating elements of disjointed geometry and convoluted organic shapes [3]. Jencks also makes very little evaluative distinction between designs with admirable environmental contributions and those with only exaggerated sculptural forms. These structures are often made in such ecologically offensive materials as stainless steel and endangered wood products, or sheathed in toxic waste producing metals like titanium, copper, and aluminum. On the other hand Wines advocate a "nature first" policy. This paper will present some recent products of design (and architecture) that has contributed to significant changes in environmental thinking. It will look at the subjects from a conceptual, aesthetic and philosophical viewpoint. Also, it will identify the motivational ideas behind designer's approach that show promise for the development of an ecologically inspired art of building in the Age of Ecology and Sustainability. Plastic materials are commonly used in household and industrial applications such as food packaging. The low cost, light weight, high strength, transparency, printing capabilities and superior barrier properties to gas and water are very important properties of plastics used in packaging materials. High strength and durability, which makes them useful and cost effective materials in packaging applications, can become a key problem after use when disposing of these plastics in landfills.

SUSTAINABLE DESIGN PROCEDURES

There have been some exceptionally creative designs accomplished in the cause of ecological design that deserves to be mentioned. At the same time there has been also much to regret as a result of the minimal effect of these efforts on any change in societal awareness in total. Wines sees this impotency as the lack of a consensus philosophy, or the absence of the philosophy that might lend communicative power and credibility of this efforts. It is significant to outline Wines' key ecological designing procedures available to the design profession [4]. Also it is important to keep these procedures in mind while analyzing examples of todays' eco-designs. Wines provided us with the eco-friendly checklist:

1. Smaller projects – modestly scaled projects is a logical alternative to mega-structures assaults on land and resources.
2. Use of recycled and renewable materials – attention should be paid on the original selection of materials; materials which have recycling potential as a result of their production technology.
3. Use of low-embodied-energy materials – designers should select materials with attention to the entire biography of their products, materials which may appear to be environmentally favorable from a manufactory standpoint.
4. Use of harvested wood – effort should be made to use only harvested wood in construction and furnishings and avoid all imported exotic woods as much as possible.
5. Water catchment system – water is essential to all life on earth; designs should include the recycling of grey water, and maintenance of reservoirs.
6. Low maintenance – reduction of fossil fuels for heating and cooling, and development of technologies adapted to regional climates.
7. Recycling of design products and buildings.
8. Reduction of ozone-depleting chemicals – refers back on material choice, recycling, and finding alternative energy sources.
9. Preservation of the natural environment.
10. Energy efficiency.
11. Solar orientation – when talking in context of architecture, buildings should be situated to take full seasonal advantage of the sun's position and its energy-generating potential.

For certain designers, the latest advances in engineering and environmental technology are central to their objectives; while for others it is important to return to the use of indigenous methods and materials. For this other group the resources of topography, vegetation, solar energy and the earth itself are the means to achieve an expanded vision of organic design. Wines gives categorical areas of design activity, this is crucial for further analyzing design examples. These general categories include:

1. The fusion of design products or buildings with the context, and usage the elements of earth and vegetation.
2. The combination of dwell and garden space, creation of microcosms.

3. The use of nature-related symbolism as a means of connecting design to cultural context.
4. A translation of the most advanced environmental technology and materials and processes into aesthetic terms.
5. Green design research and environmental technology innovations that provide the foundations of sustainable and ecologically responsible design.
6. Design ideas that encourage a new acceptance of green design.
7. Environmental attitudes that have implications for the design profession in terms of conceptual thinking.
8. Visionary and conceptual ideas in design that offer prophetic visions for future, based on changes in global communications and social and political influences that may affect the design discipline and environmental policies.

INTEGRATION OF DESIGN AND ENVIRONMENT

Certain designers and architects have constructed or conceptualized designs which represent impressive models of ecological principles. All of the works illustrated here includes admirable contributions to eco-friendly design and very high level of aesthetic invention. Emilio Ambasz, the argentine architect whose career stretched from Princeton University and the architecture-and-design wing of Museum of Modern Art to Veneto, Italy, where he designed modern medical building. His conceptual direction fits most of the admirable characteristics of green design – the fusion of the context, innovative uses of landscape, symbolism, environment technology and visionary theory. His actual elements of architecture structure are often reduced to minimal geometry, functioning as coded directional to frame the presence of landscape. For example, a classic example of Ambasz's Fukuoka Prefectural International Hall, Japan, completed in 1994, drapes foliage over one million square meters of office space, parking and retail (fig.1). This building represents one of the most important examples of architecture as the garden. People who visit or work in this building use its green façade for strolling, jogging, relaxing, and other level participation. The other, more recent project of this architect is L'Ospedale dell'Angelo (fig.2). This hospital is the world's first green general hospital with the big glace face angles over a palm and fern-studded atrium. This glass face of the building (more than seven times the length of basketball court) has created greenhouse condition in parts of the hospital. Patients' rooms line an inverted ziggurat above the garden inside [5].

Figure 1. Emilio Ambasz, Fukuoka, Japan, 1995.

Figure 2. Emilio Ambasz, Mestre, Italy, 2008.

Designers Marjan van Aubel and James Shaw set out to put wood shaving to use, after learning that fifty to eighty percent of raw timber is wasted in the milling process that makes most wooden furniture. Designers began experimenting with a mix of shavings and bio-resin, which foams to produce a lightweight yet strong material. They then used conventionally milled legs to create a chair that combines both a milled object and the waste created by the milling process (fig.3). Colors were added to create the pastel impressions [6]. Design should make an important contribution to the preservation of the environment. It conserves resources and minimizes physical and visual pollution throughout the lifecycle of the product. This kind of design is offered by furniture design company Vitsoe which turned near financial ruin into commercial success by working with designers and reducing waste in its production processes. By creating products that is built to last forever, it offers a sustainable shelf to its consumers (fig.3-right)[7].

Figure 3. Marjan van Aubel and James Shaw (left), and Vitsoe shelving systems (right)

TOWARD NEW DESIGN CODES

It has to be emphasized that virtually no form of design created today can be credited as authentically green. Everything that technologically dependent societies assume is essential for survival – including the remedial solutions offered by the most ecologically aware designers – is plugged into the same diminished sources of power. Every absorbed plate and foil insulator required to build a solar collector, every chemical detergent used in a waste-composting plant, every ream of paper needed to spread the ecological message is an additional drain on our sources. In the lager scope, green design is still nothing more than Band-Aid treatment where major surgery is required. On the other hand, every little bit counts.

In a majority of recent ecological designs, green orthodoxy is measured primarily by the degree of investment in energy-saving systems, the durability of construction materials, and the number of recycled products used in fabrication. These days, sustainable design has become a camouflage to justify the work of some vociferously righteous, but very bad, designers. Danger now is too much reliance on those people which have ideas of illusory visions of technological salvation. There is vastly more complex problem of psychological distress caused by a separation from natural environment and the lack of earth-centered philosophy. In this world, environmental commitments are mostly based on repair, not on cosmology – on salvage. Environmental commitments represent neither a significant change of priorities in consumer culture, nor any new revelations about our connections to the earth. When evaluating ecologically actions we are forced to see them as manly defensive, curatorial, and beneficial.

Day-to-day survival mechanisms of design still require the designer get up in the morning and make a living. This usually means to select one of these choices: resigning oneself to a teaching job in academia, or taking on the next available commissions for some commercial project. In job opportunities offered by conventional business or civic clients, the issue of higher aesthetic choices rarely even enters the picture, much less any sympathy for ecologically initiatives. But, there are plenty of hopes for designers and ecological visionary today. After all, the seductive visual language and new materials of industrial production, along with the revolutionary ideas emerging in physics, were absolute antithesis of 19th-century romanticism and methodological science. They gave an opportunity to develop a new aesthetic sensibility directly responsive to sustainable design.

The supporters of environmental reform and ecological stewardship tend to speak of saving the earth as though the planet were some kind of patient in a recovery zone that should be restored to health for its own good. The earth is hardly the patient and certainly does not need saving. Wines says that the only real beneficiary in any conservation program is the human race itself. Design still has one of the most important conservation and communication roles to play in any new ecologically responsible vision of the future. The goal of designs as examples of green policy and as monitors of the collective psyche tends to be compromised by designer's dependence on the ponderous elements of fabrication technology. A great part of solutions, Wines believes, is technological, but filtered through a study of the way nature solves its own engineering problems.

CONCLUSION

And on the end, nature is primal, metamorphic, and endlessly ambiguous. It is rich in associations and the one totally universal source of ideas and symbolism in the design, architecture and arts. It is a genesis of communicative content that strips away redundancies and constantly reveals new information. Through its infinite complexity, nature is an instructive and inspirational influence that can expand the aesthetic horizons of the building arts and confirm the inalienable right of humanity to try to salvage a place on this planet before its too late. The key to a truly sustainable art of design for the new millennium will depend on the creation of bridges that connect conservation technology with an earth-centric philosophy and the capacity of designers to transform these integrated forces into a new visual language.

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DEVELOPMENT OF TRAINING PROGRAMS ON RISK MANAGEMENT IN ORGANIC FARMING

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ABSTRACT

The paper presents the development of a training program concerning risk management in organic farming under EDUECO project (Education of teachers in the field of ecological food production and management) financed by TEMPUS program of the European commission. It underlines the importance of competence-based and student-centered approaches in teaching and learning processes in one hand, as well as the importance of integrated approach on the other. Conclusions are madein connection to project outcomes' sustainability underlying EDUECO successful practices in capacity development and vocational training in ecological food production through the example of the program of submodule of risk management.

Key words: risk management, organic farming, training programs.

INTRODUCTION

The main goal of the project EDUECO is to build up educational capacities in universities in Serbia, Bosnia Herzegovina and Montenegro to support sustainable economic development of food production based on ecological principles. It is focusing on the following specific objectives: capacity building and professional network development among Western Balkan universities in the field of ecological food production and management; development and implementation of vocational training programs in ecological food production and management for teachers of secondary agricultural school; development of vocational training programs for end-users (i.e. producers and entrepreneurs of organic food) by university teachers, non-university teachers and teachers/trainers from related NGO's [2].

MATERIAL AND METHODS

The development of teacher training programs in Workpackage 2 of the EDUECO project (WP2) was described in connection to other project workpackages. The teacher training program of risk management in organic farming as a part of

People &Business module was discussed and presented according to the curriculum design worksheet prepared in the project.

RESULTS AND DISCUSSION

The EDUECO project offers three teacher training programs on ecological food production – one for each Western Balkan partner country (WBC) pointed above, which development and execution are supported by the EU partner countries (Netherlands, UK, Hungary and Bulgaria). The outlined courses on the basis of training needs analysis and workshops and discussions during the implementation of the university staff development work package (WP1) are subject of changes based on local needs. The idea of establishment of broad co-operation between educational institutes in WBC and others is elaborated in establishment of an international network (WP4).

Developed teacher training programs on "Ecologic food production and management" are targeted at educational staff of secondary vocational schools in agriculture in Serbia, Bosnia and Herzegovina and Montenegro. University staff develops modules, prepares teaching materials and offers training modules to the secondary school teachers.The programs intend some school modules and LLL courses in the field to be developed. The courses' outline contains general, national (per country) and individual (per school) learning targets. The new approach of working with the concept of learning objectives and of formulating learning outcomes is used as well as student centered learning process - job profile and individual competence development. Among the teaching and learning methods used should be underlined: lecturing, coaching, working on assignments and excursions.

The results of the first audit made by an internal project team in November 2013 [3] show that the progress in the project is significant in respect to the use and the application of new approaches in teaching and learning. In particular, the execution of the corresponding teacher training courses in each country, and their programs respectively, are assessed in five criteria: relevance of the program and integrated approach, quality of training materials, applicability and adaptability, orientation towards participants and interactions between participants and trainers and sustainability. The satisfaction of the participants in teacher training courses is assessed as follows:training contents, lecturers' presentations, teaching methods and answers to questions, rational use of training time, and practical use of knowledge and skills which gives the necessary feedback for the improvements made in the programs. On the other hand, the feedback of their performance makes estimates of their thinking "organic", communication skills and skills for team work, self-initiative, motivation and wish for improvement, study and reflection skills, and skills to work with specialized literature. The main conclusions embrace five different directions: design and organization of the program, expertise shares, training materials, evaluation outcomes from participants and teachers, improvement plans, stating that teacher training programs are prepared and organized very well taking into account participants profiles and thus participants (both trainers and trainees) share valuable expertise. Training materials are provided in native languages which fact broadens the number of users and the level of understanding and use.

The outline of the teacher training modules developed in EDUECO is shown on fig. 1. Modules of plant or animal production are provided according to the participants' profiles and interests while all others are offered to all of them.

1. General*	
2. Soil & Ecology*	
3.1. People & Business*	3.2. Risk management*
4.1. Plant production**	4.2. Animal production**
5. Processing*	
6. Teaching methods*	

Figure 1. Teacher training modules developed in EDUECO
* obligatory for all participants, ** optional modules

Among the questions of special importance directly linked to organic production sector development in the countries, and to trainings needed particularly, are a number of questions about organic conversion and certification, organic management, organic marketing, food quality and safety assurance, risk assessments and management, sustainable development issues, etc. from the point of which all the modules contents are developed. That way People & Business module is one of the modules with special emphasis on the phenomenon of entrepreneurial economy and the nature of organic entrepreneurshipand management embracing topics in connection to legal aspects and certification, administration, financing and marketing in small organic farms, as well as risk management and personal development. The question of risk management and risk assessment in particular in small organic farms is a subject of many debates and very often underestimated or overlooked. It should be treated in the proper way in order to avoid some misunderstandings, especially connected to the presumption of higher production and other expenditures in organic farms, higher prices of organic products and market difficulties and opportunities. Thus, risk management is developed as a submodule (Table 1) considering topics of basics and standards and formulating competences and learning outcomes according to the most essential questions in connection to long-term goals and sustainability assurance.

Table 1. Risk management in organic farming teacher training program
Author: Dr. Vesela Radovic[4]

Job profile, main tasks and responsibilities
▪ To train participants to understand the importance of risk management concept, vulnerability, and risk perception in organic farming, as well as the different risk level and recovery after an event of adverse conditions. ▪ To encourage personal and team skills, and sharing knowledge useful for future applying risk management techniques, especially regarding to the risk communication, as well as others which lead to the successful results of the providing training program.
General topic / theme
▪ **The importance of risk management in organic farming** (identifies all the risk; analyse each risk; evaluate each risk; treat the risk; monitor and review the treatment and communication). ▪ **The basic elements in a process of development risk management plan for small organic farm.** Learn how to minimize safety risk, taking account two primary aspects of risk management: 1. Anticipating that an unfavourable event may happen and acting to reduce the chances that it will happen to you, and

2. Accept that risk management is contingency planning taking actions ahead of time to reduce the negative consequences if something bad happens. ▪ **Brief overview of risk management standards in the European Union and international community**. The importance of typical risk rankings, and its implementation in practice. Understand contradictions between standards system and regulation, and practice. 1. Risk management–procedures and guidelines (Standard Australia AS/NYS ISO 31:2009) 2. Risk management in the EU Standards (EU-regulations for organic farming (Council Directives 2007/834/EC and 2008/889/EC).
Competences ▪ To offer participants opportunity to understand the urgent need for applying risk management in organic agriculture, taking on mind the fact that in Serbia risk management is in its infancy. ▪ To disseminate specific knowledge to all actors in the organic agriculture about specific risks which threaten them: production risks, GMO risks, input risks, marketplace risks, agricultural policy risks and etc? ▪ To propose a framework for future risk management strategies this should encompass cultural practice, marketing strategies and mutual support. ▪ To prove the urgent need for risk management assistance: general programs and crop insurance.
Learning Outcomes ▪ Ability to transfer knowledge necessary for applying the risk management tools in organic agriculture. That knowledge would be useful for minimise the negative impacts that markets, finances, weather condition, pests, diseases and other factor may have on organic agriculture. ▪ Ability to improve the skills necessary in risk communication and risk management planning that can be modified to suit a producer's specific situation. ▪ Provide information about the basic requirements for organic producers which have been given trough different standards. That will enable the actors to understand specific context in which implement risk management (both in production and control).
Assessment activities ▪ Understand the need of risk management in organic agriculture (the causes and sources of risk, their consequences and the likelihood that those consequences can occur) ▪ Present gained skills about risk management ▪ Design and complete the form of risk management plan for small organic farm ▪ Present the cases of ''good practice'' from region ▪ Participants in a training program learned the need of standards in risk assessment process and applied it to issues in their jobs.
Learning in and from practice Participants would have opportunity to show their ability in solving different kind of risks, common in organic agriculture practice. They will analyze risk monitoring techniques to determine risk occurrence and effectiveness of treatment source of risk. Also, they will be able to establish creativity and show good judgement in managing of small farm.
Summary of participants activities This part of training program will contain participation activities which will help them to become acquainted with each other and creating a spirit of cooperation and interdependence (**team building**); learning about attitudes, knowledge, end experience of the participants(**on –the –spot assessment)** and creating initial interest in training topic (i**mmediate learning involvement).** It means that trainer will use open exercises, open discussion, subgroup discussions, and other appropriate methods.
Essential questions ▪ How to avoid creating unnecessary complexities and lack of understanding about risk management in organic agriculture? ▪ How to conform the necessity of risk communication in (absence of official risk management standards in country) in activities which should lead to increased consumer confidence. ▪ How to provide the permanent training for teacher about risk management in organic agriculture and do not just think about short term goals?

In development of teacher training programs, and in the Risk management submodule in particular, the following dimensions of sustainable development are taken into account: social, ecologic, economic, cultural and accountability dimension, as considered by IFOAM [1] from the point of view of sustainable agriculture and sustainable development, especially in connection to ecological food production with high levels of quality and safety.

CONCLUSION

Development of teacher training courses, and the particular example of the submodule "Risk management in organic farming", along with all other activities of the seven work packages of EDUECO, is an example how to create successful practices not only in capacity development and trainings in ecological food production, and organic farming in particular, but also in encouraging sector development based on a number of activities of regional co-operation in the educational sphere and in close connection to world trends of sector development and good practices. Formulating the modules' titles, contents and relevant assignments, the programs underline the essential competences and learning outcomes for organic sector. The established practice of including target groups in a feedback procedure for making improvements, along with the broad institutional project impact in the region, are closely connected to the assurance of sustainability of the project especially in terms of life-long learning development and encouraging entrepreneurship in organic production.

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ECO TOURISM AND SUSTAINABLE DEVELOPMENT

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ABSTRACT

Ecotourism is more dependent on the environment than any other industrial branch. Tourism depends on the environment, but also eco-tourism is the main user of the environment.The sustainable development implies the use and exploitation of today's resources in such a way that these resources (natural and social tourist attractions and ambiance) will be available for use for future generations too.

Key words : eco-tourism, sustainable tourism, development, environment.

INTRODUCTION

The increasing interest of the countries in the world for the development of the tourism sector is primarily explained by the fact that tourism produces many positive economic effects and that tourism can be used as a factor in the rapid economic development.In the second half of the 20th century in many countries, the concept of tourism developmentwas applied which took into account only the achievement of economic goals of tourism development that is actually reduced to the achievement of greater profits.However, today, even though the achievement of economic goals is a priority, many countries have begun to pay more attention to environmental interests of destinations. This is a result of the adoption of a new concept of tourism development which is known as the concept of sustainable tourism development.

Thus tourism is starting through various stages in its development, at the end of the last century it has begun a new phase of development, known as sustainable tourism. Sustainable tourism is often defined in the literature as a positive approach that seeks to alleviate the tensions that result from complex interactions between the tourism industry, visitors, the environment and society as a host.It is a modern approach to tourism development which implies the establishment of a positive relationship and links between tourism development and environmental protection and achieving complete harmony between economic and environmental interests.Only responsible tourism, ecotourism, namely tourism that is based on respect of environmental concerns, can provide permanent maintenance of a balance between the environment and tourism development.

ECOTOURISM

Discussing the ecological value of the environment as important stakeholders in tourism development, increasingly in the literature dealing with tourism issues appears so called -Ecotourism.It is consisted of tourists who are interested in exploring the natural and cultural heritage, the specific and pure natural areas, while they themselves are oriented to the protection of the environment in which we move and live.

Considering that ecotourism is motivated by learning about and conserving of natural resources, and other resource development at the regional and local level, we can say that it is a kind of selective and sustainable tourism development.

Ecotourism is based on 4 principles:

- Environment. Ecotourism includes natural areas, protected areas or places that create interest in the biological, ecological and cultural sense.
- Resource Conservation. Ecotourism must play an active role and to give its own contribution to the conservation of resources.
- Use for local residents. Ecotourism is a form of tourism that it must contribute to the development of the local population through its economic, cultural and social influences.
- Travel experience. Ecotourism should include components of education and interpretation of natural and cultural aspects of each place (a tourist destination).Visitors need to learn about the cultural achievements of the place they visit, to develop an understanding of nature and natural processes that take place at that location, thus to raise their environmental awareness and education to the higher level.

Many people think that eco-tourist is any group that takes away tourist travel to unexplored regions and societies, to enjoy the nature of the destination, or think that eco-tourism means all tourism that takes place in a protected natural environment, national park or nature park.This might lead to confusion in tourism literature and to the concept of ecotourism we should look broader and should keep the above principles. Some scientific circles, which is today an example in certain countries, believe that tourism in the 21st century will become one of the most important economic sectors.However, we should not forget the negative environmental impacts of tourism, especially a massive tourism has on the environment. Therefore, tourist and economic importance should to tracked and compared to the environmental degradation of the entire environment.In this regard, over the need is to develop tourism as an environmentally, economically and socio-culturally sustainable tourism. It is necessary to develop selective forms of tourism and to move from massive tourism in order to meet the specific interests of tourists, with the "carrying capacity of the tourist destinations" which is the most important factor in the development of tourism in order to maintain the ecological balance of the destination itself.

For the successful development of ecotourism is particularly important quality, efficient and realistic planning, management and supervision of tourism and protected valuable natural resources. Accordingly, the environmental education has been promoted among tourists and locals, which is often required by state or private grants because the costs of maintaining protected areas are quite high and cannot be covered only through tourist taxes.

THE CONCEPT OF SUSTAINABLE TOURISM DEVELOPMENT

It is noted that at the same time by increasing of environmental degradation, the awareness of the need for its preservation and protection is growing too, and thus as a result of that awakening, the concept of sustainable tourism development has been developed.In fact, it is a concept which is linked to the emergence of so-called AGENDA 12, which was adopted in 1992 by 182 countries at the World Summit of the United Nations Conference on the natural environment and development, and which is dealing with the most important issues related to the environment.It is actually about the adoption of the program of actions and measures with the aim of sustainable development of the planet in the 21st century, which is among other things, referring to the development of the tourism industry. It can be said that it was from the moment of bringing Agenda 21, concept of sustainable tourism development has become more topical and more present in the world.It is noted that since the 90s of the twentieth century, most of the tourist destinations in the world are trying to improve its position and increase its market share in the international tourism market by applying this Agenda.

The sustainable development means the using and exploitation of today's resources in such a way that these resources will be available for future generations. In other words, spending today with tomorrow in mind is the essence of responsible tourism.Sustainable tourism development is mainly related to the construction of national parks and protected areas, namely the development of ecotourism in order to preserve and protect flora and fauna.However, although necessary, these activities are not sufficient to develop sustainable tourism. First of all, you must have the help and support and that is the active participation of the local population of these destinations in activities to preserve the environment.The application of this concept is to provide an increase in the quality of tourist products based on the protection of natural and cultural resources, but in practice its implementation requires management resources that will direct the economic activities within the environmental parameters.So the essence of the concept is to develop tourism based on the alignment of economic and environmental goals, and this is accomplished in a special model called eco-tourism.

Various studies confirm that the world is constantly increasing number of tourists for whom a healthy environment is very important criteria when choosing their holiday destination. How much tourists today care about preserved environment is shown in the research conducted on the German market in 2007 (Studienkrets fur Turismus und Entwicklung).

In fact according to the results of the survey 40% of Germans are willing to pay 1 euro per day on a holiday in order to help preserve the environment in their holiday destination. The study also found that for 80% of untouched environment is important in choosing their holiday destination, then that almost 55% of them prefer to experience nature in close contact on a holiday, and that 34% of them enjoy observing wildlife, but that 17% of them are angry because of destruction of the environment.These, and similar results of some recent studies suggest that in the future we can expect a further increase in tourists interest for a clean, healthy and intact environment and that the new types of demand, ecotourism demand, must not be ignored.

CONCLUSION

The uncontrolled use of natural resources and pollution of the environment in order to achieve the highest possible economic benefits in long term has negative impact on humanity. Responsible behavior of the current generation can reduce the consequences for future generations.Sustainable tourism, or ecotourism, is a model of development that primarily involves acting responsibly when it comes to the environment and use of natural resources.Ecotourism as a goal itself sets, primarily the preservation of important environmental values as part of the tourism product, and to achieve the necessary balance in which the meet of the current needs of tourists will not jeopardize meeting the needs of future generations.

As we have seen, ecotourism intervention efforts of all stakeholders in tourism development, but also is a guarantee of the preservation of both the economic and the environmental and cultural values, and in addition, as is often pointed out, provides protection of the biosphere, steady economic growth and equal distribution of life chances and it seems that this is a form of tourism that will lead to the development of tourism in the modern world.

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THE IMPACT OF TRAVEL AND TOURISM ON THE ROMANIAN PROTECTED AREAS CASE STUDY: MEHEDINŢI COUNTY

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ABSTRACT

Tourism in protected areas, a true "outdoor classrooms", is a growing attraction for advised tourists and for responsible lovers of tourism. By practicing responsible tourism man discovers, learns and meets new tourist destinations. At the same time, tourism involves a bi-univocal relationship, all tourists leaving their mark on the visited place through its interactions with the locals, other tourists or simply with the environment.

The protected areas in Romania are about two times lower than the European average, despite the efforts put on by authorities to expand these perimeters.

So far, in Romania 963 protected areas of national interest were declared, which cover over 7% of the country. Also, 400 Natura 2000 sites have been identified (273 pSCIs and 108 SPAs), whose area represent 17.84% of the Romanian national territory. 5 wetlands (Ramsar sites), 3 biosphere reserves and one natural and cultural world heritage site obtained international recognition.

Key words: protected areas, tourism destination, tourism, site, heritage.

INTRODUCTION

Officially 7% of the country is constituted from protected national areas, while the European average is 12-15%.

The area of protected natural areas in the Mehedinti county is 76582.5 ha, including the related area of the two county parks (74203 ha), respectively the Iron Gates Natural Park (total area 115 656 ha – across the Mehedinti and Caras-Severin counties) and the Domogled Valley National Park - Cernei (covers parts of Mehedinti, Gorj, Caraş-Severin counties - stretching over 60,100 ha), protected areas outside of parks (1287 ha) and the two wetlands (1102 ha), Hinova - Ostrovul Corbului and Gârla Mare – Salcia. This area represents 15.6% of the county (490,000 ha).

The protected natural areas of Mehedinţi County according to the 5/2000 Law, are in number of 32 with an area of 2205.5 ha. An example of sustainable and ecological development of a benchmark tourist area in the Mehedinţi county is (and hopefully will

remain) the Iron Gates Natural Park which brings its geographical space a series of "superlative" such as:
Danube Gorge - the longest gorge in Europe (134 km);

- the most stretched Natural Park of Romania (115655 ha);
- the largest hydropower station in Romania (Hydropower and Navigation System Iron Gates I)
- protected area with the greatest ethnic diversity in Romania
- geological and geomorphological diversity that can confer special status of an outdoor geological museum;
- high biological diversity - over 1600 vegetal taxons (higher plants) and over 5200 faunistic taxons;
- high diversity of plant associations, in this space **171** associations being **identified**, of which **26 are endemic to Romania** and **21 of community interest**;
- presence of some wetlands which are important habitats for protected bird species worldwide;
- traces of human settlements during the Paleolithic, Mesolithic, Neolithic era - historical evidence attesting the living of the area: cities, monasteries, churches;
- buildings with historic and architectural value, unique operating system watermills;

Picture 1. Image from the Iron Gates Natural Park

A **National Park** is a protected area whose primary goal is the protection and conservation of landscapes created by the harmonious interaction of human activities with nature over time (Law no. 462/2001).

The objectives of the Iron Gates Natural Park are: conservation of landscape and biodiversity, the ethnic and folk traditions, the cultural values, development of harmonious relations between nature and society by promoting activities without impact on the environment and also the international cooperation in the Danube River Basin biological conservation.

After 1990, the **Iron Gates Natural Park** has been mentioned in several legislative acts, the declaration and legal recognition is accomplished only through the

Law no. 5/2000. The spatial delimitations and management structure of the Iron Gates Natural Park was done by the **Government Decision no. 230/2003**.

The Iron Gates Natural Park covers an area of 115 655 ha. Located in the south-western Romania, its space belongs to the Caraş-Severin and Mehedinţi counties. The Natural Park limits are represented by the navigable channel Danube to the south, the River Nera on the west, the watershed tributary rivers of Danube to the north (partly) and the sinuous line that starts downstream of Gura Văii to the Peak Motărăţ on the east. This natural reservation, adjoining the National Ecological Park in Yugoslavia, on the Belgrade-Timoc segment - based on a joint program of cooperation with Serbia in the perspective of the **Danube Strategy** - would create a broad ecological region of large expanse, with interest for the three neighboring countries with particularly conducive economic and social implications to the Balkans, with perspective of sustainable integration (including tourism) in the EU.

Conducting touristic activities, the second phase of running sustainable tourism lies in the active involvement of all those involved (local suppliers of travel services with the local authorities and local population) in actions of solving environmental problems using economic or legal leverage to compel firms to use environmental protection equipment.

On the other hand, tourists are also required to limit environmental pollution during holidays, by better informing and educating them by other travel agents (tour operators, suppliers, tourism organizations, NGOs, etc.), having the joint purpose to support the development of sustainable tourism.

Continuing the work of education in the spirit of ecotourism should be achieved by the development of the environmental awareness of the population, twinned with feelings of love and respect for nature, historical places, monuments of art and architecture from throughout the ages.

It is necessary to sustain the environment and the tourist potential in the area in order to raise awareness of the communities about the benefic evolution of eco-tourism. To prevent an environmental catastrophe that would irreversibly change the current parameters of the area are biotope and biocenosis (the Danube ecosystem) we highlight the main causes of the ecological impacts in the area and the occurred changes:

1) *The pollution of the tributary waters of Danubei* from the Baziaş spring and from Baziaş to the end of the Mehedinţi county – Salcia and down to the shedding of the Olt river, with:

- pesticide;
- oil;
- heavy metals;
- chemical fertilizers;
- basic or acidic bases loaded with chemical residues, from tannery, wood and cellulose industry.

2) *radioactive pollution of the Danube tributaries* with sources from the Yugoslav territory in the Maidanpek mining area and Kozloduy in the Bulgarian territory.

3) *air pollution with various gas* (SO_2, NO_2, CL, F, etc.) with sources from the Heavy Water Aggregate, Drobeta Turnu Severin Cellulose Aggregate and their involvement in the Danube area affecting the flora, fauna and even the Danube waters.

As a result of the concentration of the pollutants referred to above, in the Danube adjacent area deep changes occurred in the biosphere system, namely:

a) *the deterioration of the Danube system* by altering the biocenotic structure through:

- The disappearance of plant species mainly forests as a result of the change of ratio in the components of air and the acid rain loaded with SO2;
- The disappearance of fish due to the eutrophication of lakes and the bays formed by the Danube, or in connection with the eutrophication caused by the increased concentration of nitrogen in the water. The growth is determined by washing the nitrogen fertilizers in the vicinable arable area, the discharge of untreated stormwaters and manure from livestock and urban settlements;
- almost the complete disappearance of sturgeons determined by the changes in the breeding habits and the appearance of less valuable species of fish, determined by constructing the Iron Gates I and II dams;
- Danube river gaining dangerous microorganisms for human and animal life;
- Accidents caused by discharging into the Danube and tributary waters of heavy metals (Pb, As, Cd, Hg, etc.) pesticide, oil, radionuclides.

b) *The deterioration of the danube aquatic ecosystem* by constructing dams and irrigation canals:

- The upstream construction of hidropower plants;
- The construction of hidropower plants in Mehedinti county;
- Building irrigation systems particularly in the Mehedinti, Dolj and Olt counties, affecting nearly half a million hectares of which a fifth in the Mehedinti county.

The deterioration of the danube ecosystem can be explained as follows:

- Blocking the flow of sturgeon reproduction and consequently their disappearance from the Iron Gate (I and II) ecosystem, just as happened in lakes from Asuan, Egipt, Kariba (Zambia), or the construction of the Panama Canal.
- Modifying the parameters of life of the evolved and relatively valuable fish such as: carp, bream, perch, tench, pike, due to the increased pressure and intra aquatic temperature accompanied by the decreasing oxygen. This is due to the increase of depth, the decrease of flow rate, the increased amounts of nitrogen, phosphorus, sulfur, etc. accompanied by eutrophying elements.

c) *The deterioration of the Danube* by introducing new species, deterioration obvious by replacing specific species of meadow with more valuable but obviously unsuitable species.

d) *The deterioration of the Iron Gates ecosystem* by overexploitation of species of trees manifested by unrational wood cutting and deforestation, made for giving back agriculture land for hunting and fishing without particular concern for species regeneration.

A possible program for environmental protection in the Danube ecosystem and particularly in the Iron Gates area refers to:

1) *protecting the atmosphere* through adequate measures in the Heavy Water Power Plant, the Cellulose Aggregate, the Tire Factory from Turnu Severin, referring only to the polluted objectives from the Romanian territory;
2) *applying the law severly*, making it known to the public and giving penalties that can go to the closing of the polluting agents.

An important role comes to the biological-geographical research station subordinated to the Romanian Academy and the University of Bucharest, Faculty of Geography, whose role should be enhanced, restructuring its activity regarding areas such as: wildlife, wild flora, flora cultivation, forestry, fruit viticulture and in the territories:

- ✓ Belgrad – Baziaş area;
- ✓ Baziaş Şviniţa area;
- ✓ Şviniţa – PF1dam area;
- ✓ PF1 dam – PF2 dam area;
- ✓ PF2 dam area – confluence with Olt river.

In this case higher levels steps need to be taken in order to transform the Orşova resort in the Central Resort with predominantly ecological character which must have corresponding territory branches. Also, the resort must be equipped with adequate laboratory to the ECE system, which can be able to determine the gradual pollution of air, water and foods: heavy metals, pesticides, SO2, NH3, Cl, F, oil, fertilizers, bacteria, viruses, fungi , radionuclides, toxic substances.

3) *Organizing an laboratoy that can* begin tracking the inventory, setting the frequency of the structures in the ecosystem of individuals and populations specific to the biocenosis of the Danube area.
The actions of protecting the ecosystem include:
a) compliance with applicable law and especially the law on environmental protection:

- 🕮 Protecting the forests;
- 🕮 Protecting the meadows;
- 🕮 Protecting the acquatic and terrestrial fauna;

b) recycling the household wastes in burning or composting plants;
c) practicing ecological agriculture by replacing the pesticide based on heavy metals, phosphorus and chlorine by combating the biologically integrated;
d) protecting the population and the bordering settlements;
e) Further development and investment only in locations where the change does not affect the ecological balance;
f) organizing joint actions with Serbia and Hungary;
g) integrating the Danube ecological zone in the tourist circuit by:

- ⇨ The enhance of value of the natural treasure and unique natural area with the development of activities in order to conserve and not disrupt the ecosystem balance;
- ⇨ tourist valorization of the Iron Gates Gorge (Cazanele Mari, Cazanele Mici, Drumul Roman, Cetatea Romană Drobeta, formaţiunile carstice, traseele Craiova-Turnu Severin-Orşova-Herculane, Orşova-Moldova Nouă, Turnu Severin-Ostrovul Mare-Calafat).

Among the **ecotourism activities** that can be performed in the Iron Gates Natural Park we can specify:

- *mountain tourism* (marked tourist routes - Pemilor Route, connecting all villages inhabited by Czechs in the Iron Gate park);
- *Danube Cruises* (leaving from Orşova);
- *Scientific tourism* (for habitats and species of protected plants and animals);
- *speology* (in the limestone areas of the Park: Cazanele Dunării, Coronini-Moldova Nouă-Gârnic, Sirinia),
- *birdwatching* (in the wetlands in the west of the Iron Gates Natural Park)
- *Recreational fishing* (on the Danube - catfish, carp, pike, sterlet, etc and in the interior rivers - trout, barbel, etc..);
- *traditional festivities and celebrations* (Neda, minority celebrations);
- *Traditional cuisine* (fish, goat meat, dairy products, vegetables, sweets specialities);
- *Nautical danube sports* (canoeing, kayaking, jet skiing);
- *bike touring and mountain biking*;
- *ski fond* (on forest roads);
- *cultural sightseeing* (arheological, religious);
- *visiting water mills in the* Elişeva, Povalina, Cameniţa valleys;
- *visiting museums and collections* (museums of ethnographic and religious collections)
- *visiting villages populated by ethnic Czech and Serbian.*

Scientific tourism in protected areas is mainly done by experts in disciplines related to natural and biological support of the area; it has development conditions because of the existing natural reservations and reservoirs in the county. The areas that can be promoted in this form of tourism are: the National Park "Iron Gates", the "Domogled - Cerna Valley" and other protected monuments, provided the principles of sustainable tourism[2] are applied, thus avoiding the negative effects of tourism phenomenon in the protected space.

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[2] Mirela Mazilu,Turism și Dezvoltare Durabilă,Editura Universitaria,Craiova,2012,p.31

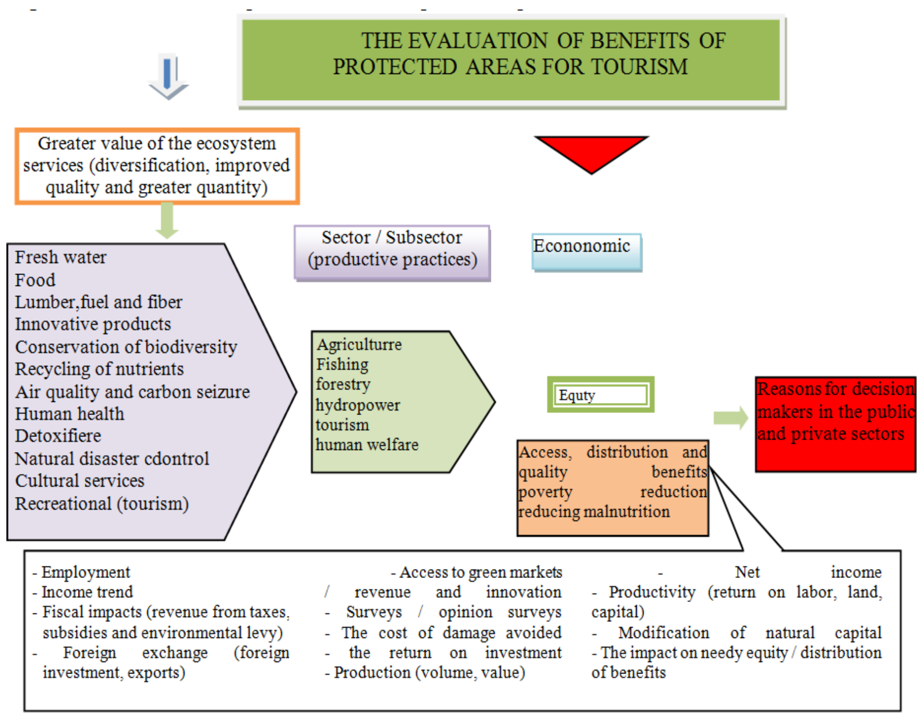

Figure 2. The benefits of protected areas for tourism

In the last decade, international bodies like the World Tourism Organization and the United Nations stressed the importance of a responsible, sustainable development and preservation of natural and anthropogenic elements engaged in tourism, taking into account the following documents, discussions and recommendations:

The Global Code of Ethics in Tourism, adopted by the World Tourism Organization, which aims to promote responsible and sustainable tourism that adheres to fair tourism, responsible and sustainable, with an ultimate goal: the elimination of poverty by practicing responsible tourism;

Agenda 21 with its latest additions, adopted by the World Tourism Organization, which stresses that progress in tourism necessitates the provision of distinct interest in the environment, the development of responsible tourism gaining more and more followers;

Tourism Industry Report (2002) conducted by UN agencies recommending the promotion of responsible tourism in partnership with the private sector, NGOs, civil society and governments;

The first International Conference on Responsible Tourism destination (Cape Town 2002), in which it was emphasized that responsible tourism should not be seen as another expression of tourism, but as a distinct approach to programming and implementation of sustainable tourism activity.

The recent (2014) amendments to the law on protected areas made by Members of the Committee for Public Administration, Ecological Territorial Planning and Balance of the Chamber of Deputies contains prohibitions on equestrian tourism, camping and cycling tourism in the protected areas.

Also recently, the evaluation of the Romanian[3] National Strategy for Tourism **(SDNT)**, having as a central base the Master Plan for the Romanian National Tourism (2007 – 2026) is vital because it corelates the variety of documents regarding the tourist planing from the ECE countries, and it underlines the considerable influence of tourism on the economy, quality of life and long term benefits in the tourism industry.

As well as all the East and Central European countries, Romania needs a complex national strategy for developing tourism, that can respect and administer the natural and cultural resources as a competitive advantage, in the context of the european and international tourism markets.

The evaluation showed that the Romanian tourism strategy only **fulfills 42,4%** (medium) the analised indicators (table 1):

Table 1. Fulfilment of assessment criteria in analysed national documents (in %).

Document / Thematic field	Bulgaria	Moldova	Poland	Romania	Ukraine	Ivano-Frankivsk
Description and elaboration process	75	43	60	47	41	49
Situation analysis and programming	94	37	71	45	18	82
Sustainable approach to tourism in policies	81	71	58	20	52	67
Participation of institutions in tourism management	95	56	78	69	80	80
Business, supply and PAs	83	27	70	17	43	57
Strategy measures	83	32	19	59	6	63
Financing and implementation	68	43	75	46	11	64

Source: The results of the National Tourism Development Strategy Assessments - 2012

Also one of the recommendations that were made in the final assessment emphasizes that **sustainable tourism development should not only be a simple statement**, **but a real priority**, supported **by clear objectives, expected results**, **consistent actions and monitoring**. In 2014, after seven years from finding "*the environment is damaged and on nationwide level there is no concern about the environment*" recognized in the Romanian Tourism Master Plan by international specialists, we immediately see that nothing has changed.

The impact of tourism on the protected areas in Romania, shown in the following table truly shows the "economic contribution" of the protected areas in the tourism industry, unfortunately omitting the total cost of repairs needed in the areas of ongoing irresponsible, unchecked tourism phenomenons.

[3] *http://www.ceeweb.org/wp-content/uploads/2012/02/CEEweb_STWG_NTDS-Assessment-Methodology-final.pdf*

Table 2. The impact of travel and tourism on protected areas in 2012 (million euros)

	Total internal and international tourism [1]	**Total leisure trips [2]**	**AP Tourism [3]**
a. Visitor export	1.356,3	1.274,9	112,2
b. Domestic expenditures	2.069,0	1.944,8	171,1
c. Individual expenses of the state	46,0	43,2	3,8
d. Purchases by tourism service providers	-1.816,1	-1.707,1	-150,2
Direct contribution to GDP (million euros)	**1.655,2**	**1.555,9**	**136,9**
Other impacts (indirect and induced)			
Internal purchasing chain	1.724,1	1.620,7	142,6
Capital investments	2.344,8	2.204,1	193,9
Collective expenditure of the state	252,9	237,7	20,9
Imported goods with indirect costs	-2.436,8	-2.290,6	-201,5
Induced	873,6	821,1	72,2
Indirect and induced contribution to GDP (million euros)	**2.758,6**	**2.593,1**	**228,1**
The total contribution to GDP (millions of euros)	**4.413,8**	**4.149,0**	**365,0**
Employment ('000 jobs)			
Direct Employment	234,3	220,2	19,4
Indirect Employment	214,3	201,4	17,7
Total Employment ('000 jobs)	448,6	421,7	37,1

Source: [1] WTTC 2012, [2] derivated from the WTTC figures for 2010 and 2011, [3] calculated proportionately on the basis of tourists data records managed by NIS and INCDT.

CONCLUSIONS

It is important for local and regional tourism development that sustainable development requires harmonized support to national processes. On the other hand the state policy has to be connected to international sustainability agreements.

The criteria of the strategy assessment were elaborated in light of the EU biodiversity policies (EU Biodiversity Strategy to 2020) and the Agenda 21 for a Sustainable and Competitive European Tourism[4].

These include sustainable conservation and management of natural and cultural resources, minimizing use of resources and pollution at tourist destinations including the production of waste, managing changes in the interests of the well being of the community, reducing the seasonality of demand, addressing the environmental impact of transport linked to tourism, making tourism experiences available to all without discrimination, and improving the quality of jobs in tourism.

The tourism policy expressed in a strategy should focus on climate change, habitat destruction and the loss of species, potable water availability, solid and liquid waste pollution and others problems expressed in agreements and policy documents on European level.

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According to the sustainability concept which has been developed in last 20 years tourism development should be carried out in a way that:

- ✓ use of resources, both natural and cultural, should be non consumptive, making them renewable,
- ✓ supports the local economy, being an opportunity for remote communities,
- ✓ provides a linkage between different sectors like private-public sector, forestry, agriculture, handicrafts etc.,
- ✓ provides an economic incentive to conserve natural and cultural assets,
- ✓ foster greater understanding between people (and interested parties).

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ASPECTS REGARDING THE POSSIBILITY OF DEVELOPING ECOTOURISM IN BAZOŞ, TIMIŞ COUNTY, ROMANIA

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ABSTRACT

Ecotourism can be considered a chance given for the population of major urban areas, for those who appreciate nature and respect it. Favored for the development of tourism in general and ecotourism in particular, are mountainous and hill areas.

The existence of protected areas, even in plain areas creates the possibility of developing this type of tourism.

A nature reserve forest is located near Timisoara, one of national interest, the Arboretum in Bazoş where there are opportunities to develop ecotourism.

Key words: sustainable tourism, ecotourism, protected area, nature reserve.

INTRODUCTION

The environment consists of all elements, natural and artificial phenomenon existing on Earth, which conditions life. It underwent many changes over time, due to human activities and this has led to the concept of sustainable development. Pollution means contamination of the environment with materials that affect human health, the quality of life and the natural functioning of the ecosystems. The causes of appearance are: natural (volcanic eruptions, erosion, the decay of plant and animal residues) and artificial (human, industrial, agricultural, domestic activities). In urban areas polluted air and daily stress are issues that have not yet been solved, so the possibility of residents to spend a few days in a natural, unpolluted area is "saving". The duration of such outflows may be a day or even a month, depending on the free time, work program and income of the population. The natural environment has a major role in the decision to temporarily shift out of your personal residence to a chosen destination.

Usually the uniqueness, age, originality are the characteristics of tourism resources that draw potential tourists. The natural resources are better represented in the hilly and mountainous areas.

Tourism development and the enhancing of global tourist traffic is primarily due to the desire to escape from the polluted environment in one of relaxation and rest.

Avoiding degradation of tourism resources and ensuring an unpolluted environment is achieved by implementing and practicing sustainable tourism.

Tourism is the recreational activity that is dependent on the natural environment. Through sustainable tourism we understand the travelers' needs today, protecting the environment so that future generations benefit from current resources. In other words, the issue of tourist exploitation of the environment without degradation is put into consideration.

The known forms of sustainable tourism are rural, cultural, scientific and ecotourism, but sustainable tourism can be implemented in other forms of tourism as well. Vanguards propose theme parks and a virtual tours as forms of sustainable tourism. Ecotourism can be defined as a form of sustainable tourism that takes place in natural areas, preserving the environment and supporting local welfare.

At the basis of ecotourism development are several principles, namely:

- To minimize the negative impact on nature and local culture;
- Informing tourists about the importance of nature conservation;
- Raising funds for the conservation and management of protected areas;
- Operators need to cooperate with the public and local authorities to meet community needs;
- Regional tourism zoning and careful planning of tourist flows towards protected areas considered tourist destinations;
- Conduct studies, both social and environmental policies and programs for long-term monitoring to avoid imbalances;
- Maximizing the economic benefits of population in the area, companies and local communities;
- Development of tourism up to the specialists calculated (environmental pressure indicators and environmental status);
- General and specific development of the infrastructure in harmony with the natural environment and cultural ties in order to minimize negative impacts on vegetation, wildlife and culture.

Tourists eager to practice this form of tourism has to abide by a code of conduct which refers to:

- Preparing the holiday;
- Respecting the rules of the protected area;
- Respecting the flora, fauna and their habitat;
- Own impact on the environment;
- Relations with local communities.

Those interested in ecotourism are generally people who love nature, who respect it and want to be part of it. The characteristics of such a tourist are of socio demographic order, motivation and the related to travels. The age of ecotourism is in the range of 35-54 years, their education is superior and they have above average income. Regarding the gender, there are no differences, both women and men love ecotourism. Such holidays last between 8 and 14 days, the spending per person hovering between 1,000 and 1,500 dollars, the money being invested in various equipment, magazines and even donations. Ecotourists prefer not to travel alone, but in couple or with friends. Their motives are related to nature, they want to get to know it, to study it, looking for a new adventure and that their preferences are not high the accommodation accepted are in tents, lodges, motels and B & B.

Promoting ecotourism we can say that we seek to maintain life in its natural habitat and environmental quality. However, the escape of humans in nature and rebuilding their health is important and supported by ecotourism.

PROTECTED AREAS IN TIMIŞ COUNTY, ROMANIA

According to current legislation „the protected area is the area of land, and / or groundwater and aquatic area, whose perimeter has a legally established special protection and conservation regime, in which there are species of plants and wildlife, elements of biogeographic formations, landscape, geological, paleontological, speleological or otherwise, the ecological, scientific of cultural value".[5]

The categories at national level are scientific reserves, national parks, natural monuments, nature reserves and natural parks. In order to declare an area as a protected area, regardless of its category it is necessary to submit the documentation that includes a study of scientific substantiation, a topographic map of the area, the exact area of land and legal situation and the opinion of the Romanian Academy.

In Romania 1,234,608.12 ha are protected areas in which there are scientific reserves, nature reserves and natural monuments represent 8%, the rest being national parks, natural and biosphere reserves.

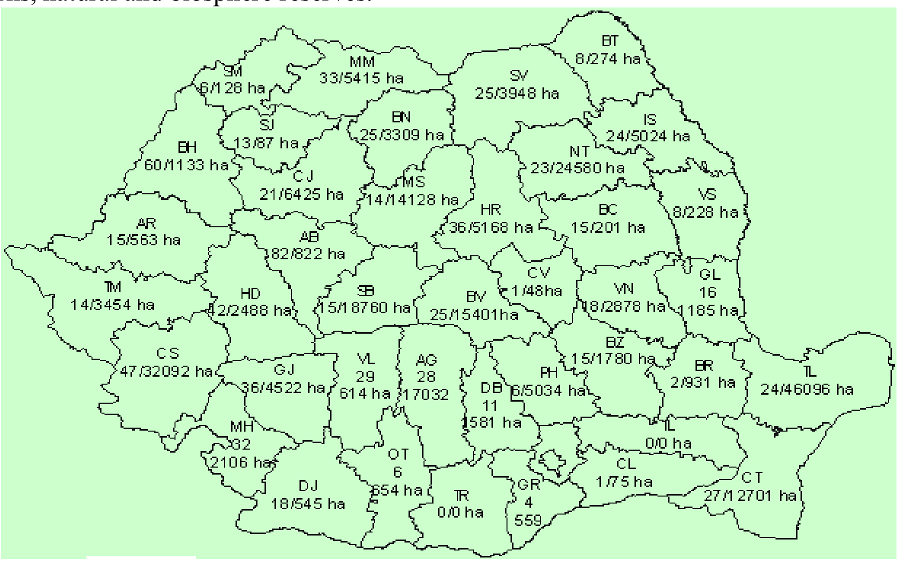

Figure 1. Biosphere reserves and national natural parks in Romania
(Data from MAPM)

[5] Ordonanţa de Urgenţă a Guvernului nr.236/2000 privind regimul ariilor naturale

Timis County is located in the south-western Romania, in the historical area of Banat, the most sprawling county of the country (8696.7 km ² - 3.6% of Romania's total area) and having the westernmost point of the country, the city of Beba Veche, $20^{0}16$'eastern longitude. By its geographical position is considered as a gateway to the West, the distances between the residence city and also the most important city in the county, Timişoara and some European capitals are relatively small, Belgrade (170 km), Budapest (280 km), Vienna (520 km), Bucharest (550 km), Zagreb (551 km), Prague (851 km).

Forever this part of the country was regarded as a model of tolerance and coexistence area between ethnic populations and a multicultural area. According to statistics in that county the share of population by ethnicity is 83.4% Romanian, 7.5% Hungarians, 2.4% gypsy, 2.1% German, 2.0% Serbs and 2.6% other nationalities.

The county predominant landform is the plain area, low in the west and high in the middle, it represents 75.9% of the total area of the county, followed by hills -7.3%, 7.2% hill-mountain, plain-hill - 6.3% and 3.3% mountains.

However, in Timis county protected areas of national interest can be found, declared by the Law no. 5 in 6 March 2000 relating to the approval of the National Spatial Plan - Section III - protected areas.

Table1. Protected areas in Timis county, Romania

Protected area name	Location	Type of protected area IUCN	Type	Area (ha)
Bazoş Arboretum	Remetea Mare	IV	Forest	60
Igriş island	Sânpetru Mare	IV	Mixed	3
Big island of Cenad	Cenad	IV	Mixed	3
Surduc lake	Fârdea	IV	Mixed	362
Pogănişului meadow	Sacoșu Turcesc, Tormac	IV	Botanical	75,5
Rădmăreşti fossil place	Bara	IV	Paleontological	4
Șișitak mound	Sânpetru Mare	IV	Botanical	0,5
Murani swamp	Murani	IV	Ornitological	200
Satchinez swamp	Satchinez	IV	Ornitological	236
Daffodils meadow Bătești	Făget	IV	Botanical	20
Bistra forest	Ghiroda	IV	Forest	19,9
Cenad forest	Cenad	IV	Forest	279,2
Ornithological reserve Beba Veche	Pordeanu	IV	Ornitological	2187
Sărăturile Diniaş	Peciu Nou	IV	Pedological	4

Source: Landscaping plan of Timis County (PAJT) - Phase II, Volume 3, protected areas, tourism January 2013

As shown, these protected areas all fall under the IUCN, category IV (habitat management area / species) being natural reserves of national interest. Their aim is conservation through active management interventions. In the county, special protection areas for birds (SPA) are ROSPA0047 Hunedoara Timişană, ROSPA0069 Lower Mures Meadow, ROSPA0078 Satchinez swamp, ROSPA0079 Murani swamps, ROSPA0095 Macedonia Forest, ROSPA0029 Lower Mures Gorge and Lipovei hills.

Sites of Community Importance (SCI) are ROSCI0064 Lower Mures Gorge, ROSCI0108 Lower Mures Meadow, ROSCI0109 Timis Meadow, ROSCI0115 Satchinez swamp, ROSCI0250 Pădureni area. One can talk about the existence of a wetland of international importance and considered a natural park, the Mures Floodplain Natural Park (only a small part of 3157.59 ha which is in the county).

The protected areas of local interest complement to the protected areas in the Timis County.

Table 2. Protected areas of local interest

Area name	Location	Type	Area (ha)
Buziaş forest park	Buziaş	Mixed	25,16
Dumbrava forest	Buziaş	Forest	310
Banloc park	Banloc	Mixed	8
Secular oaks from Lovrin	Lovrin	forest	6

Source: Landscaping plan of Timis County (PAJT) - Phase II, Volume 3, protected areas, tourism January 2013

The importance of protected areas, regardless of their type and surface is special for maintaining the "health" of the environment.

DEVELOPING ECOTOURISM IN BAZOS

Just 20 km away from Timisoara is the Bazoş Arboretum, a nature reserve forest type which covers an area of 60 hectares.

Since 1867 the Oak Forest and land was property of the Ambrozy family. During 1909-1914, Ludovic Ambrozy arranged the forest as a park, bringing specimens of collection trees from the breeding grounds at the Harvard University. This transformation was performed using the German landscape painter Franz Von Engerhord, director of the botanical garden in Düsseldorf. With the start of the arrangement of the park the construction of a castle begins as well, which unfortunately was demolished in 1934. Agrarian reform of 1922 determines the Hungarian Count Louis Ambrozy to leave Romania and settle in Vienna.

The park where there were 194 species of trees and shrubs was bought in 1934 by the State House of Rangers. This park contains one of the most valuable collections of trees and shrubs in Romania, with over 800 taxons.

The presented arboretum was declared in 1954 a scientific reserve, in 1988 a natural monument and in 1994 a protected area for biodiversity, ecofund and genofund protection.

The park structure is as follows:

- The Central Park - Oak Forest for over 160 years that spans 36 hectares;
- The American park - North American species (American oaks and Carya) with an area of 1.5 ha;
- Collection of Asian species naturalized in the area, and they stretch over an area of 1.5 ha;
- the Dendrological park with various species which runs on 11.5 ha;
- Seed nurseries and experimental crops totaling 9.5 ha.

According to current legislation that protected area has been assigned in custody by Convention 292 / 30.11.2011, under code 2738 to the Forest Research and Management Institute of Timisoara (ICAS). This public institution has legal personality and is under the Ministry of Environment and Forests (Law nr.46/2008). The Institute is aimed at scientific research, technological development, investment design, providing expert advice and implementation of technologies for sustainable forest management.

For tourism development so far has been done:

- Identification of sightseeing routes;
- Arrangement of paths (without concrete);
- Mounting plates for the recognition of protected species;
- Realization and installation of a map of the park;
- Remaking the entrance gate;
- Installation of traffic signs in Remetea Mare, which show the access point for the park.

A project to support the development of ecotourism is the arrangement of the former water tower, a building, the only one that remains from the castle of Count Ambrozy.

Tourism activities reffer to:

- Walks on arranged alleys;
- Actions of "tourism orientation"type;
- Observing species during the spring-summer-autumn time;
- Photographing trees and shrubs.

The accommodation and food for tourists can be provided at the edge of the protected area, where there is a parking and the entrance gate (Stejarul hotel and restaurant - 4 stars), and in the neighboring village guest houses (Casa Celia 3 stars hotel in Bucovăţ and Pension Zetas 3 stars in Remetea Mare).

Developing ecotourism in the natural reservation in the Arboretum from Bazoş can be achieved after developing and implementing a management plan that includes a series of actions to protect the environment and offer tourists a relaxing time and the information sought.

CONCLUSIONS

Ecotourism is a form of sustainable tourism that respects the environment, offering guests relaxation, leisure and awareness. The protected areas in Romania are diverse and they offer the possibility of developing ecotourism.

Located in the middle of the plains, 20 km from Timişoara, the natural reservation the Arboretum in Bazoş has a particular scientific value and is a great place for leisure. Now the area is not equipped to stay, only for one day recreations but it can be combined with an instructional activity. Lately the first steps towards improving the park for visitors keen for fresh air from Timisoara have been made. From spring to autumn the forest provides dreamlike images and relaxation.

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PRODUCTION PROCESS OF PROTECTIVE GLOVE, ASSESSMENT AND MANAGEMENT OF CHEMICAL HAZARDS

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ABSTRACT

Protective equipment factory, AD Trayal corporation, is one of the oldest industrial companies in Serbia . In all processes of production of protective devices a wide range of chemicals is used, that can cause large chemical accidents. For the known dangers of used chemicals, in the phase of their use in the production process,of their storage or transportation , assesses the existing chemical risk, provides for specific actions for its removal in order to manage it, in accordance with the Hazardous Substances and their threshold quantities, with the list of hazard classes and threshold quantity of hazardous substances. The aim of this work is that throughout the analysis of the technological process of production of protective gloves determines the risk of chemical contamination, estimates the risk and determines the necessary steps to manage with it.This paper presents the development of possible events and consequences in those critical areas where the estimated probability of occurrence of an accident is increased, such as leaking and evaporation of hazardous substances. Reviewing the applied preventive and technical and technological and organizational measures at the plant, as well as the fact that in the previous work were not recorded accidental situations, it can be concluded that the management of chemical risks in the production process is successful, and that there is low probability of accidents. Based on the possible effects on human life and health, and the environment, the risk is assessed as medium, which makes possible consequences serious, but the important conclusion is that the risk can be managed.

Key words : Accident, chemical risk level, risk management, probability and frequency of risk.

INTRODUCTION

Risk is the possibility of the formation of undesirable circumstances or events that in the case of exercise may significantly impair or endanger human lives, property, and ecosystem functioning. The interest in risk analysis is very increased in the last few decades. The reasons for the research and development of new methods of risk analysis arise from practical problems and needs. Systems in which the man is are becoming more complex, with both technical and technological aspects, as well as the organizational and social. A large and complex industrial systems, power plants, weapon systems, refineries, storage of hazardous materials, as well as many other similar objects, as a rule, contain potential failures that threaten the safety, health, life, or human environment.Thebuilding aim of this methodology is to,with preventative care, as much as possible avoid unintended consequences for different types of accidents, as well as the consequences of the accident amortized in the best possible way .

The risk assessment methodology or the risk existence of accidents and environmental pollution consists of three phases:

1. Risk of accidents analysis,
2. Measures of prevention, preparedness and response to accidents and
3. Elimination of accident consequences .

GENERAL CONSIDERATIONS

TRAYAL Corporation was founded in 1889. as a powder magazine Obilićevo . It was destroyed and renewed several times . After the Second World War in 1948. was named after the national hero Miloje Zakić . They built a factory of activated charcoal , tires and protective masks . From June in 1995. it function under the name TRAYAL Corporation AD. The factory was privatized in November 2006th , and privatization was terminated in December 2013th year. This year the factory celebrates 125 years of existence. Production at the factory Trayal Corporation AD today is organized into three core segments: protective equipment, industrial explosives and rubber manufacturing industry.[1,2]

Factory for protective equipment

Factory for protective equipment is the largest and most famous manufacturer of protective equipment for defense and civilian needs in Serbia . It has a long tradition. Within the bureau"Obilićevo" after World War I and the first use of poison gas, was initiated the development of products for respiratory protection from poison gas. In 1927. year was produced the first protective mask. In World War II many of the factory facilities were destroyed and after the war started with the construction of new facilities for the production of respiratory protection, face, hands and body, rubberized fabrics, collective filters, filters for purifying water and air as well as other related programs and products.

Funds from the program for personal protection covers a wide range of products intended to protect the body and respiratory system designed to provide durable and secure survival in contaminated areas. These products include: respirators and half masks, protective masks, protective gloves, protective clothing, protective suits - NBC, helmets, etc. .

Production of protective latex glove by dipping technology began in 1994. They are used for multiple hand protection against mechanical injury with sharp or rough objects. The anatomical design provide comfort while working. They are available in two sizes and are widely used in all areas of work. Protective gloves are harmonized with the European standards for hand protection. The glove set is shown in Picture 1. [3]

Figure 1. Protective gloves

The technological process for the production of protective gloves

In the operation of making rubber gloves with cotton pad by dipping technology, the raw material used is natural latex, toluene, acetic acid, sulfur, zinc oxide, sodium carboxymethyl cellulose, potassium hydroxide as well as various catalysts, antioxidants and pigments. From the listed chemicals, the greatest danger is natural latex, spending 500kg/day, toluene , 200kg/day consumption and acetic acid, the daily consumption of 3.24 kg.

The technological procedure of making gloves is shown in Figure 2 .The production process is continuous and is carried out in 10 phases. The production process is directly involving seven workers per shift, in the presence of technicians and supervisors. Capacity development glove on a monthly basis is 90 000 pairs. [4]

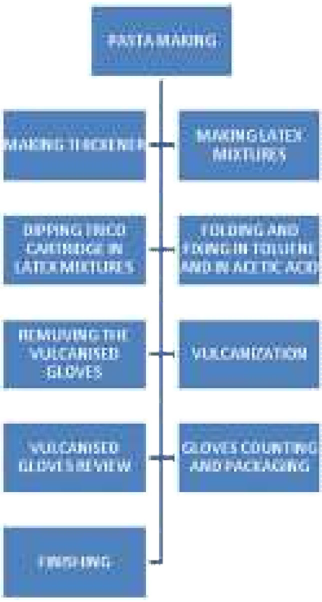

Figure 2. Schematic representation of the technological process of production of protective gloves. [4]

ASSESSMENT OF CHEMICAL RISK IN PRODUCTION OF PROTECTIVE GLOVES

In the operation of making the protective gloves used materials have the standard quality, out of which as potential contaminants emerge powder, emulsion, and liquid materials. Powders are Vulkacit LDA, sulfur and carboxymethyl cellulose etc . These substances are not combustible or toxic, the particle size is about 60 microns. Production of these substances on a daily basis is in grams. They are taken by ventilation through filters and retain there. Of liquid materials toluene is used so as acetic acid, whose daily production is below the maximum allowable concentration. They are taken by a local fan - mounted above the tub for dipping, which filters the air before it is discharged into the surrounding atmosphere. The operating ventilation is also used, which is equipped with air filters, so the potential air pollution does not exist .

An aqueous solution of latex is an emulsion containing 4 % bound ammonia on its own does not constitute a hazardous substance. Ammonia removal is done locally by operating ventilation through appropriate filters. The concentration of ammonia in the work environment is under maximum permitted. [5]

Institute for Prevention Novi Sad, was testing these substances presents in the workplace, and found that they do not exceed the maximum allowable concentrations in the working environment, according to the Rule book of inspection procedure and work equipment testing and working environment testing. Article 12 The results of these tests are shown in Table 1.

Table 1. The concentration of chemical hazards in the plant for the production of protective gloves [6]

Workplace	Type of chemical harmfulness	sampling location	concentrations found mg/m^3	MDK mg/m^3	comment
Dipping into a bath with acetic acid and toluene	acetic acid	Area of work of the employees in the hight of respiratory organs	1,25	25	Satisfying
	Toluene	Area of work of the employees in the hight of respiratory organs	45	375	Satisfying
Dipping gloves in latex mixture	Ammonia	Area of work of the employees in the hight of respiratory organs	2,90	18	Satisfying
On the platform- near Latex mixture mixer	Ammonia	Area of work of the employees in the hight of respiratory organs	4,80	18	Satisfying

Of these substances, the greatest danger is natural latex, toluene and acetic acid, while other raw materials are in powder form, and does not represent a significant threat because they are used in small concentrations.

Based on estimates of the probability of accidents and the possible consequences in the plant, with particular considered the most critical positions in the most adverse situations, the risk to human health and life, as well as the risk of material goods at the factory, can be quantified as a small to medium. Depending on the scope of the accident, and the risk to life and health of the population and material goods outside the complex would be in a different level. In the event of an accident less intensity risk would be practically negligible, while in the worst-case developments, the level of risk would be medium to very large. [7]

Overview of possible chemical accidents

In the production of protective gloves, the transport and storage of hazardous materials accidents that may occur are highlighting certain quantities of dangerous substances which are in the process (toluene, acetic acid), due to a malfunction, accident or any other event, or scenarios that can be classified as an accident. Also one of the most dangerous potential accidents at this location is a fire, or explosion in certain circumstances. Of possible, probable accidents that increase the chemical risk and can affect the quality of the working environment, are **1.**Fire in the discharge of toluene cistern to toluene tank**2.** Fire while pouring the toluene tank in toluol barrels, **3.** The fire in the folding and fixation of toluene and acetic acid, **4.** Poisoning with ammonia in latex barrels transport barrels to the factory and **5.** Ammonia poisoning if loosening the valve mixer for latex mixture.

In the first case, the discharge of toluene cistern to toluene tank leads to the ignition of toluene and the large-scale fire. Since the tank is bordered by flameable materials warehouse, fire can lead to disaster. This level of risk is assessed as very high.

In the second case, as in the first, there may be an accident . If not, the danger is the barrel transport to section. If the barrels in transport got damaged or overturned, there would be a effusion of toluene. Since it is a small amount of toluene, the fire would have been small-scale, but it could affect the whole plant. This level of risk is assessed as medium to very large .

In the third case, the wrinkling and fixing toluene and acetic acid, the improper handling of these chemicals, would come to its effusion from the tubs, sparking and high temperatures, and thus the appearance of fire. The fire would spread to the whole plant, but would not affect the wider range of plants. The dosing of chemicals is computerized ,and in case of failure, the tub should be doused larger amount of toluene and acetic acid, there would be a effusion of chemicals and fire. This level of risk is assessed as small to medium.

In the fourth case, duringlatex barrels transport to the factory,the barrels could be damaged due to unexpected traffic accidents, all quantities of chemicals could be poured out from the barrels. Every single barrel contains 205 liters of latex. An aqueous latex with content of related ammonia does not constitute dangerous substance itself, but at an elevated temperature, the ammonia fumes. In this case, it may cause poisoning drivers and persons present in the area and overruns permitted maximum concentration of ammonia in the air. This level of risk is assessed as small to medium.

In the fifth case, the easing of the mixer valve in which real latex compound for dosing in the manufacturing process, there would be a gradual evaporation of ammonia gas that would pollute the working environment and endanger the health of workers present. This level of risk is assessed as medium.

CHEMICAL RISK MANAGEMENT

Response to the accident involves a method response to the accident, as well as actors and agents response to the accident .

Critical emergencies, spread of fire, spilling fuel and etc. often preceded by certain " warning ", vibration, sound, leak, sudden variations of process parameters (temperature, pressure) than normal, and more. Instantly identification of the signal and the proper corrective action in many cases can prevent the further development of critical situations. In each of these cases, the employee must have a current overview of the entire situation and inform the immediate supervisor, who further informs the fire department and other relevant institutions. All workers must be skilled, trained and familiar with the potential hazards and the measures to be taken in order to react quickly in order to prevent large-scale accidents. In this respect Trayal Corporation workers are trained in the management of fire extinguishers, and tested every three years to verify their knowledge [8]. The Directorate for Security of Trayal Corporation Inc operates a fire unit, which is responsible for intervening in accidents, whose commander assessed, and if necessary, notify the fire brigade city of Krusevac . Officer for Safety and Health at Work, with license, train workers on safety measures at work with hazardous materials and keep records of periodic medical examinations of workers at workplaces with high risk, which include the production of protective gloves [9,10,11]. The facility can be operated only by workers who have been laid previously mentioned training and who have medical authorization to work in this workplace. [12,13]

CONCLUSION

Reviewing the extent possible accidents can be concluded that under the most unfavorable conditions possible level of accidents can be extended to parts of the colony, which is the level of risk is determined as the second level. Reviewing the applied technical and organizational measures that are in force at the plant and the fact that in previous work are not recorded any incidents, as well as the production is based on ready raw materials which are delivered to the factory, it can be concluded that the probability of accidents is low. Based on the possible effects on human life and health, and the environment, the risk is assessed as medium. Based on the adopted medium risk it can be concluded that the potential consequences can be serious . By all indications, it can be concluded that the Chemical risk can be managed in the production of protective gloves. Protective equipment factory at all times has a team of trained employees. All rooms are fitted with fire extinguishers, and the company section is incorporated with ventilation system to exhaust hazardous gases, it can be concluded that the current level of risk is acceptable .

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ADVANTAGES VERSUS DISADVANTAGES OF ECOLOGIC STUDIES IN ASSESSING ENVIRONMENTAL HEALTH

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ABSTRACT

A classical ecologic study examines the rates of disease in relation to a factor described on apopulation level. In spite of some limitations, asecologic fallacy, possibleconfounding, lack of preexisting databases quality data, ecologic studies remain a popular study design in assessing environmental health for several reasons:they can be done quickly and inexpensively,their analysis and presentation are relatively simple and easy to understand,they have the ability to achieve a wider range of exposure levels than could be expected from a typical individual-level study, they are particularly important for studies of the transmission of infectious disease.

Key words: epidemiologic methods, ecologic study, environmental health, advantage, disadvantage.

INTRODUCTION

A classical ecologic study examines the rates of disease in relation to a factor described on apopulation level. Thus, “the units of analysis are populations or groups of people rather than individuals”(1). The population-level factor may be an aggregate measure that summarizes the individual members of the population (for example, the proportion of individuals above the age of 65 years), an environmental measure that describes the geographic location where the population resides or works (for example, the air pollution level), or a global measure that has no analog on the individual level (such as the population density or existence of a specific law or health care system)(2).

Thus, the two key features that distinguish a traditional ecologic study from other types of epidemiologic studies are: the population unit of analysis and an exposure status that is the property of the population. Ecologic studies usually identify groups by place, time, or a combination of the two (2).

For example, researchers conducted an ecologic study with groups identified by place to determine the association between air pollution and mortality rates (3). The study authors obtained 1978–1981 air pollution levels from monitoring stations throughout the United States and 1980 mortality rates for 305 Standard Metropolitan Statistical Areas (SMSAs). SMSAs are geographic areas that typically include a city and its surrounding areas (1). The investigators examined correlations between the air pollution variables (such as total suspended particulates and sulfates) and mortality. They observed a positive association between annual mean sulfate concentration and total mortality. That is, SMSAs with high sulfate concentrations tended to have high mortality rates (for example, Scranton, Pennsylvania), while those with low sulfate concentrations tended to have low mortality rates (for example, Salt Lake City, Utah). Ecologic studies that identify groups by time often compare disease rates over time in geographically defined populations (2). A special type of time-trend ecologic study tries to separate the effects of three time-related variables: age, calendar time, and year of birth (2).

Some investigations cannot be classified as traditional ecologic studies because they have both ecologic and individual-level components. Consider, for example, a "partially" ecologic study that was recently conducted in Norway to determine if chlorinated drinking water was associated with the occurrence of birth defects (4). Chlorinated water contains numerous chemicals called disinfection byproducts that may be harmful to developing embryos. Because the study used group-level data on the exposure and individual-level data on the birth defects and confounding variables, it is considered partially ecologic. The study population consisted of children born in Norway from 1993 through 1995 who lived in an area with information on water chlorination (n = 141,077 children). Investigators examined the prevalence of birth defects in relation to the proportion of the population served by chlorinated water. They examined four groups of municipalities: those with 0% chlorinated water, 0.1% to 49.9% chlorinated water, 50 to 99.9% chlorinated water, and 100% chlorinated water. Individual-level characteristics that were controlled included maternal age and parity and place of birth, as obtained from the children's birth records. The study suggested there was a 15% increased risk of birth defects overall and a 99% increased risk of urinary tract defects among women whose water was chlorinated. However, the authors acknowledged that the study did not directly measure the concentrations of the disinfection byproducts on the individual level. The lack of individual-level information leads to a limitation of ecologic studies known as the "ecological fallacy" or "ecological bias." The ecological fallacy means that "an association observed between variables on an aggregate level does not necessarily represent the association that exists at the individual level"(1). In other words, one cannot necessarily infer the same relationship from the group level to the individual level. In the Norway study, we do not know if the women who drank chlorinated water were the same women who gave birth to babies with defects. This is particularly true for the two middle exposure groups (municipalities with 0.1 to 49.9% and 50 to 99.9% of the population with chlorinated water), because women with chlorinated and unchlorinated water were grouped together. On a practical level, the ecological bias means that the investigator cannot fill in the cells of a two-by-two table from the data available in a traditional ecologic study.

The aim of this review is to summarise main characteristics, advantages and disadvantages of the ecologic approach in assessing environmental health.

MATERIAL AND METHODS

We usedrelevant literature evidence on classical ecologic design in assessing environmental health. Main advantages and disadvantages of the ecologic approach were than discussed.

RESULTS AND DISCUSSION

Advantages. The main advantage of the ecologic approach is that it allowsthe study of very large populations. Because exposure and healthinformation are used on a group basis, there is a considerable increasein cost efficiency as compared to designs where individualdata are required. Alternative designs such as the case-controlmethod typically involve samples of at most several hundredcases and controls; the typical prospective cohort design mightinvolve at most several thousand individuals. But an ecologicdesign is capable of studying populations that are orders ofmagnitude larger. Ecologic studies have even been done to makeinternational comparisons, thereby including populations ofmany millions. An example is an analysis of the relationship ofcoronary heart disease mortality to the polyunsaturated/saturatedfat ratio in the diet of approximately 20 countries (5).

Another practical advantage of many ecologic studies is thatthey use existing databases. For instance, ifwaterquality data areroutinely available in a particular geographic area, and ifdiseaseoutcomes (e.g., incident casesofcancer) are recordedin a registry,then the two sources of data may be used directly, without thenecessity for contact with individual population members.

Both the ability to study large populations and the frequent useof available data imply that the ecologic design may be one ofthemost cost-efficient epidemiologic approaches. Further cost savingsmay result because it is often possible to execute an ecologicstudy in a relatively short period of time. There is no necessityto await the occurrence ofincident cases ofdisease, as is requiredin a cohort study; similarly, there is no need to wait for a caseseries of sufficient magnitude to accrue, as is required in case-control studies.

Because large populations can be studied using ecologicdesigns, one may investigate relatively small increases in risk.Environmental exposures that are associated with small ormoderateincreases in risk, but which apply to large segments ofthe population, are capable of generating quite large numbers ofcases of disease. Such factors can be of great significance topublic health. The overall impact of such exposures can be conveyednumerically by use of the population attributable risk index,which represents the proportion of all cases of disease in apopulation that might be associated with exposure (6,7). Thepopulation attributable risk is a function both of the relative riskof individuals exposed versus not exposed to the hazard in questionand of the proportion of the population which is exposed. Itis possible for the population attributable risk to attain quite highvalues when the exposure prevalence rate is high, even though therelative risk is only modest (8). However, in order to demonstratethe statistical significance of a small relative risk, largepopulations must be studied. The ecologic design is often wellsuited for this purpose.

An example of the "small risk, large population" scenario is that of low-level carcinogenicity in well water. Crump and Guess(9) have calculated an upper limit on the risk for all carcinogensidentified in well water in the United States. This is an estimated0.1% increase in lifetime excess risk for all cancers, and less thana 10% increase in the number of cases of rectal, colon, or bladdercancer individually. Crump and Guess concluded thatepidemiologic studies may overestimate the effect of drinkingwater on cancer rates, possibly because of confounding withother environmental risk factors not measured, because of collinearitybetween organic concentrations in water and other factorsin the environment, or because humans are more susceptiblethan animal species tested for carcinogenicity of the samecontaminants. They have concluded that "increased risks of rectal,bladder, and colon cancer of the magnitude suggested bythese studies are large enough to be ofconcern yet small enoughto be very difficult to separate from confounding risks associatedwith other environmental risk factors" (9).

Another advantage of the ecologic approach is its usefulness in the investigation of suspicious clusters of disease in relativelysmall geographic areas. Examples of this type include studiesof apparent increases in cancer rates near locally contaminatedwater supplies. Communities that suspect they are experiencingsudden or sustained increases in health event rates often demandthat epidemiologic investigations be carried out. Examples ofthiskind include an investigation of an outbreak of leukemia associatedwith industrially contaminated ground water in Woburn,Massachusetts (10), and the Upper Ottawa Street Landfill Studyin Hamilton, which investigated the health of residents near alandfill site, possibly subjected to airborne and waterborne contaminants (11).

A common feature of investigations of local health problemsis that a suitable comparison must be made to an appropriate controlgroup ofindividuals not exposed to the hazard in question.Some of these studies involve the use of mortality or cancerincidence registry data and can therefore be completely ecologicin nature, without requiring contact with the individuals in thestudy area. However, in practice the ecologic information is oftensupplemented with personal interviews concerning health and/or exposure to the postulated contaminant. If questionnaire or other individual data are used, the study ceases to be one with a pure ecologic design but assumes mixed design.

The population-level factor is particularly important for studies of the transmission of infectious disease. For example, investigators conducted an ecological analysis to determine the risk factors for dengue fever (a viral infection transmitted by the *Aedes aegypti* mosquito) in 70 Mexican villages(12).They measured exposure by the average proportion of *Aedes* larvae among households in each village in relation to the proportion of affected individuals in the village. The study found a strong relationship between dengue antibody levels and the village-level larval concentrations. This association was not seen when an individual-level study was carried out, because it did not take into account transmission dynamics at the population level.

*Disadvantages.*The strongest disadvantageof the ecologic design arisesbecause of its inherent feature ofusing aggregated data. Becausethejoint distribution ofexposure and health at the individual levelremains unknown, there is the possibility that the so-called"ecologic fallacy" would apply; this fallacy leads to possible distortion ofthe association between exposureand disease. It is possible for two variables to be apparentlyassociated in ecologic data, when no association exists at theindividual level; similarly, it is possible that two variables which are correlated at the individual level show no associationwhen studied in aggregated data. By careful attention tomethodologic issues in the design ofecologic studies, it may bepossible to minimize the effects ofthe ecologic fallacy; however,it is usually difficult to assess the likelihood ofan ecologic fallacyhaving occurred once a study has been completed.

The possibility of fallacious ecologic associations has ledmany epidemiologists to be critical ofthe ecologic method. Mostwould agree that it is generally preferable to use a nonecologicdesign ifthis is feasible. At the same time, ifan ecologic designis selected, it requires considerable attention to methodologic rigor in order to minimize the potential ecologic fallacy problem.

A second disadvantage ofthe ecologic approach is more practicalin nature. If existing databases are to be used with theecological method, then obviously one is limited by the extent ofthose databases. The use of routinely collected laboratory dataon water quality will by necessity restrict attention to thosevariables that have been measured. These variables may or maynot include the most relevant quantities for health investigations;specific carcinogens or bacteria may not have been explicitlymeasured and so cannot be studied.

The same type of limitation may apply to routinely availablehealth data. Disease registries may not include disease events ofinterest or may classify them with coding schemes that are inappropriateto the research study question. Mortality data, forinstance, areascertained onalmost 100% ofdeaths,butthecodedcause ofdeath may notalwaysbeaccurate. Inaddition, one mightbe interested in contributory causes ofdeath, ratherthanunderlyingcauses of death, and these may be difficult to extract fromroutine vital statistics.

For less serious health events such as nonfatal gastrointestinaldisorders, there may be no suitable disease registry or databaseavailable atall. Muchofthis type ofmorbidity may gocompletelyunrecorded ifindividualsdonotseekhealthcare. Evenifthey doseekcare, the informationthey providemay be widely dispersedinphysicians' notesorhospitaladmission forms, andtherefore difficultto access for a largepopulation group. Generally speaking,it is more likely that serious health events (such as diagnosis ofcancer or death) will be recorded in a centralized database,whereas dataonminormorbidity will either notberecordedatallor recorded in a nonsystematic way on a noncentralized basis.

There may be further difficulty in drawing causal conclusionsfrom ecologic data because of possible confounding. Forexample, ifan association is found of increased health events with poorer water quality, then it is possible that the association is due to confounding with socioeconomic status. If persons oflowsocioeconomic status tend to reside in regions where publicservices in general and water quality in particular are poorer,then an apparent association of health with poor water qualitywould be induced through the general effects ofa social class gradientfor several diseases. Ifthis scenarioapplied, the true risk factor would be low socioeconomic statusrather than poor water quality. It would be difficult for anecologic analysis to separate the effect of water quality and lowsocioeconomic status and might falsely conclude that waterquality was indeed the causal variable.

CONCLUSION

In spite of mentioned limitations, ecologic studies remain a popular study design among epidemiologists for several reasons (2). They can be done quickly and inexpensively because they often rely on preexisting data. Their analysis and presentation are relatively simple and easy to understand. They have the ability to achieve a wider range of exposure levels than could be expected from a typical individual-level study. And, last but not least, epidemiologists have a genuine interest in ecologic effects. For example, ecologic studies can be used "to understand how context affects the health of persons and groups through selection, distribution, interaction, adaption, and other responses." As Susser states, "Measures of individual attributes cannot account for these processes; pairings, families, peer groups, schools, communities, cultures, and laws are all contexts that alter outcomes in ways not explicable by studies that focus solely on individuals"(13).

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DO ANTHOCYANINS SHOW ANTI-DIABETIC PROPERTIES?

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ABSTRACT

Anthocyanins are the largest group of water-soluble pigments in the plant kingdom, known collectively as flavonoids. Anthocyanins are believed to display an array of beneficial actions on human health and well-being.The aim of the present article is to summarise and discuss some anti-diabetic properties, regarding insulin secretion, diabetic cataracts, and capillary permeability and vasorelaxatio.Although several *in vitro* and animal studieswith anthocyanins strongly suggest their beneficial effectsin cardiovascular complications in diabetes, clinical evidencefor the use of anthocyanins and anthocyanin-richextracts in diabetes is not convincing.

Key words: anthocyanins, disease prevention, insulin secretion, diabetic cataracts, capillary permeability, vasorelaxatio.

INTRODUCTION

Anthocyanins are an important group of water-soluble plant pigments. They belong to the most common class of phenolic compounds, known collectively as flavonoids with more than 8000 flavonoid and 500 anthocyanin structures reported by the year 2000(1).Anthocyanins are water-soluble glycosides of polyhydroxyland polymethoxyl derivatives of 2-phenylbenzopyrylium orflavylium salts. The six anthocyanidins commonly found inplants are namedcyanidin, delphinidin, malvidin, peonidin, pelargonidin and etunidin.

Anthocyaninsare widespread in food plants, occurring in 27 families. The worldwide annual consumption has been estimated as 10 000 tonnes from black grapes alone. It is generally accepted that anthocyanins are the most important group of water-soluble pigments in plants. In the plant tissues the anthocyanins produce blue, purple, red and intermediate hues and appear black in some products.

Anthocyanins form the colours of many fruits and vegetables and are probably the most widespread food colours occurring as red colours in fruit juices, wines and jams. These pigments have been identified in edible plant materials as diverse as apple, berries (blackcurrant, boysenberry,blueberry, bilberry, strawberry, blackberry,raspberry, cranberry, elderberry, lingonberry, chokeberryetc.), black carrot, cabbage, cherry, grape, radish, red onionsand sweet potato, to mention only a few of the vastarray known(2). The discovery of more stable bis- andpolyacylated anthocyanins has attracted the attention ofthe food industry for use as safe and effective food additives.

Duringthe past two decades an increasing number of studies haveinvestigated the diverse protective effects elicited by polyphenolicspresent in various fruits and vegetables. Theseeffects include antioxidant, anti-allergic, anti-inflammatory,anti-viral, anti-proliferative, anti-mutagenic, anti-microbial,anti-carcinogenic, protection from cardiovascular damageand allergy, microcirculation improvement, peripheralcapillary fragility prevention, diabetes prevention, andvision improvement(3). Polyphenolic research has recentlyintensified because of this increasing understanding andawareness of the potential beneficial human health effects.

The aim of this review is to summarise and discuss some anti-diabetic properties of anthocyanins.

MATERIAL AND METHODS

We used relevant literature evidence on some anti-diabetic properties of anthocyanins. Some future considerations were than discussed.

RESULTS AND DISCUSSION

The consumption of a diet low in fat and rich in antioxidantsmay reduce the risk of obesity and insulin resistance (4). A number of recent reports indicate that consumptionof fruits and vegetables, especially rich in polyphenols,decrease the incidence of type-2 diabetes, a conditionassociated with insulin resistance (5). Insulin resistance isa disorder in which insulin inadequately stimulates glucosetransport in skeletal muscle and fat and inadequatelysuppresses hepatic glucose production. The mechanismsthat prevent the β-cell of the pancreas from secreting sufficientamounts of insulin to overcome peripheral insulin resistance are not yet fully understood. Oral hypoglycemicagents that directly stimulate insulin release from β-cells (e.g., sulfonylurea-based drugs), however, can elevateinsulin secretion from islets of type-2 diabetic patientssufficiently to overcome peripheral insulin resistanceand normalize blood glucose levels. One of the disadvantagesof using sulfonylurea-based drugs is that theyfail to control normal blood glucose levels (6). These drugsalso adversely affect the ability of β-cells to secrete consistentinsulin level and cause weight gain (6). Hence, itwould be beneficial if dietary constituents could regulateblood glucose levels or induce insulin production by pancreaticβ-cells in the type-2 diabetic condition. However, there is little clinical evidence that food factors can do this.

*Insulin secretion.*It is well known that dietary antioxidants, including anthocyanins, protect pancreatic β-cells from glucoseinducedoxidative stress (7). Recently Jayaprakasam *et al.* (8)demonstrated glucose-induced insulin release from pancreaticβ-cells by anthocyanins and anthocyanidins. Similarly, the dimethoxy ether and the glycoside of leucopelargonidin isolated from the bark of the Indian banyan tree*Ficus bengalensis* showed significant hypoglycaemic,hypolipidemic and serum insulin-raising effects in moderatelydiabetic rats with close similarities to the effects ofglibenclamide (an oral hypoglycaemic sulfonylurea-baseddrug) (9). Previously *Cornus* fruits (cherry), a rich sourceof anthocyanins, have been reported anecdotally as havinganti-diabetic activity (10).Results indicated that pelargonidin- 3-galactoside and its aglycone, pelargonidin, causeda 1.4-fold increase in insulin secretion. Zhang *et al*.(11) alsoreported that several compounds present in grape skin orwhole grapes are capable of enhancing insulin secretionas well as selectively inhibiting COX-2 enzymes. Theysuggested that cherries, grapes, and berries containinganthocyanins might be useful for the prevention of type-2diabetes. In few *in vitro* and animal studies (12),anthocyaninextracts were found to have potent alpha-glucosidaseinhibitory activity, suppressing the increase in postprandialglucose level. However, no further extensive *in vivo*studies and clinical evaluation of these compounds haveyet been carried out to validate the *in vitro* observations.

Diabetic cataracts. Continuous hyperglycemia is well known to cause toxicreactions in organ tissues. Loss of lens opacity control islinked with high levels of reducing sugars in *in vitro* and*in vivo* studies, i.e. experimental diabetic cataract formation.Diabetic cataract, a complication of diabetes, occursin about 10% of diabetic patients. In the U.S.A. about 20,000 patients are reported to develop retinopathy/cataract and loss of sight annually. In Japan, about aquarter of total blindness cases annually are caused bydiabetes, including diabetic retinopathy and diabetic cataract.It is said that caloric and food intake influence the progress of diabetes and diabetic complications (13). Flavonoidsare well known for their possible role in the preventionof diabetic cataracts (14).Over forty flavone derivativeswere tested and found to be potent inhibitors of aldosereductase, the enzyme that initiates cataract formation indiabetes (14). Five anthocyanin monomers isolated from theextract of grape skin showed inhibitory activities for lensopacity (13). Flavonoids can also prevent or delay the occurrenceof cataracts in rat lenses perfused in a high-glucosesolution or in diabetic rabbits (14).Several naturally extractedor synthetic anthocyanins combinations with novelanti-cataract/anti-glucoma activity have been reported inpatents (15). Therefore, it is important to discover whetherdiabetic complications can be restrained with food constituentsin humans.

*Capillary permeability and vasorelaxatio.*Various microcirculatory disorders have been described indiabetes. Several of them may occur before the onset ofmicroangiopathic lesion (thickening of capillaries in manyareas including the eye in diabetics) and are assumed crucialin the pathogenesis of microcirculatory complicationsin diabetes. In the diabetic microangiopathic condition,microvascular permeability and the number of leucocytessticking to the venular endothelium are increased (16). Delphinidin chloride elicited increased microvascular permeability and a reduction of leucocytes adhering to the venular vessels in diabetic hamsters (17).Anthocyanosides from berries are currently used in ophthalmology for theircapacity to improve vision and prevent diabetic retinopathy (18). Various flavonoids including anthocyanosideshave been shown to be effective against experimentallyinduced capillary hyperfiltration (19). In one animal study,Cohen-Boulakia *et al*. (20) showed that anthocyanosides canimprove and even normalise capillary filtration of albumin.It was reported that blueberry extracts act as inhibitorsof cyclic adenosine monophosphate and cyclicguanosine monophosphate phosphodiestase (21), as scavengersof superoxide anions and as antioxidants on humanlow-density lipoproteins (22).Considering all these effects,together with the lack of significant adverse effects (21),the clinical interest in anthocyanins and anthocyanin-richextracts is increasing.In several pathological conditions including diabetes,endothelium-dependent vasorelaxation by different vasodilatoragonists is reduced (23). One of the mechanisms accountingfor the dysfunction of the endothelium is a decreasedrelease of nitric oxide (NO) (24). It was shown thatextracts from red wines, other grape products, and variousplants that contain polyphenols (mainly anthocyanins),can induce endothelium-dependent vasorelaxation, probablyvia NO release or enhanced biological activity of NO (25). A mixture of anthocyanins extracted from bilberry(*V. myrtillus* L.) was reported to have biological andpharmacological properties, including vasorelaxation (26)and ophthalmic activity (27). Nakamura *et al*.(28) investigatedthe effect of blackcurrant (BC) concentrate on smoothmuscle in rat thoracic aorta. They reported that BC concentratedose-dependently relaxed the norepinephrineprecontractedaorta, and the response was abolished afterendothelium removal. Therefore, they hypothesized thatthe prevention of eye and lower back fatigue probablyresulted from increased blood supply to these areascaused by vasorelaxation induced by BC concentrate viathe histamine H1-receptors on the endothelium. The exactidentification of the anthocyanins having this vasorelaxationactivity was lacking in this study. It could be a synergisticrelaxant effect of a number of polyphenols.

CONCLUSION

The Diabetes Control and Complications Trial (DCCT,1993) (29) demonstrated that tight control of blood glucoseis effective in reducing clinical complications of diabetessignificantly, but even optimal control of blood glucosecould not prevent complications completely, suggestingthat alternative treatment strategies are needed. A multitudeof *in vitro* and *in vivo* studies have been performedutilizing the antioxidant properties of anthocyanins in cellculture and experimental diabetic models. There are differencesin response to anthocyanin-rich extracts measuredthrough certain observable biomarkers. These studies provide a foundation for further clinical trials. Resultsshould be interpreted cautiously since these studies involveda wide variety of experimental models of diabetes,duration and type of the treatment and markers of oxidativestress. Although several *in vitro* and animal studies with anthocyanins strongly suggest their beneficial effectsin cardiovascular complications in diabetes, clinical evidencefor the use of anthocyanins and anthocyanin-richextracts in diabetes is not convincing.

It is important to studyisolated and purified anthocyanin components, along with extracts of the food from which they are derived, to comparetheir activities and determine how they interact witheach other, so that their role in diabetescan be assessed both at the mechanistic level and whenthey are part of the food matrix that forms the basis of ourdiet.

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INTERNAL EXPOSURE TO NATURAL RADIONUCLIDES FROM SOIL AND RELATED HEALTH RISK ASSESSMENT

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ABSTRACT

Purpose of this paper is to assess lifetime cancer mortality risks related to inhalation and ingestion of natural radionuclides from soil, using Monte Carlo method. Twelve soil samples were taken from the alluvial horizon of stream Kladoroba and Skrapez River which is tributary of the West Morava River. Activity concentration of radionuclides ^{232}Th and ^{238}U in soil samples were measured using gamma spectrometry. Assessed risks are approximately 10^{-7} for lifetime exposure to ^{232}Th and 10^{-8} for lifetime exposure to ^{238}U for inhalation and ingestion exposure. Monte Carlo method is applied in health risk assessment because measurement uncertainties are usually with the same order of magnitude as estimated values, and the risk probability distributions significantly deviate from Gaussian.

Key words: natural radionuclides, internal exposure, cancer, risk assessment, Monte Carlo method.

INTRODUCTION

Ionizing radiation interacts randomly with atoms in cells where it can change molecular structure of the cell constituents. Critical and the most important alteration is damage to DNA. Unrepaired damage to DNA or inaccurately repaired damage can lead to cancer development [1]. Relationship between induction of many cancers by low-LET radiation and dose appears to be sigmoidal function. Dose-response relationship of high-LET radiation is more linear [2]. Internal exposure to the natural ionizing radiation sources arises from the ingestion, inhalation or dermal absorption of the natural radionuclides from environment [1]. Inhalation of the radionuclides from soils is possible due to their intake through dust particles that are resuspended in the air. Ingestion includes direct soil/dust ingestion or radionuclides transfer from soil to vegetables wherefrom they enter into the food chain [3].

Point risk estimates are conservative and they provide very limited information to the public and decision-makers. Monte Carlo method is important tool in environmental and health risk assessment because it introduces uncertainty analysis in convenient and reliable way [4]. Important steps in Monte Carlo risk analysis include: *i*) determination of input quantities that have influence on the assessed risk and model function; *ii*) determination of probability density functions for input quantities; *iii*) sampling and propagation of probability density functions (PDF) for the input quantities through the model in order to obtain probability density function for the output quantity; *iv*) implementation of parameter sensitivity analysis in order to quantify influence of input quantities on the risk; *v*) graphical representation of the results with quantified uncertainties that provides information about the range and likelihood of risks to receptors from exposures to contaminants in the environment [5, 6, 7].

In quantitative uncertainty analysis, a distinction is made between uncertain and variable input parameters. Whereas uncertain input parameters are result of the lack of the information about that parameter, variable input parameters are characterized with sufficient data but they have inherent heterogeneity in the population. Input parameters that describe exposure conditions to receptors in environmental and health risk assessment could be variable and uncertain in the same time. In Monte Carlo simulations, input quantities are described with probability density functions which represent their uncertainty and variability [5, 8].

Purpose of this paper was to assess lifetime cancer mortality risks related to inhalation and ingestion of natural radionuclides from soil using Monte Carlo method.

METHODS

Twelve soil samples were taken from the alluvial horizon of the stream Kladoroba and Skrapez River at the depth of (15-20) cm with sample weight of 5 kg. Skrapez River is tributary of West Morava River. Selected locations were part of the wider research of West Morava basin, its natural radionuclides content in sediment and soil and possible detection of contamination related to industrial activity. Gamma spectroscopic measurement was performed for determination of the ^{238}U and ^{232}Th activity concentration in soil samples. Gamma spectrometry was performed with high purity, low energy, germanium semiconductor detector (HPGe), manufactured by ORTEC, with accompanying electronic equipment and ORTEC software for spectra evaluation. The relative efficiency of HPGe detector was 28 % with energy resolution of 2 keV in measurements at the 1.33 MeV reference transition of ^{60}Co. Detectable energy range was up to 2 MeV. The expanded measurement uncertainty of radionuclide activity concentration was 15 % (coverage factor $k = 2$).

Lifetime cancer mortality risk *per capita* was calculated based on the determined radionuclide activity concentrations in soil samples [9]. It was calculated using risk coefficients that represent average risk per unit exposure to members of a population [9]:

- exposed throughout life to a constant concentration of a radionuclide in soil;
- acutely exposed to the radionuclide from soil.

Risks refer to average member of population because cancer mortality coefficients are averaged over age and gender distribution of hypothetical closed stationary population.

Considered exposure pathway was inhalation and direct ingestion of soil [3, 9, 10].

Lifetime cancer mortality risk *per capita* from lifetime exposure via direct ingestion pathway was calculated using equation:

$$Risk = R_c \times A \times IR_s \times EF \times ED$$

where *Rc* represents risk conversion factor (risk/Bq), *A* is activity concentration of radionuclide in soil (Bq/kg), *IRs* is ingestion rate (mg/day), *Ef* is exposure frequency (day/year) and *Ed* is exposure time (year).

Lifetime cancer mortality risk *per capita* from lifetime exposure via inhalation pathway was calculated using equation:

$$Risk = R_c \times A \times C \times IR_i \times EF \times ED \times \left[ET_0 + \left(ET_i \times DF_i \right) \right]$$

where *Rc* represents risk conversion factor (risk/Bq), *A* is activity concentration of radionuclide in soil (Bq/kg), *C* is concentration of dust particles from soil in air (μg/m^3), *IRi* is inhalation rate (m^3/day), *Ef* is exposure frequency (day/year) and *Ed* is exposure time (year), ET_0 is fraction of time spent outdoor, *ETi* is fraction of time spent indoor, *DFi* is indoor dust dilution factor.

Probability density functions were assigned to the model input quantities in order to perform risk assessment and uncertainty analysis using Monte Carlo method.

RESULTS AND DISCUSSION

Exposure parameters for inhalation and ingestion of ^{232}Th and ^{238}U were presented in Table 1 and Table 2. Appropriate single value estimates or probability density functions were assigned to every input quantity. PDF for the risk conversion factor, R_c, is log-normal distribution (defined with two parameters). Probability distributions for R_c factor was developed based on the description of the factor in the guides published by US Environmental protection agency (EPA) [9, 11]. Uniform distribution was assigned to the activity concentration and it is characterized with minimum and maximum values that are calculated from the relative standard measurement uncertainty. Normal distribution (defined with mean value and standard deviation) was assigned to the inhalation rate, *IRi*, according to EPA Exposure Factors Handbook [12]. PDF for concentration of dust particles in air, *C*, was developed based on meteorological conditions and periods in the year with wind. Log-normal distribution was developed for the soil ingestion rate, *IRs*, so that probability is 0.95 for the soil ingestion rate in the rage of (0-100) mg/day and 0.5 for soil ingestion rate in the rage of (50-100) mg/day. Single values were taken for the exposure frequency, *Ef*, and exposure duration, *Ed*, as the representation of stationary lifetime exposure.

Table 1. Single value estimates and probability density functions of input quantities for inhalation exposure

Inhalation		
Input quantity	Single value estimate	Probability density function
R_c(^{238}U) (Risk/Bq)	/	log-normal (-15.2; 1.12)
R_c(^{232}Th) (Risk/Bq)	/	log-normal (-13.7; 1.12)
A (Bq/kg)	/	Uniform (min, max)
C (μg/m^3)	/	p=3/4 for C=(5-15) μg/m^3 p=1/4 for C=(60-80) μg/m^3
IR_i (m^3/day)	/	Normal (17.48; 2.81)
EF (day/year)	365	/
ED (year)	70	/
ET_0	0.5	/
ET_i	0.5	/
DF_i	0.4	/

Table 2. Single value estimates and probability density functions of input quantities for ingestion exposure

Ingestion		
Input quantity	Single value estimate	Probability density function
R_c(^{238}U) (Risk/Bq)	/	log-normal (-20.3; 0.95)
R_c(^{232}Th) (Risk/Bq)	/	log-normal (-19.8; 1.36)
A (Bq/kg)	/	Uniform (min, max)
IR_s (mg/day)	/	log-normal (4; 0.4)
EF (day/year)	365	/
ED (year)	70	/

Results of assessed cancer mortality risks using Monte Carlo method, for inhalation and ingestion exposure cases with range of uncertainty for probability of 95 % are presented in Table 3 and Table 4. Lower and upper bounds of uncertainty range (for probability of 95 %) are the 2.5th percentile and the 97.5th percentile. It can be seen that lower and upper bounds of uncertainty range are very asymmetrically distributed relative to mean. Cancer mortality risks *per capita* are approximately 10^{-7} for lifetime exposure to ^{232}Th via inhalation and ingestion exposure and 10^{-8} for lifetime exposure to ^{238}U for inhalation and ingestion exposure. Figure 1 presents obtained probability density functions for assessed cancer mortality risks.

Table 3. Assessed cancer mortality risks for exposure related to inhalation and ingestion of ^{232}Th with range of uncertainty for probability of 95 %.

^{232}Th		Ingestion		Inhalation	
Location	Activity concentration (Bq/kg)	Cancer mortality risk ×10^6	Uncertainty bounds (min, max)×10^6	Cancer mortality risk ×10^6	Uncertainty bounds (min, max)×10^6
Kladoroba	25.1±3.8	0.201	0.008-0.952	0.382	0.011-2.85
Skrapez	30.1±4.5	0.240	0.009-1.14	0.457	0.013-3.41

Table 4. Assessed cancer mortality risks for exposure related to inhalation and ingestion of ^{238}U with range of uncertainty for probability of 95 %.

^{238}U		Ingestion		Inhalation	
Location	Activity concentration (Bq/kg)	Cancer mortality risk $\times 10^6$	Uncertainty bounds (min, max)$\times 10^6$	Cancer mortality risk $\times 10^6$	Uncertainty bounds (min, max)$\times 10^6$
Kladoroba	21.3±3.2	0.073	0.007-0.274	0.070	0.002-0.525
Skrapez	20.8±3.1	0.071	0.007-0.268	0.069	0.002-0.512

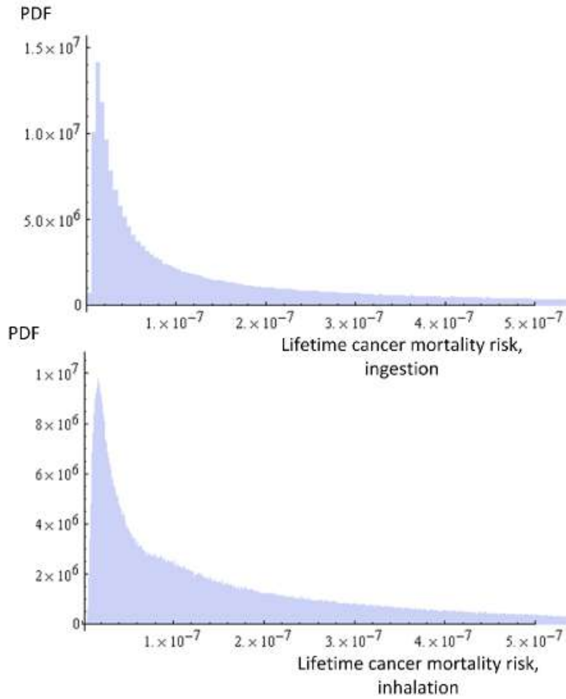

Figure 1. Probability density functions for lifetime cancer mortality risks obtained using Monte Carlo method, related to ingestion and inhalation of ^{232}Th.

CONCLUSION

Monte Carlo method is very important tool in environmental and health risk assessment because it introduces uncertainty analysis. Only assessed risks with explicitly stated measurement uncertainty represent reliable information for further decision-making process. Assessed risks in this paper have low priority for further investigation because they are less than 10^{-6}.

The use of Monte Carlo method in cancer risk assessment is justified for uncertainty propagation because output quantity has measurement uncertainty with the same order of magnitude as the estimated value and probability density distributions of risks deviate from Gaussian.

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APPLICATION MINERAL WATER MATARUSKA SPA TO PREVENTIVE AND GENERAL MEDICINE

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ABSTRACT

Mataruška Spa is located in the southwestern part of the vast Kraljevacke valley on the right bank of the mountain river Ibar River to the south and east it is surrounded by branches of mountain Stolovi (1375m) ia the west and southwest side branches Troglava (1177m) and Čemerna (1579m). It has geothermal mineral water alkaline sulfuric acid hyper-temperature 37-51^{0}C.

Due to its properties, is used for the treatment of chronic rheumatic diseases of the joints and muscles, conditions after injuries of bones and soft tissues, as well as for many other diseases and general preventive medicine.

This paper presents a short overview of the characteristics of thermal mineral water Mataruška and possible applications in spa preventive and general treatment.

Key words: Mataruska Spa, Medicine, Prevention, Treatment, Thermal water.

INTRODUCTION

Mataruška Spa, dates from 1898. and is one of the youngest known spa in Serbia, which provides treatment, rehabilitation, recovery, rest and recreation. It is located 8 km southwest of Kraljevo, at an altitude of 211m, on the right bank of the mountain river Ibar. It is only 2km from the Monastery Žiča, some distance from the monastery of Studenica and Ljubostinja, a very close Bogutovačka Vrnjačka and Josanicka spa.

Mataruška Spa is known for its geothermal mineral water alkaline sulfuric acid hyper little salt, temperature 37-51^{0}C, comes from the depths of the earth over 1000m, and due to its temperature rises raselnom cracked to a depth of 3 m below the surface.

The most general terms, mineral water Mataruške Spa is very suitable for the treatment of chronic rheumatic diseases of the joints and muscles, conditions after injuries of bones and soft tissues, infertility and other gynecological diseases, various neuralgia, chronic poisoning metals, catarrhal diseases of the mucous membranes, diseases of the stomach and bowel disorders to modify materials and other diseases and preventive cases, which will be discussed in this paper.

MATERIAL AND METHODS OF WORK

Geological structure and relief mataruska

Right bank of the Ibar to Mataruska Spa is composed of serpentine, mainly as he is in other parts of the Ibar serprentinskog belt, which also belongs to this part of the field. Him near Spa intersects South Morava fissure zone, the north-west - south-east, along the serpentine belt is sinking, and then covered with tertiary lacustrine sendimentima. This area stands out as a separate thermal area because intersects the Rhodope mass until its eastern odboda and there are thermal springs. Between the king and Bogutovac, along the right bank of the Ibar river, extends another fissure zone prevailing direction of southwest - northeast. This line is a former crack through which in ancient times emanated sulphurous water, before the terrace down below the present level.

Symbol Mataruške Spa is a fountain "Kupačica", which is located in the central part of the park, and is shown in Fig. 1.

Figure 1. Symbol Mataruške Spa-fountain "Kupačica".

Digging in the area of thermo-mineral water, first encountered the humus layer, ie. earth mixed with fine sand, the thickness of about three to three and a half meters. This layer and the layer contains a mainly originated from the sediment during flooding Ibra and stone comminution due to the effects of atmospheric and mechanical forces. Digging deeper you come to a layer of clay, and beneath the layer of finer and coarser all large stones.

Sulphurous water from wells located about 3 meters below the surface, but this level of mineral water lowers and rises depending on the level of groundwater, so-called vadose water, the quantity or amount, depending on the amount of rainfall and snowmelt. Interesting is the fact that Ibar flows like in a laterally confined bed of non Its floods the underground left and right. This can be concluded from the fact that the drinking water from the pump, pobodenih next to the riverbank, lime, and water from Ibra does not contain any lime. This is why drinking water in Mataruska Spa pure mountain water from the mountain Stolovi, and without a mixture of water from the river Ibar.

RESULTS AND DISCUSSION OF RESULTS

Natural healing Mataruška Spa

By definition, mineral waters are a special group of groundwater, due to its physical properties and chemical composition favorable effect on the human body and can be used for prophylaxis and treatment.

Mataruške Mineral Water Spa, magmatic origin, from greater depths (some sources to get water depth of about 1000m) arriving at the Earth's surface and are a group of juvenile water. They are very complex chemical composition, more complex than many pharmacotherapeutic agents because they contain more than 10 elements. Represent solutions of weak electrolytes, and are characterized by the ionic composition.

The thermal zones, in which the upper parts of the aquifer is hot or lukewarm water, the surface was of about 10.000 m^2. In this zone, is constructed of eksploatcionih trap, but has not been used a larger number of separate sources. The total abundance of mineral water is 26.5 liters/sec. The amount of water is almost the same throughout the year.

The first complete chemical analysis of mineral waters was published in 1922., and with them the main part of the water is hydrogen sulfide and sodium bicarbonate. Based on these results, the water has been included in the Red sulfuric acid hyperthermal alkali with a weak character muriatic water (slightly salty). The temperature of the water, depending on the operation of, from 37°C to 51°C. Radioactivity in drinking cold water was determined to 1.14 MJ, a hot sulphurous water 0.74 MJ. This analysis showed that this is an important mineral water, but it is a negative trait very little radioactivity. However, more recent studies that are underway indicate the occurrence of radioactive contents from big depth.

According to a survey by the rehabilitaiciju Belgrade, executed in 2001. Were determined by the following characteristics of thermal mineral water Spa Mataruške:.

Table 1. Physical - Chemical analysis of water (48.5^{0}C)

No.	Element	Grama (gr.)	milimola	milivala
1	**Ions**			
2	Natrium(Na)	0,2730	11,880	11,880
3	Calium (K)	0,0250	0,6390	0,6390
4	Ammonium (NH_4)	0,0008	0,0440	0,0440
5	Calcium (Ca)	0,0415	1,0355	2,0710
6	Magnesium (Mg)	0,0320	1,3160	2,6320
	Anions			
1	Bircabonata(HCO_2)	0,8640	14,160	14,160
2	Hlorida (Cl)	0,0790	2,2280	2,2280
3	Sulfate (SO_4)	0,0412	0,4280	0,8570

Table 2. Koloidnio dissolved oxide

No.	Colloidal dissolved oxide	
1	Silicon oxide (SiO_2)	0,1200
2	Iron oxide (Fe_2O_3)	0,0030
3	Aluminium oxide (Al_2O_3)	0,0400
4	Dryness at 180^{0}C	1,0560
5	Free carbonic acid (CO_2)	0,4000
6	Free hydrogen sulfide (H_2S)	0,0210

MEDICINSKE INDICATIONS AND TREATMENT IN MATARUSKA SPA

Water Mataruške Spa in late nineteenth-century was in use for treating a disease of the skin, and soon began to be used for the treatment of chronic rheumatic diseases, posttraumatic conditions, chronic gynecological diseases that cause infertility in order to access the last fifty years and treatment of hemiplegic patients after stroke, intracranial condition. Indication area is expanded to various types of damage to the peripheral nervous system as well as by paraplegia, post-traumatic etiology or any other etiological factors (diseases of the spinal cord, the state of the process after the post-operative tumor treated). In the last twenty years have treated children with cerebral palsy before operatively and postoperatively. At the beginning of the 90s with orthopedic clinic in Belgrade was sent to 170 wounded in the former Yugoslavia affected by war.

Physiological effect - Balneological factor, sulphurous mineral water, is a stimulus to the receptors of the skin and mucous membranes, causing over neuroflexne and humoral regulation of the complex reaction of the organism to adapt. These changes occur as a result of the effects of mechanical, thermal and chemical factors on the skin and mucous membranes.

Mechanical effect - The hydrostatic pressure body apparently loses weight (mineral water and up to 91%), which facilitates the movement expressed in pain and neuromuscular injuries followed aggravated motion. Hydrostatic pressure leads to more intensive discharge depot venous pressure in the body cavity and veins, coronary flow better, increasing the stroke volume and heart rate, and increases the re-absorption of tissue fluid under the skin. Hydrogen sulfide sticks to the skin in the form of bubbles and is a mechanical stimulus to the receptors, causing effects micromassage.

Heat effect - Is based on a large thermal conductivity and high specific heat of water. At the entrance to the warm bath from which the so. "Paradoxical reaction of the skin", which was soon replaced shudder redness and relaxation. The temperature of the skin and subcutaneous tissues may be increased by 2-4 degrees, warming the blood in the blood and lymph vessels, which then goes into the circulation, leading to an increase in body temperature. Neuroreflexive mechanisms leading to vasodilatation and hyperemia. Cells from the skin is released acetylcholine, which enters the bloodstream, causing vasodilation and lowering blood pressure.

The effect of hyperemia is so present in distant parts of the body. Dilation of blood vessels of the skin leads to a redistribution of blood from the internal organs and blood depots to the periphery. Reduces the viscosity of the blood as it comes to the passing fluid into the circulation, which causes sweating (excrete harmful products of metabolism), evaporation of liquid from the surface of the skin and diuresis - generated so. physical thermoregulation. Chemical thermoregulation is accompanied by increased needs for oxygen, leading to improved nutrition of tissue.

Hyperventilation leads to increased pH levels blood. Prolonged increased respiration can cause detrimental and it is necessary dosing the amount of heat supplied to the body. Different temperatures of gas bubbles (which accumulate on the surface of the body), and water are also thermal stimulus. Warm mineral springs reduce skeletal muscle tone and smooth muscle and after baths may feel fatigue. Noted also decrease arterial blood pressure and increase heart rate at the inlet and adverse effect upon exiting the bath with a drop in heart rate expressed.

Chemical effect - Sulfur water are the only mineral water whose ingredients involved in the construction of proteins, important structural elements of tissues. Biologically active substances, hydrogen sulfide, can be easily absorbed through the skin and mucous membranes. Resorption is increased at higher temperatures, and the water thus formed kože.Dilatation morphological changes of the blood vessels to improve blood circulation, and it is applied in the treatment of eczema and other skin diseases accompanied by a loss of the epidermis. It also affects the metabolism of the skin, cholesterol, tissue oxygenation, exowing secreting glands, amino acid synthesis. Resorption of sulfur into the cartilage of the joints has a particularly beneficial effect in rheumatic patients as partially compensate for the lack of these substances. Hydrogen sulfide reduces uric acid and blood sugar. Has a detoxifying effect in mercury poisoning, lead, some toxins. Sulphurous mineral water acting stimulant, increasing muscle tone of smooth muscle fibers.

Indications: inflammatory and degenerative rheumatism, conditions after injuries of the locomotor apparatus, neurological diseases, skin diseases, metabolic disorders, sterility.
contraindications for the application of sulphurous thermal mineral water: general state of disorder, unregulated hypertension, acute inflammatory diseases, exacerbation of chronic inflammation, malignancy, bleeding specific processes, varices.

Sulphurous mineral water is used as a bath, local and general, in hot tubs or swimming pools; combined Hydro therapy pools, Hubbard tub. It is applied in the form of underwater massage and spraying. Out of the water hydrogen sulfide is toxic but is rapidly oxidized to non-toxic compounds, and have a safe bath.

Balneological reaction is a transient deterioration of general condition and occurs as a reaction to the application of thermal mineral baths (worsening of rheumatic pain). It manifests itself as a general - with headache, by fatigue, nervous irritability, loss of appetite, insomnia: a local or in the form of pain in the musculoskeletal apparatus.

Special Institute for Rehabilitation "Agens" is a modern medical facility that has a highly trained staff and medical equipment for the diagnosis, prevention, treatment and rehabilitation. Hospital has 230 beds including modern fitted part of the "Agens" through a special outpatient services provide services to other guests.

At the Institute applied the most advanced methods of medical rehabilitation and physical therapy: power Chinese therapy pools tubs for underwater massage and hydro-galvanic treatment, electrotherapy, phototherapy, sonotherapy, paraffin, manual and vibration massage, Chinese and occupational therapy as well as a variety of recreational activities.

The Institute can treat:

- rheumatic diseases (inflammatory rheumatism, systemic connective tissue diseases, degenerative diseases of the spine and connective tissue rheumatism)
- gynecological diseases (primary and secondary sterility)

- posttraumatic conditions and their consequences (injuries and fractures and joint, muscle hypertrophy)
- a neurological disease or damage to the central and peripheral nervous system (paresis and plegia limbs, multiple sclerosis lesions, intervertebral discs and after surgery)
- peripheral vascular disease (Buerger's disease, atheromatosis, arteriosclerosis, varicose veins).

The indicator areas:

- Gynecological diseases (chronic andeks-parametritis including primary and secondary sterility)
- Rheumatic diseases inflammatory rheumatism (rheumatoid arthritis, juvenile arthritis, Behtrevljeva disease), degenerative diseases of the spine (spondylosis, spondiloartritis, to cure), rheumatism and other diseases and deformities of the musculoskeletal system
- All post-traumatic conditions and their consequences (contraction joints, muscle hypotrophy, Sudek's disease)
- Neurological diseases damage the central and peripheral nervous system (hemiplegia, hemiparesis, kvadriplegia, paraplegia and paraparesis, cerebral palsy, multiple sclerosis, Parkinson's disease, polyneuritis, various etiology, peripheral nerve lesions and conditions after surgery operatovnih)
- peripheral vascular disease (Buerger's disease, arterio-sclerotic diseases of the blood vessels, varicose veins, vibration disease)
- Some skin diseases (eczema, psoriasis, a condition after burn)

Therapies:

- HIDROTHERAPY (swimming in the tub (underwater massage and pearl bath), swimming in the pool, the local baths (alternating and Haufeove baths), spraying)
- THERMOTHERAPY (paraffin, peloidotherapy (mud: hot and cold)
- CHINESETERAPY (individual and group exercises)
- ELECTROTHERAPY (galvanization, electrophoresis, eksponencijlne current, DD, KTD, interferential current, TENS)
- PHOTOTHERAPY (solux and quartz lamps)
- MECHANOTHERAPY (manual and apparatuses of massage)
- LASERTHERAPY
- SONOTHERAPY
- MAGNETICTHERAPY
- OCCUPATIONAL THERAPY

Other medical Services:

- DIAGNOSTICS (ultrasound of the abdomen and the thyroid gland, x-ray)
- SPECIALIST CLINICS (internal medicine, gynecology, physical therapy, orthopedic, rheumatic)
- CONSULTATIVE EXAMINATION (gynecological, neuropsychiatric, pneumophysiological)

Disorders alter matter: Gout (inflammation of the joints caused by deposition of uric acid salts).

Chronic toxicity of metals: Chronic lead poisoning (with typesetters and miners).

Chronic poisoning, bismuth, mercury, arsenic.

Other services: prevention and rehabilitation workers, recreation and relaxation program sports teams, schools in nature for children of preschool and school-age children.

CONCLUSION

Spas can be characterized as a complex natural motifs, with hydrographic, climatic, geomorphological and biogeographical elements, all of which are prerequisites to the implementation of activities in the enrichment of the overall tourist offer spas. Modern development of the tourism sector is based on an integrated approach and fusion of recreational and cultural facilities in the tourist industry.

Among spas in Serbia, stands a group of a dozen spas that have gained market recognition as an independent tourist motives (Vrnjačka, Niska, Soko, Mataruška, Gornja Trepca, Sijarinska, Koviljača, Prolom, Bukovička, Vranjska Spa), some of which are grown in urban urban centers with extended functions. This group spa has the best prospects of development in the future, especially in the short and medium term, due to the influence of various factors (tradition, the results achieved in the previous period, heterogeneous motif basis, the solid material base, a favorable geographic location, etc.).

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THE INFLUENCE OF POWDER METALLURGY ON HUMAN HEALTH AND ON THE ENVIRONMENT POLUTION

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ABSTRACT

This paper describes ecological aspects of powder metallurgy and influence of some metal powders on human health. The paper discusses the advantages the powder metallurgy process over the other comparable manufacturing alternatives. Toxicity and other harmful properties of copper, nickel, and gold metal powders are also discussed.

Key words: powder metallurgy, powders, toxicity, human health.

INTRODUCTION

Powder metallurgy (PM) has been used for over 60 years to produce a wide range of structural PM components, self-lubricating bearings and cutting tools. The PM process involves compressing the powder, normally in a container, to products a compact having sufficient cohesion to enable it to be handled safely, and then heating the compact, usually in a protective atmosphere. The ISO definition of the term *sintering* is „The thermal treatment of a powder or compacts at a temperature below the melting point on the main constituent, for the purpose of increasing its strength by bonding together of the particles“ [1-5]. The basic procedure in the manufacture of PM parts is: mix the metal powders with a suitable lubricant, load the mixture into a die or mold and apply pressure (this gives what is called *compact*), heat the compact – *sintering*. There are a number of reasons for making engineering components by powder metallurgy and these lead to the groupings: refractory metals, composite materials, porous materials, structural or mechanical parts, special high – duty alloys.

In this paper are present the influence of metal powders and PM technology on the environmental and human health.

ENVIRONMENTAL ASPECT OF POWDER METALLURGY TECHNOLOGY

Could a technology be connected with powder production and its processing in a way that is friendly to both environment and humanity, especially when our every-day practice shows that metallurgy is a main natural pollutant? We want to show here the achievements of a technology that is not only economically profitable but environmental favorable. Powder metallurgy is closely connected with technologies that determine its relationship to environmental protection. Obtaining and manipulating solids in powder state is an essential feature of powder metallurgy. If powder metallurgy is limited to the production of metal or metal-like powders, it would be just a part of metallurgy and could not be a progressive, technologically, and economically attractive method combined with metallurgy, materials science, and metalworking. Elimination (in most cases) or at least minimization of machining of the end article leads to economic advantages. As more than 97% of the starting materials reach the finished product, powder metallurgy is a process that conserves both energy and materials. Elimination of scrap losses, which directly reflects on environmental protection, is another privilege of the PM method, providing many possibilities to create waste-free and waste-free and environmentally friendly processes.

Sometimes, metal powder production is a contradiction of technological and work safety viewpoints. Low temperature reduction of metal oxides, in order to obtain fine-grained metal powders that lead to high sinter-ability, may result in products with pyrophoric properties. These powders, in contact with air, tend to self-ignite. The burning proceeds at very high speed and very high temperatures. Iron (Fe) and cobalt (Co) powders, which find numerous applications in PM, are good representatives of these materials. Strict safety measures should be taken during manipulation and storage of fine (< 10 μm) and ultrafine (< 0.5 μm) Fe and Co powders. Organic liquids, vacuum techniques, and an inert atmosphere of argon (Ar) are used to protect such powders from self-ignition [3,4].

ADVANTAGES OF POWDER METALLURGY

Powder metallurgy is recognized as a superior way of producing high-quality parts for variety of applications. Powder metallurgy industry fabricates products using several different technologies: pressing and sintering, injection molding, hot isotactic pressing. Producing near shape samples with tight dimensional tolerances provides powder metallurgy with a distinct advantage over other metal forming techniques. Powder metallurgy minimizes finishing operations and energy use. It is design flexibility and lowering costs to end use costumers' technology. From ecological point of view, powder metallurgy affect environment in a more positive manner than classic ingot metallurgy.

Powder metallurgy components fall into two groups. The first group is consisted from components difficult to make by any other methods, like Mo, W, WC, filters, hard and soft magnetic component. The second group is consisted from components for which powder metallurgy is cost effective alternative to other methods [1-4].

TOXICITY OF SOME METALS POWDERS

Following metals are cancerous: Cd, Be, Hg, Pb, Cr, and Ni, and significant effort are being done to remove them from usage, even as alloying elements. Even though Cu-Be alloy is known for exceptional hardness and tensile strength, it is best to replace beryllium with titan as alloying element. Some metals are cancerous and all metals in powders form are toxic and pyrophoric, due to their big specific surface. These two hazardous characteristics increase with finer powder particles. That is why extreme caution handling with metal powders is necessary. There are fully automated production lines for forming and sintering metal powders today. There is a great interest in powder metallurgy in transporting, storing and handling metal powder and overall ecological validity.

The toxicity of metals powders is specific for each of them, but it depends on the physical properties and the degree of the dispersion of the particles [6].

Copper is a reddish-brown metal, fig 1. It is widely used in the electrical industry, plumbing, heating, and in building construction. It is also used in chemical and pharmaceutical machinery. Because copper is essential to the metabolic function of humans, it is normally occurs in all organs, tissues, and fluids. Despite of practical benefits of copper to human, over the ages there have been repeated discussions is the copper poison in a medicine.

Copper powder can affect the body if it is inhaled or if it comes in contact with the skin or eyes. Short-term exposure to copper powder may cause a feeling similar to the common cold with sensations or chills and stuffiness of the head. Powder can irritate the skin and eyes on contact. Irritation to the eyes will cause watering and redness. Reddening, scaling, and itching are characteristics of skin inflammation. Inhalation causes irritation to the lungs and mucus membrane. Repeated or prolonged exposure to copper powder may cause skin irritation or discoloration of the skin and hear. Chronic copper poisoning is typified by hepatic cirrhosis, brain damage and demyelination, kidney defects, and copper deposition in the cornea as exemplified by humans with Wilson's disease. It has also been reported that copper poisoning has led to hemolytic anemia and accelerates arteriosclerosis.

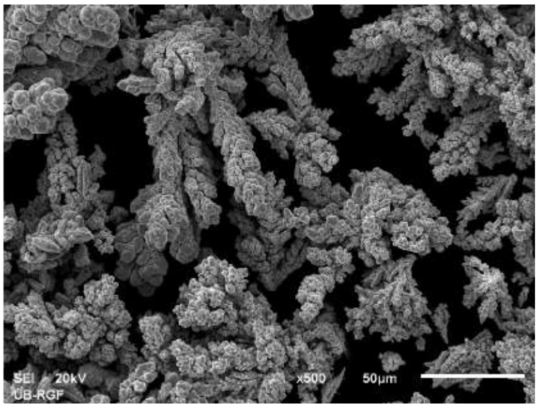

Figure 1. SEM image of electrolytic copper powder particles

In spite of this, no poisoning of workers in copper mines, smelters, and refineries has been demonstrated. A 1967 study of Chilean copper miners whom had worked in the mines, smelters and refineries for at least 20 years, showed no indication of copper toxicities. There is evidence that workers in copper smelters have an increased risk of lung cancer, but this is thought to be due to arsenic-trioxide and not copper. Inhalation of copper powder may cause "metal fever", which disappears after one-two days [7].

The best protection is to enclose operations and/or provide local exhaust ventilation at the site of chemical release. Isolating operations can also reduce exposure. Using respirators or protective equipment is less effective than the controls mentioned above, but is sometimes necessary. Copper powder below 50 µm size range is classified as weakly explosive.

Nickel is one of many carcinogenic metals known to be an environmental and occupational pollutant. Like other metals, nickel can react with acids to liberate hydrogen gas, which can form explosive mixtures in air. Under special conditions nickel can react with carbon monoxide in reducing atmospheres to form nickel carbonyl, $Ni(CO)_4$, a toxic gas. Like other metal powders, nickel powder can react explosively or incandescently with substances such as ammonium nitrate, perchlorates, phosphorous, selenium, sulfur, etc. Fig. 2 shows SEM images of nickel powder obtained by the thermal decomposition of nickel carbonyl $Ni(CO)_4$.

A small amount of nickel is essential for humans, although luck of nickel has not been found to affect the health of humans. Lung effect, including chronic bronchitis and reduced lung function, have been observed at workers who breathed a large amount of nickel. Current levels of nickel in workplace air are much lower than in the past [8].

Nickel metal is a well-known skin sensitizer. Direct and prolonged skin contact with metallic nickel may induce nickel allergy and skin reactions in those people who are already sensitized to nickel (so called nickel allergic contact dermatitis). Repeated contact may result in persistent chronic dermatitis in a smaller number of individuals, despite efforts to reduce or avoid nickel exposure. Animal studies on rats [8] show that repeated dose inhalation of nickel damages the lung.

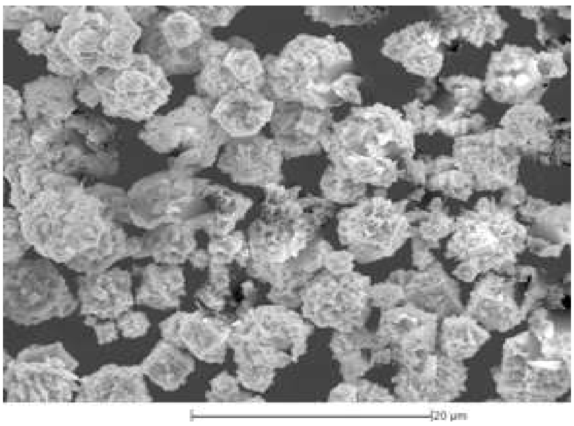

Figure 2. SEM image of nickel powder particles

The International Agency for Research on Cancer (IARC) [9] found there was inadequate evidence that metallic nickel is carcinogenic to humans, but since there was sufficient evidence that it is carcinogenic to animals, IARC concluded that metallic nickel is possibly carcinogenic to humans. But certain forms of nickel are carcinogenic, but these forms are not likely to be encountered outside of industrial settings, such as factories where metals are processed, particularly where nickel ore is refined and where stainless steel is produced. Other workers who may be exposed to these forms of nickel are welders, electroplaters, battery makers, jewelers, spray painters, paint makers and varnish makers. Workers in metal industries who were exposed daily to nickel dust in the form of nickel carbonyl or nickel sub sulfide have been found to have a higher incidence of nasal, sinus and lung cancers. Inhalation exposure to nickel dust can also result in chronic bronchitis, acute respiratory distress syndrome and pulmonary fibrosis.

In the presence of an ignition source, fine nickel powder disperses in air in sufficient concentrations, and it became potential dust explosion hazard. Metal powders when heated in reducing atmospheres may become pyrophoric.

Fig. 3 shows SEM images of gold powder obtained by the chemical process. Gold is considered to be the least corrosive and most biologically inert of all metals [10]. However, that does not mean that gold is completely inert in humans. As a result of exposure to dental restorations, gold jewelry, and use of gold in food, allergic contact dermatitis may occur at some people. It is proposed that gold toxicity to mammals is associated, with formation of the more reactive Au^{+} and Au^{3+} species [11]. In contrast to silver nanoparticles that are known to be ionized in biological media, gold nanoparticles are not normally ionized in biological media. Thus, inhalation exposure to gold nanoparticles provides the potential to separate the behavior of nanoparticles as particles from chemical effects [12].

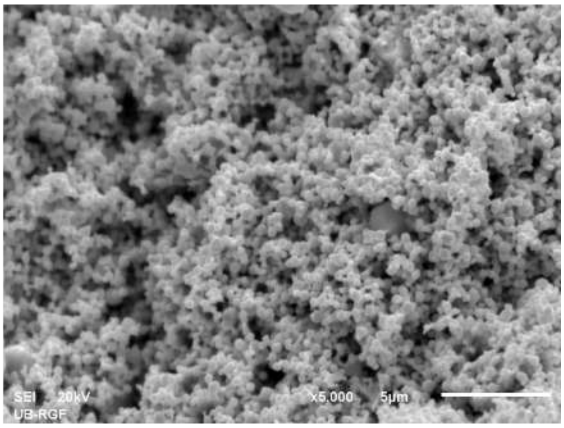

Figure 3. SEM image of gold powder particles

Metal and alloys are often used at high temperatures operations in the workplace. These may include welding, brazing, soldering, plating, cutting, and metallizing. At the high temperatures reached in these operations, metals often form metal fumes which have different health effects and exposure standards than the original metal or metal compound, and require specialized controls.

There are many materials that can be toxic, but they are safe to use when handled in the right way and exposures kept at acceptable levels. Wearing protective clothes and respiratory masks as well as strict control of dust levels in the air are necessary to minimize the risk of inhaling powders.

CONCLUSIONS

Powder metallurgy is energy efficient and ecological friendly technology for metal forming, and it offers the some manufacturing advantages and benefits: cost savings compared with alternative processes and unique attributes attainable only by the powder metallurgy technic. Porous materials with a huge flexibility in material selection justify why the powder metallurgy technology has a long way ahead to its development.

The toxicity of metals powders is specific for each of them, but it depends on the physical properties and the degree of the dispersion of the particles. The best protection from metal powder toxicity is to enclose operations and/or provide local exhaust ventilation at the site of chemical release. Isolating operations can also reduce exposure. Using respirators or protective equipment is less effective than the controls mentioned above, but is sometimes necessary.

Acknowledgment

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ARSENIC DISTRIBUTION IN THE ENVIRONMENT AND ITS INFLUENCE ON HUMAN HEALTH

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ABSTRACT

The metalloid arsenic is a natural environmental contaminant to which humans are routinely exposed in food, water, air, and soil. Arsenic has a long history of use as a homicidal agent, but in the past 100 years arsenic, has been used as a pesticide, a chemotherapeutic agent and a constituent of consumer products. In some areas of the world, high levels of arsenic are naturally present in drinking water and are a toxicological concern.

This paper gives an overview of findings and distribution of arsenic in the environment (air, water and soil), the most significant impacts of arsenic and its compounds on wildlife and human health.

Key words:arsenic, toxic, exposure, environment.

INTRODUCTION

The word "arsenic" elicits a fearful response in most people. This is because arsenic has a long history of being a poison, both intentional and unintentional, to humans. However, most laymen do not know or understand that we are constantly exposed to arsenic because it is naturally present in the environment, is used in commercial products, and has medical applications. Although most typical environmental exposures to arsenic do not pose a health risk, several areas of the world contain arsenic from natural or anthropogenic sources at levels that create a toxicological concern. Many of these areas have been identified, and efforts are being made to either remediate these areas or limit access to them [1].

Arsenic (As) is a ubiquitous element found in the atmosphere, soils and rocks, natural waters and organisms. It is widely distributed in the Earth's crust, which contains about 3.4 ppm arsenic [2]. It is mostly found in nature in minerals, such as realgar (As_4S_4), orpiment (As_2S_3), and arsenolite (As_2O_3), and only found in its elemental form to a small extent. There are over 150 arsenic-bearing minerals [3,4], While arsenic is released to the environment from natural sources such as wind-blown soil and volcanoes, releases from anthropogenic sources far exceed those from natural sources. Anthropogenic sources of arsenic include nonferrous metal mining and smelting, pesticide application, coal combustion, wood combustion, and waste incineration. Most anthropogenic releases of arsenic are to land or soil, primarily in the form of pesticides or solid wastes. However, substantial amounts are also released to air and water.

Arsenic found in soil either naturally occurring or from anthropogenic releases forms insoluble complexes with iron, aluminum, and magnesium oxides found in soil surfaces, and in this form, arsenic is relatively immobile. However, under reducing conditions, arsenic can be released from the solid phase, resulting in soluble mobile forms of arsenic, which may potentially leach into groundwater or result in runoff of arsenic into surface waters. In aquatic systems, inorganic arsenic occurs primarily in two oxidation states, As(V) and As(III). Arsenic may undergo a variety of reactions in the environment, including oxidation-reduction reactions, ligand exchange, precipitation, and biotransformation [5-8]. These reactions are influenced by Eh (the oxidation-reduction potential), pH, metal sulfide and sulfide ion concentrations, iron concentration, temperature, salinity, and distribution and composition of the biota [9]. Much of the arsenic will adsorb to particulate matter and sediment. Arsenic released to air exists mainly in the form of particulate matter. Arsenic released from combustion processes will generally occur as highly soluble oxides. These particles are dispersed by the wind and returned to the earth in wet or dry deposition. Arsines that are released to the atmosphere as a result of microbial action are oxidized to nonvolatile species that settle back to the ground.

Arsenic naturally occurs in soil and will be present in the atmosphere as airborne dust. It is also emitted from volcanoes and in areas of dormant volcanism (e.g., fumaroles). Gaseous alkyl arsenic compounds may be released from soil that has been treated with inorganic arsenic compounds as a result of biogenic processes [10,11].

Arsenic naturally occurs in sea water and vegetation and is released into the atmosphere in sea salt spray and forest fires. Anthropogenic sources of arsenic include nonferrous metal smelting, coal, oil and wood combustion, and municipal waste incineration. Arsenic naturally occurs in coal and oil and therefore, coal- and oil-fired power plants release arsenic to the atmosphere in their emissions [12]. Arsenic's use in agriculture and industrial processes also contributes to its emissions. One important source of arsenic emissions is cotton ginning in which the cotton seeds are removed from the raw cotton.

ARSENIC IN THE ENVIRONMENT

Because arsenic is a natural component of the Earth's crust, low levels of the element are found in all environmental media. Atmospheric levels of arsenic in remote locations (away from human releases) range from 1 to 3 ng/m^3, while concentrations in urban areas may range from 20 to 100 ng/m^3. Concentrations in water are usually <10 μg/L, although higher levels may occur near natural mineral deposits or anthropogenic sources. Natural levels of arsenic in soil usually range from 1 to 40 mg/kg, with a mean of 5 mg/kg, although much higher levels may occur in mining areas, at waste sites, near high geological deposits of arsenic-rich minerals, or from pesticide application. Arsenic is also found in many foods, at concentrations that usually range from 20 to 140 μg/kg. Total arsenic concentrations may be substantially higher in certain seafoods.

The impact on the environment of the use of arsenical compounds, at least locally, will remain for some years. Of the various sources of arsenic in the environment, drinking water probably poses the greatest threat to human health. Airborne arsenic, particularly through occupational exposure, has also given rise to known health problems in some areas.

Arsenic in air

Estimates of yearly emissions from anthropogenic sources ranged from 12,000 to 25,600 metric tons with a median value of 18,800 metric tons. Natural sources contributed 1,100– 23,500 metric tons annually. Chilvers et al. [13]estimated global natural and anthropogenic arsenic emissions to the atmosphere as 73,500 and 28,100 metric tons per year, respectively. Copper smelting and coal combustion accounted for 65% of anthropogenic emissions.

Arsenic in the particulate phase is the predominant (89–98.6%) form of arsenic in the troposphere [14]. Inorganic species, most commonly trivalent arsenic, is the dominant form of arsenic in the air over emission areas; methylated forms of arsenic are probably of minor significance. Arsenic-containing air samples of smelter or coal-fired power plant origin consist largely of trivalent arsenic in both vapor and particulate form. Oxides are the primary species evolved from fossil fuel and industrial processes. Additionally, arsenic trisulfide has also been reported from coal combustion, organic arsines from oil combustion, and arsenic trichloride from refuse incineration.

Arsenic is released into the atmosphere primarily as arsenic trioxide or, less frequently, in one of several volatile organic compounds, mainly arsines. Trivalent arsenic and methyl arsines in the atmosphere undergo oxidation to the pentavalent state, and arsenic in the atmosphere is usually a mixture of the trivalent and pentavalent forms [15].

Arsenic in water

Arsenic may be released to water from the natural weathering of soil and rocks, and in areas of vulcanism. Arsenic may also leach from soil and minerals into groundwater. Anthropogenic sources of arsenic releases to water include mining, nonferrous metals, especially copper, smelting, waste water, dumping of sewage sludge, coal burning power plants, manufacturing processes, urban runoff, atmospheric deposition and poultry farms [16]. A contributory part of mining and coal burning power plants is leaching from abandoned mine tailing and fly ash waste piles. Significant amounts of arsenic are released in liquid effluents from gold-milling operations using cyanide.

People who produce or use arsenic compounds in occupations such as nonferrous metal smelting, pesticide manufacturing or application, wood preservation, semiconductor manufacturing, or glass production may be exposed to substantially higher levels of arsenic, mainly from dusts or aerosols in air. Exposure at waste sites may occur by a variety of pathways, including inhalation of dusts in air, ingestion of contaminated soil or water, or through the food chain. The magnitude of the exposures can only be evaluated on a site-by-site basis; however, exposures generally do not exceed background intakes from food and drinking water. Leaching of arsenic from soil, landfills, or slag deposits is a source of arsenic in groundwater [17, 18].

The arsenic in soil may be naturally-occurring or a result of the application of arsenic-containing pesticides or sludge. Wood treated with chromated copper arsenate (CCA) is used in piers, piling and bulkheads and arsenic can leach from the treated wood [19]. Ammoniacal copper zinc arsenate (ACZA) is another arsenic-containing waterborne preservative; however, it is not as widely used as CCA [20]. Arsenic in water can undergo a complex series of transformations, including oxidation-reduction reactions, ligand exchange, precipitation, and biotransformation [21].

Arsenic in soil

The soil receives arsenic from a variety of anthropogenic sources, including ash residue from power plants, smelting operations, mining wastes, and municipal, commercial, and industrial waste. Ash from power plants is often incorporated into cement and other materials that are used for roads and construction. Arsenic may be released from such material into soil. Pacyna et al. [22]estimated global anthropogenic inputs of arsenic into soil for 1983. Excluding mine tailings and smelter slag, annual estimated inputs ranged from 52,000 to 112,000 metric tons with a median value of 82,000 metric tons. Mine tailings and smelter slag were estimated to add an additional 7,200–11,000 and 4,500–9,000 metric tons, respectively. Old abandoned mine tailings undoubtedly contribute still more. Wood treated with CCA used in foundations or posts could potentially release arsenic into the surrounding soil. CCA preservatives have been shown to leach to varying degrees from wood, as well as through soils in both field and laboratory studies [23, 24].

Arsenic may also be released on land through the application of pesticides and fertilizer. Terrestrial plants may accumulate arsenic by root uptake from the soil or by absorption of airborne arsenic deposited on the leaves, and certain species may accumulate substantial levels. Yet, even when grown on highly polluted soil or soil naturally high in arsenic, the arsenic level taken up by the plants is comparatively low [25].

Arsenic in soil exists in various oxidation states and chemical species, depending upon soil pH and oxidation-reduction potential. Under most environmental conditions, -inorganic As(V) will exist as a mixture of H_2AsO_4 and $HAsO_4^{2-}$, and inorganic As(III) will exist as H_3AsO_3. The arsenate and arsenite oxyanions have various degrees of protonation depending upon pH [26]. As(V) predominates in aerobic soils, and As(III) predominates in slightly reduced soils (e.g., temporarily flooded) or sediments.

ARSENIC INFLUENCE ON HUMAN HEALTH

Arsenic is one of the most toxic elements that can be found. Despite their toxic effect, inorganic arsenic bonds occur on the Earth naturally in small amounts. Humans may be exposed to arsenic through food, water and air. Exposure may also occur through skin contact with soil or water that contains arsenic. Levels of arsenic in food are fairly low, as it is not added due to its toxicity. But levels of arsenic in fish and seafood may be high, because fish absorb arsenic from the water they live in. Luckily this is mainly the fairly harmless organic form of arsenic, but fish that contain significant amounts of inorganic arsenic may be a danger to human health. Arsenic exposure may be higher for people that work with arsenic, for people that live in houses that contain conserved wood of any kind and for those who live on farmlands where arsenic-containing pesticides have been applied in the past. Arsenic poisoning is a slow process, taking many years to appear after continual consumption of arsenic-laden water. Tell-tale signs are having pigmentation changes, hyperkerotosis and skin cancers.

While As exposure can occur from food, air and water, all major chronic As poisonings have stemmed from water and this is usually the predominant exposure route. Exposure to As leads to an accumulation of As in tissues such as skin, hair and nails, resulting in various clinical symptoms such as hyperpigmentation and keratosis. There is also an increased risk of skin,internal organ, and lung cancers. Cardiovascular disease and neuropathy have also been linked to As consumption. Verbal IQ and long term memory can also be affected, and As can suppress hormone regulation and hormone mediated gene transcription. It is therefore important to carry out clinical tests of As exposure[27].

CONCLUSIONS

The knowledge base of the exposure and toxicological effects of arsenic has expanded greatly, particularly in the past 10–20 years. It is known that exposure to arsenic for most people is an everyday occurrence because it is a natural component of the environment. Other types of exposure can come from soil contaminated with arsenic, from its occupational use as a pesticide or a by-product of metal ore smelting, from its use as a chemotherapeutic agent, and what interests many people, but occurs rarely, as a homicidal agent. More research is still needed to understand arsenic exposure, metabolism, effects, and MOA for cancer. Nevertheless, with recent findings and advances in technology, many of the unanswered questions regarding the toxicology of arsenic may soon be answered. This knowledge will lead to better protection of populations at risk from arsenic-related illnesses.

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