University of Belgrade, Technical Faculty, Bor, Serbia
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University of Applied Sciences Trier, Environmental Campus Birkenfeld, Germany

1st International Symposium on Environmental and Material Flow Management

EMFM 2011

PROCEEDINGS

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PREFACE

As the first co-organizers of the 1st International Symposium on Environmental and Flow Material Management – EMFM 2011, it is our pleasure to begin a new tradition, a new scientific meeting, in the jubilee year of 50th anniversary of Technical Faculty in Bor, University of Belgrade.

The International Symposium on Environmental and Material Flow Management is organized this year for the first time by the Technical Faculty in Bor, University of Belgrade (Serbia), Faculty of Mechanical Engineering, University of Zenica (Bosnia and Herzegovina) and Environmental Campus Birkenfeld, University of Applied Sciences Trier (Germany), presenting a forum for representation and discussion of scientific research and practice on the subjects of environmental and material flow management.

Main topics of this Symposium are: environmental management, ISO 14001 and EMAS, material flow management, life cycle analysis, sustainable development, industrial ecology, energy management, cleaner production, eco-efficiency.

It should be mentioned, that the symposium presents a joint activity initiated in the frame of Resita Network – academic network within the field of "Entrepreneurship and Innovation", formed in 2008 by numerous participant universities from Albania, Austria, Bosnia and Herzegovina, Bulgaria, Croatia, Germany, Macedonia, Montenegro, Romania, Serbia and Slovenia, and successfully functioning under DAAD support.

Prof. dr Dragana Živković

President of the Scientific Committee EMFM2011

Prof. dr Živan Živković

Vice-president of the Scientific Committee EMFM201

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MATERIAL FLOW MANAGEMENT – BEST PRACTISE FOR SUSTAINABLE EDUCATION AND APPLIED RESEARCH PROJECTS AT THE ENVIRONMENTAL CAMPUS BIRKENFELD

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Abstract

Material flow management (MFM) represents the basic principle for all activities conducted at IfaS. MFM is a tool to implement sustainable concepts such as Circular Economy or Zero Emission strategies and involves the goal-oriented, efficient use of materials, material streams and energy as well as the necessary steps and measures for the conversion from a linear economic system ("throughput society") into a durable "circular" society.
The Institute for Applied Material Flow Management (IfaS) is a higher research institute of Trier University of Applied Sciences located at Environmental Campus Birkenfeld (ECB). ECB offers students an interdisciplinary education at the only "Zero Emission University" in Europe. Innovative and ecological building standards are complemented by modern utility technology and sustainable management systems. The electricity and heat demand of the campus is covered by renewable energy sources, provided by a neighbouring biomass-combined heat and power plant.
IfaS was founded in 2001 thanks to the initiative of committed professors from various disciplines, namely Material Flow Management, Ecology, Business Management, Physics/Process Engineering and Communication/ Ethics. The aim of IfaS is to promote the sustainable optimisation of regional and operational material flows in specific and practice-oriented projects worldwide. IfaS features long and demonstrable experience in education (i.e. IMAT master programmes, www.imat-master.de), research and project development. The intelligent, resource-efficient utilisation of material and energy flows is the backbone of a sustainable society. For IfaS the optimisation of material and energy flows is rather a question of management than a technical challenge. The analysis of the present situation, the creation of networks, the innovative combination of new and proven technologies as well as the development of innovative financial mechanisms are the focus of IfaS work.
The paper will provide an overview about the educational and applied research solutions developed by IfaS and ECB. Practical examples of successful material flow management projects will be used to demonstrate that material flow management is a tool to implement sustainable solutions.

The term of Material Flow Management (MFM) goes back to 1994, when by the Enquête Commission of the German Bundestag it was defined as: "[...] goal-oriented, responsible, holistic and effective influencing of material flows[…]".

STATE OF ENVIRONMENT IN BOSNIA AND HERZEGOVINA

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Abstract

Legal regulation of environmental protection, and making strategic plans as well as the organization of the institutional framework in this area has created the conditions for environmental management in Bosnia and Herzegovina. It was favorable overall global climate of the need to reduce pressures on the environment, obligations to the international regulations and growing awareness about the consequences of increasing pressures on the environment.
The real situation of the environment in B&H can be best assessed through analysis of environmental protection strategy, plans and reports on the state of the environment and the available data on the effects of particular interventions on the environment.
On the basis of available data, it can be concluded that environment quality is quite favorable, because the pressures on the environment do not exceed the critical limit. It is primarily the result of reduced economic activity and lower production in the last two decades, and undertaking effective measures to protect the environment. It should be noted that pressures on the environment even before they were high compared to European averages. With the revitalization of economic resources and economic development activities, in recent years, pressures on the environment have been growing. Although, these pressures are not disturbing, it is essential to future economic development with the needs of environmental protection, it actually means that economic development is planned and implemented in accordance with the concept of sustainable development.

Keywords: environmental management in B&H, situation of the environment in B&H.

1. Introduction

Bosnia and Herzegovina, although late, began to accept the European environmental principles and standards. Meeting the standards on environmental protection, or progress toward these standards represents a major challenge. Much has been done to develop a framework for the desired directions and goals in terms of environmental protection and sustainable development. The legal and institutional framework is established, and many activities in the field of environmental protection that provide specific results are initiated. However, in the future it is necessary to build the necessary environmental infrastructure, administrative capacity, and undertake activities to implement the objectives of sectoral policies in the field of environmental protection [1].

According to the Constitution and applicable legislation, environmental management is the responsibility of the entities and cantons in the Federation. In both entities there is a ministry responsible for environment in FBiH - the Federal Ministry of Environment and Tourism, and in the RS - Ministry of Urbanism, Civil Engineering and Ecology. In the Federation also exists a ministry for the environment in each of the ten cantons and the Federation and the cantons are jointly responsible for environmental management. The international-legal obligations in the field of environmental protection, development and utilization of natural resources are implemented through the Ministry of Foreign Trade and Economic Relations. At the same time, this Ministry is responsible for performing duties related to defining basic principles and policies, coordination and harmonization of strategies and plans of entities government and authorities at the international and national level in the field of environmental protection, development and utilization of natural resources.

In the period 2002-2004 the Entities and Brcko District have been prepared (with the help of the CARDS EU project) and adopted a set of laws on environmental protection. On the basis of these laws were drafted and adopted many regulations so that it can be concluded that BiH has satisfactory regulated environment issues. Legal regulation of environmental protection, the adoption of strategic plans and the organization of the institutional framework in this area has created the conditions for environmental protection management. It was favorable by global awareness of the need to reduce pressures on the environment, obligations to the international regulations and growing awareness about the consequences of increasing pressures on the environment.

Priorities in this area are:

- adopting the Law on Environmental Protection, which would create legal framework for the single management of environmental protection at the level of the country and implementation of international obligations in this area,
- implementation of ratified international conventions and ratification of the remaining relevant conventions,
- the establishment and creation of conditions for the functioning of the State Agency for Environmental Protection,
- implementation of strategic plans, with special emphasis on collecting and treating wastewater, drinking water supply and solid waste management,
- Integration of basics of environmental policies in other sectors, etc. [2]

BiH is a part of BELLS movement, and some of the standards of this movement are the incorporation of European values of sustainable development and environment in the political agenda and all elective programs at the national, regional and local level. BELLS movement is the result of the regional project "Regional Environmental Advocacy (REA) Action and Cohesion in Western Balkans", which aims to environmental issues are given priority by policy makers and to find the focus in decision making at all levels, because they are one of the important segments of reaching EU standards and better quality of life of citizens [3].

The real situation of the environment in B&H can be best assessed through analysis of achieving the goals of environmental protection strategies, plans and reports on the state of the environment and the available data on the effects of particular interventions on the environment.

BiH has developed and adopted a strategic document in the field of environmental management that includes following:

1. National Environmental Action Plan in BiH (NEAP), developed and adopted in 2003, which identifies short and long-term priority activities and creates the foundation for the preparation of long-term strategy for environmental protection in accordance with the economic development of BiH;
2. Environmental Management Plan was developed for the electricity sector which identifies the pressures on the environment, measures to improve performance, cost and dynamic of implementation of measures;
3. Strategy of environmental protection in FBiH and RS for 2008-2018 were developed and adopted in 2010. They defined the main objectives of environmental policy for individual

sectors, and defined a series of measures to achieve the set goals. The success of the implementation of the strategy depends fundamentally on the extent and manner of involvement of key stakeholders in the process of decision-making, to ensure the integration of environmental objectives and measures to the other sectoral strategies.

4. Strategy of the water management of the Federation BiH for period 2010 - 2022, made in 2010, which defines the objectives in the field of water management and measures for achieving the goals.
5. Strategy on solid waste management in BiH provides management at the regional level and builds regional sanitary landfills for municipal waste disposal.
6. Technical guidelines on best available techniques (BAT) in the sectors of food industry and agriculture, made in 2007/08.

The adoption of these and other strategic documents created conditions for effective protection and environmental management.

2. Air protection

On the basis of available data, it can be concluded that the air quality situation in BiH is better due to significantly lower emissions of pollutants, primarily as a result of reduced economic activity and lower production volume in the last two decades, but also because of taking measures to protect the air. According to the NEAP, the main sources of air pollution are quite outdated power plant in Tuzla, Kakanj, Ugljevik and Gacko, a lot of outdated industrial and metallurgical plants, burning poor quality coal with high sulfur content in thermal power plants and households, use of outdated motor vehicles and other sources such as municipal landfills, etc. [2]

According to calculations, the annual SO_2 emissions from the energy sector in the period 2000-2005 was between 182 and 279 kt and it is significantly lower compared to 1990 in which the SO_2 emission was 422 kt [4]. A decreasing of SO_2 emissions was a result of significantly lower amount of burned coal and using better quality fuels, and the restructuring of the economy. The SO_2 emission from energy sources for the period 2000-2005 is shown in the following table.

Table 1. The SO_2 emissions from energy sources in BH [4]

SO_2 emission (t)	2000.	2001.	2002.	2003.	2004.	2005.
Federation of BiH	105.493	137.834	153.375	130.960	139.794	133.182
R. Srpska	76.868	86.876	125.702	143.331	89.407	105.415
Brčko District	454	449	460	390	400	447
Total	182.815	225.159	279.537	274.681	229.601	239.044

The trend shows an increase in SO_2 emissions in the period 2000-2002 and since this year has a slight decrease. The SO_2 emission from power plants is 83.3%, emissions from non-industrial (small) furnace 6.8%, transport 1.4% and 8.5% other sources [4].

Emission of particulate matter in the period 2000-2005 was 29.3 to 35.7 kt what is significantly lower compared to 1990 when it was 56.2 kt. Particulate matter emissions from energy sources for the period 2000-2005 is shown in the following table.

Table 2. Particulate matter emissions from energy sources in BiH [4].

SO_2 emission (t)	2000.	2001.	2002.	2003.	2004.	2005.
Federation of BiH	19.227	23.255	24.892	20.654	21.456	23.415
R. Srpska	10.189	10.265	9.332	11.659	11.034	12.088
Brčko District	485	510	497	516	505	569
Total	29.901	34.030	34.721	32.829	32.995	36.072

The highest emissions of particulate matter were from non-industrial combustion plants (55.1%), thermal plants (35.7%), transport (3.0%) and other sources (4.5%).

The main causes of excessive air pollution are the following:

- character of the industry (basic and outdated industry)
- lack of technical systems for the mitigation of emissions and air protection,
- inadequate maintenance of installations and technical systems for air protection,
- high energy intensity in industry,
- lack of integration of measure of environmental protection management in production processes and inadequate treatment of air protection,
- poor organization of traffic in urban areas and vehicle age, etc.

Monitoring air quality is carried out sporadically in some industrial-urban centers and there is no established a systematic monitoring at the level of the entity for the purpose of monitoring air quality under the regulations and obligations of international regulations. Monitoring of air quality is the responsibility of the entity Meteorological Bureau. The following tables provide data on the state of air quality in some cities in BiH, which performs continuous monitoring of air quality.

Table 3. The results of air quality monitoring at the automatic station in Zenica in 2010

Polutant	Sampling period	The limt value for annual average (μg/m^3)	The limit value for high values (μg/m^3)	Average (μg/m^3)	Maximal value for measured period (μg/m^3)	The number of high value exceeding
SO_2	1 hr	90	500 [1)]	117,4	986,08	79
SO_2	24 hrs	90	240 [2)]	117,4	503,68	20
NO_2	1 hr	60	300 [3)]	8,2	43,52	0
NO_2	24 hrs	60	140 [2)]	8,2	24,57	0
PM10	24 hrs	50	100 [2)]	67,16	741,9	32
CO	8 hrs	150	10.000	2558,4	9450	0
O_3	8 hrs	30	150 [4)]	42,1	174,05	0

[1)] It must not be exceeded more than 24 times in a calendar year
[2)] It must not be exceeded more than 7 times in a calendar year (98th percentile)
[3)] It must not be exceeded more than 18 times in a calendar year
[4)] It must not be exceeded more than 21 times in a calendar year (98th percentile).

Table 4. Concentrations of sulfur dioxide and smoke in Sarajevo – Bjelave station[5].

Year	Concentration of SO_2 (μg/m^3)					Concentration of smoke (μg/m^3)				
	C_{sr}	C_{med}	C_{95}	C_{98}	C_{max}	C_{sr}	C_{med}	C_{95}	C_{98}	C_{max}
2003	21	11	68	122	162	41	20	152	290	634
2004	24	14	74	93	134	47	27	154	241	749
2005	33	17	103	142	435	47	25	155	270	713
2006	29	21	69	94	130	35	18	132	232	285
2007	28	22	61	71	247	27	15	88	121	146
2008	22	18	49	71	167	27	16	78	162	309
2009	28	21	54	134	401	27	17	72	157	422

Table 5. Parameters of the air quality in Sarajevo – Bjelave station [5].

Parameter	SO_2 (μg/m^3)				O_3 (μg/m^3)	NO (μg/m^3)	NO_2 (μg/m^3)	NO_x (μg/m^3)
Year	2006	2007	2008	2009	2009	2009	2009	2009
Average	24	29	17	29	49	13	26	35
Max	334	1075	761	506	156	267	299	523
C_{95}	86	105	46	79	101	63	81	125
C_{98}	128	149	103	160	113	96	122	189

Table 6. Parameters of the air quality in Tuzla - Station1 [5].

Parameter	SO_2 (μg/m^3)					NO_2 (μg/m^3)	O_3 (μg/m^3)	PM2.5 (μg/m^3)
Year	2004	2005	2006	2008	2009	2009	2009	2009
Average	38	73	63	60	71	28	30	77
Max	1561	967	959	829	733	178	155	784
C_{95}	162	267	244	241	225	62	74	274
C_{98}	268	362	328	315	323	77	86	362

Table 7. parameters of the air quality at the Ivan Sedlo station (project EMEP) [5].

Parameter	SO_2 (μg/m^3)	NO (μg/m^3)	NO_2 (μg/m^3)	NO_x (μg/m^3)	O_3 (μg/m^3)	PM10 (μg/m^3)
Year	2007	2007	2007	2007	2006	2007
Average	33,6	1,2	4,9	5,7	61,0	228
Max	302,7	335,9	58,8	540,8	153,3	225,8
C_{95}	71,3	4,0	18,4	21,6	102,9	73,7
C_{98}	103,7	5,0	27,3	29,3	110,7	97,6

Monitoring of air quality showed that the air in the industrial-urban areas is mostly polluted, especially in the winter season when there is a periodically air pollution, although industrial activity is significantly reduced in that time.

BiH submits information on air quality monitoring by the European Environment Agency (EEA). Data on imission can be found in the Airbase EIONET portal EEA.

The strategic aims of the air protection policy are:

- limit emissions,
- management of air quality and
- improving energy use by reducing energy intensity and encouraging use of renewable energy sources [6].

According to the NEAP main strategic objective in the field of air protection is participation in international activities to reduce transboundary air pollution and global climate protection, and at the local level reducing air pollution.

Measures to achieve this goal are:

- institutional strengthening,
- establishing a registry and database on emissions of acid and greenhouse gases including information on trends in local emissions and quantities of greenhouse gases,
- research impact of polluted air on human health, the components of the environment and economic activities,

- stabilization and gradual reduction of acid emissions and greenhouse gases by increasing energy efficiency, technological restructuring, greater use renewable sources of energy and revitalization of forest ecosystems,
- improving the information systems and adequate inclusion of BiH into operating systems (EIONET, the World Meteorological Organization, etc.)
- inclusion of emissions issue, changes in air quality and climate in the curricula for all levels of education and improving public awareness on protection of air and the environment, etc. [2].

According international obligations in the protection of the atmosphere, BiH among others, included in:

- implementation of cooperation programs for monitoring and assessment of transboundary transfer of pollutants in the atmosphere over long distances in Europe (EMEP) trough the Ivan Sedlo station
- data collection of emissions of greenhouse gases as part of national reports/communications to the UNFCCC convention,
- implementation of the project excluding the use of substances that threaten the ozone layer (SOOO). In 2009 is banned the import of all SOOO than HCFCs, which BiH has fulfilled obligations under the Montreal Protocol,
- creating, implementing, publishing and regularly updating the program of measures to mitigate climate change,
- sustainable use of sinks and reservoirs of greenhouse gases,
- the inclusion of impact assessment of climate change in the relevant national strategies,
- Co-operation in technology transfer, research, systems monitoring and data exchange,
- cooperation in education and awareness, etc. [2,4,7].

BiH has a relatively small effect on global climate change, and low emissions of other pollutants in the region, but suffers from significant climate change. BiH Presidency adopted the Decision on BiH accession to the Protocol Water and Health to the Convention on the Protection and Use of Transboundary Watercourses and International Lakes.

3. Water protection

BiH has two different water basins that have significant local and regional impact of European basins. Neretva River and its tributaries flowing south to the Adriatic Sea, while Bosna, Drina, Vrbas and Una flowing north to the Sava and Danube, and belong to the Black Sea basin. Protection and prevention of pollution of these waters is therefore of great national and international importance.

Condition of water management in BiH is characterized by a complicated distribution of competences between the two entities and Brcko District, and therefore the institutional structure does not reflect the real needs of this sector.

Harmonization with EU water legislation appeared a new era in the management of water resources in terms of developing the legal and institutional framework for water management. Progress has been determined by a shift in the direction of finding a new, modern management solutions to new social requirements (including in respect of environmental protection, integrated water management and water management within river basins, taking into account the ecosystem approach) were satisfied with the extent of the transitional possibilities of BiH.

Monitoring of surface water is carried in certain measuring profiles of water streams which are the long-term monitored. Based on the results of water monitoring can be stated as follows:

- generally can be concluded that the quality of surface water has improved due to restructuring the economy, closing some industrial capacity, ie the reduction of industrial pollution,
- water of sub-basin of the river Bosna is significantly more polluted than water of sub-basins of the rivers Una, Vrbas and Drina,
- greatest pollution is observed in rivers Miljacka Jošanica and Stavnja which discharged untreated wastewater of Sarajevo, Breza and Vares
- Una River is the least polluted and is the cleanest river in BiH,
- largest sources of pollution in the sub-basin of the river Bosna are municipal wastewater of Sarajevo, Visoko, Kakanj, Zenica, Tuzla and other towns,
- urban centers such as Sarajevo and Tuzla produce the greatest burden of pollution of water of sub-basin of Bosnia and industrial centers in Zenica and Maglaj produce much less of a burden than they were before the 1991,
- all waterways of the Sava river basin still have the possibility of selfcleaning.

The total pollution load of the population in river basin / sub-basin areas is shown in the following table [8].

Table 8. Overview of the total pollution load of the population in river basin and sub-basin areas in FB&H [8].

River basin / sub-basin	Population	Percent	BPK_5	N	P
	2007.	%	t/y.	t/y.	t/y.
A water area of Sava river					
Sub-basin of Una with Korana and Glina	302.487	13	6.624	1.214	276
Sub-basin of Vrbas river	120.868	5	2.647	485	110
Sub-basin of Bosna river	1.341.727	58	29.402	5.390	1.225
Sub-basin of Drina river	57.526	2	1.260	231	52
Basin of Sava river	135.557	6	2.969	544	124
Total:	1.958.166	84	42.902	7.865	1.788
A water area of Adriatic Sea					
Sub-basin of Neretva river with Trebišnica	311.262	14	6.817	1.250	284
Sub-basin of Krka and Cetina river	58.084	2	1.272	233	53
Total :	369.346	16	8.089	1.483	337
Total in FBiH:	2.327.512	100	50.991	9.348	2.125

The following table gives an overview of the total pollution load of industrial production by basin and sub-basin whose calculation is done on the basis of measurement.

Table 9. Overview of the total pollution load of industrial production by basin and sub-basin in FB&H [8].

River Basin / sub-basin	With pretreatment	Without pretreatment	Total	Estimation	Total industry
	EP				
A water area of Sava river					
Sub-basin of Una with Korana and Glina	12.683	0	12.683	2.386	4.297
Sub-basin of Vrbas river	1.442	1.024	2.466	1.831	2.110.662
Sub-basin of Bosna river	769.792	1.321.844	2.091.636	19.026	6.850
Sub-basin of Drina river	5.924	486	6.410	440	7.742
Basin of Sava river	3.591	1.682	5.273	2.469	2.144.620
Ukupno:	13.128	1.325.036	2.118.468	26.152	2.144.260
A water area of Adriatic Sea					
Sub-basin of Neretva river with Trebišnica	13.128	11.110	24.238	187.642	211.880
Sub-basin of Krka and Cetina river	0	2.355	2.355	3.402	5.757
Total :	13.128	13.465	26.593	191.044	217.637
Total in FBiH:	806.560	1.338.501	2.145.061	217.196	2.362.257

Comparison of pollution load from the population and pollution from industry can be concluded that the pollution load from industries covered by the billing system for water pollution is approximately the same as pollution load from the population. Taking into account that one part of the industry is not covered by the collection of discharged water and wastewater as a part of the population that is released into the soil as a recipient, it can be concluded that the industry is in a slight advantage in terms of contribution to overall pollution the water.
Indicators in the field of water management show:

- The capacity for wastewater treatment is minimal, a very small number of devices for treatment of urban waste water were built, from the 79 municipalities in FBiH only eight have plants for wastewater treatment (Gradačac Srebrenik, Zepce, Trnovo, Ljubuski, Čitluk, Grude and Neum) and thus covered only about 3% of wastewater treatment in Federation,
- Wastewater from most of the population (90%) is discharged without treatment into the nearest streams or underground,
- Part of population that is covered wit sewerage systems in urban areas is about 56%,
- Commercial facilities excessive burden surface water due to irrational use of water and lack of wastewater systems (a small number of industrial plants have facilities for wastewater treatment),
- 50% of tap water supply is "lost" along the way and never reach the consumer,
- low level of sewerage coverage of the population,
- surface water is burden with solid waste [8,9].

According to the NEAP, the main causes of the unsatisfactory condition of water resources and water management are as follows:

- lack of integrated water management system,
- lack of development plans and the coordination of different levels of decision-making,
- lack of financial resources,
- lack of systems for water monitoring
- lack of expert personnel and equipment,

- irrational consumption of water,
- lack of information system,
- lack of research and education, etc. [2].

To improve the situation in the field of water protection and water management is necessary to implement the following measures:
- execute restructuring and modernizing the water sector in line with EU directives (Model "integrated river basin management")
- intensify activities in the water sector, primarily due to the fulfillment of international obligations,
- preparation and completion of river basin management plans,
- rehabilitation of existing and building new systems for wastewater treatment,
- the establishment of water monitoring and information system,
- strengthening the water sector and education of personnel.

Obligations regarding the protection of water quality resulting from domestic water legislation and international treaties and agreements such as: the SAA (Stabilization and Association Agreement), the ICPDR (International Commission for the Protection of the Danube River), the Sava Commission, MAP (Mediterranean Action plan), etc.

Ultimate goals are clean water, without the presence of hazardous materials and sustainable use of water resources. The goal is clear, but the path to its realization is very long, complex and requires the implementation of many technically demanding measures.

4. Waste

In BiH annually per capita 270 kg of waste is produced. Waste is usually collected without selection. In municipal waste certain categories of industrial, medical and other wastes are often found. It is estimated that 40% of the total collected waste is disposed of in unprepared landfills, there are 54 of them, and 36% of waste produced is not at all disposed of by the utility companies. In the situation of poor coverage of waste collection services there are large number of unregulated and uncontrolled landfills. Thus, in the Federation is about 2,000 so-called uncontrolled locations (wild) municipal waste landfill in an area of 974 221 m2. At this landfill is disposed municipal, industrial, and inert wastes of animal origin, and often medical waste [10].

Although neglected in the past, this sector has gained an important place among the priorities of local, entity and state institutions. A comprehensive strategy was developed through three important documents: NEAP, solid waste management strategy from 2002 and medium term development strategy (2004-2007). Both entities have harmonized laws related to waste management, and the existing legislation of the European Union is taken for the frame. The implementation of these laws has yet to come an adequate way.

Solid Waste Management Strategy in BiH provides waste management at the regional level, i.e. the construction of regional sanitary landfills. It is a defined policy and strategic directions for waste management based on the general principles of EU legislation. In accordance with this fact an agreement with the World Bank was signed on the IDA credit for the project "Solid Waste Management." The project envisages the rehabilitation of existing municipal landfills and the construction of 16 new regional sanitary landfills for municipal waste disposal for several municipalities in each region. The implementation includes six regions: Sarajevo, Zenica, Tuzla, Bihac, Banja Luka and Bijeljina. The regions have formed new teams with utilities to implement this project (PIT teams). Due to a very pronounced problem with the deposit of solid waste, which is present in both entities, the activities to include the region of Livno, Gorazde, Prijedor, Doboj, Zvornik in this project were undertaken [10].

Indicators in this field show that:

- the degree of coverage of organized waste collection is low,
- most municipal landfills do not meet the technical requirements which guarantee minimal environmental impacts,
- the frequent occurrence of uncontrolled waste disposal in the area unprepared for such purposes,
- inadequately disposed waste is a source of infectious diseases,
- municipal landfills are supposed to be closed and repaired for use until 01 January 2008, but it is not done,
- information on the separate collection, recycling and composting waste show a very low level of practical implementation of the principles of waste management,
- lack of landfill cadastre, register type, quantity, and waste streams,
- lack of qualified personnel, etc.

The basic objective of the Solid Waste Management Strategy is the protection of the environment, encourage sustainable use of resources through the establishment of an integrated waste management system. The realization of the fundamental objectives can be achieved by implementation of the following strategic objectives:

1. Reducing the risk to the environment and human health and the establishment of priority infrastructure for integrated waste management;
2. Reducing the amount of waste for final disposal with more efficient use of resources;
3. Ensuring the implementation of an integrated waste management system through legal, institutional and economic framework;
4. Ensuring systematic monitoring parameters for the assessment of environmental conditions [10].

Based on the strategic objectives the operational objectives are defined that are specific and measurable changes that will be achieved during the implementation of measures from the Strategy of Environmental Protection and Waste Management Strategy.
The first strategic goal is achieved through the realization of the following operational objectives:

- reducing production of waste to a minimum, especially hazardous waste,
- increase the population covered by organized waste collection,
- create conditions for a sanitary waste disposal in all regions,
- remove illegal ("wild") landfills and remediation of them,
- rehabilitate and close the existing municipal landfill.

The second strategic goal is achieved through the realization of the following operational objectives:

- establishing a system of separate waste collection,
- collection and recycling of packaging waste,
- separate collection of biowaste from gardens and parks in order to compost it
- the establishment of regional waste management centers in all regions with all the necessary amenities (such as Sarajevo, Zenica, Banja Luka, Mostar, etc.).

The third strategic objective has been realized to a significant extent in the part relating to the structure and the legal part of the institutional and economic framework. Integrated system meet the regional concept and is created on the territory of several municipalities joined in the region. The purpose of the regional centers of waste management is to reduce waste disposal through lower production and recycling of useful materials, sanitary waste disposal in order to minimize the negative impacts of landfills on the environment and self-sustaining funding of waste management.

The fourth strategic objective relates to ensuring systematic monitoring of the parameters for the assessment of environmental conditions. To achieve this goal it is necessary to establish an information system first as one of the basic components of integrated waste management. The information system integrates the information flow of technical, legal, institutional and economic character of all types of waste in order to better planning of activities in this field.

5. Conclusion

On the basis of available data, it can be concluded that the state environmental quality in BiH is quite favorable, because the pressures on the environment do not exceed the critical limit. It is primarily the result of reduced economic activity and lower production volume in the last two decades, and taking effective measures to protect the environment. It should be noted that pressures on the environment even before were not high compared to European averages, making it easier to achieve the set objectives in this area. With the revitalization of economic resources and economic development activities pressures on the environment in recent years grows. Although these pressures are not disturbing, it is essential to future economic development harmonize with the needs of environmental protection and economic development plans and implements in accordance with the concept of sustainable development.

The organization of the legal and institutional system, and adopting strategic plans are created the basic conditions for the efficient management of environmental protection in BiH. In future it is necessary to build the necessary environmental infrastructure, administrative capacity, and take action to implement all the objectives of sectoral policies in the field of environmental protection.

Implementation of strategic objectives in the field of environmental protection and sustainable development of guidelines allow long-term development of BiH, and following that strategy BiH has adopted a set of laws and a number of implementing regulations on environmental protection, which are based on key principles of environmental protection. Legal protection of the environment is consistent with the legal norms of the European Union. In addition, BiH has acceded to most relevant international conventions and protocols related to environmental protection, indicating that it was determined in the adoption and implementation of EU environmental principles and standards.

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ASSESSING THE SUSTAINABILITY OF MODERN VEHICLE DRIVES – HOW ECO - EFFICIENT IS THE ELECTRIC CAR?

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Motorized traffic is among the dominating CO2-emitting sources, worldwide and even more in highly developed countries. Also, motorized traffic is responsible for environmental damages and high health costs all over the world due to toxic emissions. Since one and a half decades, CO2-reduction of cars has been a primary political goal in EU in order to minimize GHG emissions as required by Kyoto protocol. EU commission and EU car industry subsequently initiated a Diesel car boom nearly all over Europe to reduce CO2 emissions. This way, toxic emissions (NOx, fine dust) were partly neglected in threshold regulations, public opinion as well as in the scientific sustainability discussion.
Alternatives in vehicle drives other than combustion engines and fossil fuels are discussed in this contribution and assessed with respect to the development described above, to energy and eco-efficiency as well as availability. In conclusion, there seems to be no reasonable alternative to electric cars which are locally emission free. The critical sustainability discussion on the electric car in Germany, focussed on CO2, is reviewed. Data beyond CO2 (NOx, fine dust) and from additional approaches (health improvement) are provided. A new attempt to improve the sustainability of electro mobility (E-conversion) will be presented.

Reference

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SPATIAL DISTRIBUTION OF HEAVY METALS IN VICINITY OF COPPER SMELTING PLANT IN BOR, SERBIA

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The presence of the pollutants in the environment and their impact on human health, are great ecological attributes for the most copper smelters in the world. Thus, an elementary step towards a quantitative assessment of the risk of pollutants to the environment is to estimate their environmental concentrations and spatial distribution. This paper presents developed multicriteria method to evaluate distribution of heavy metals in surrounding of copper smelter plant in Bor, Serbia, as well as their fate in environment. In order to establish a reliable state of dispersion of pollutants and marking the most critical zone, the required samplings of environmental parameters, in accordance with proper procedures, were made in the air and soil in urban and rural areas of the townsite around the copper smelter. The obtained results clearly indicate that the most contaminated sites are located in the town center. Also, a strong correlation was found between the results of multcriteria analysis in the air and soil, where, a very important role in the mechanism of formation of pollution, play the meteorological parameters and distance from the sources of pollution.

Keywords: atmospheric distribution, soil pollution, heavy metals, ecology, copper production

1. Introduction

Due to increased industrialization, the problem of environmental pollution has been increasing for several decades. These problems are caused by the disposal of industrial wastes whether solids, liquids or gases, which have potential of ultimately polluting soil and water they come in contact with. Several studies have shown that the area in close proximity with industrial activity is marked by contamination of soil, water and agriculture fields [1–4].

Copper-smelters are one of the most significant pollution sources of SO_2 and heavy metals in the environment [5-6]. More than 80 primary copper smelters around the world employ various conventional pyrometallurgical techniques to produce more than 90 % of the total copper production [7]. Generally there are three steps in this process: roasting of ores to remove sulphur; smelting of roaster product to remove a part of the gangue for production of the copper matte; and converting the copper matte to blister copper. Atmospheric emissions of sulphur dioxide and heavy metals on fine particles PMx, occur during all the above mentioned processes [8-9]. The amount of sulfur dioxide released depends on the characteristics of the ore (complex ores may contain lead, zinc, nickel, and other metals), and on whether facilities are in place for capturing and converting the sulfur dioxide. SO_2 emissions may range from less than 4 kilograms per metric ton (kg/t) of copper to 2,000 kg/t of copper. Particulate emissions can range from 0.1 kg/t of copper to as high as 20 kg/t of copper. Various trace elements from impurities are present in the copper ores, which are emitted during the production process. The process is a major source of atmospheric arsenic and copper (50 % of the global emissions of this element), indium (almost 90 %), antimony, cadmium and selenium (approximately 30 %) and nickel and tin (approximately 10 %) [10].

Heavy metals can enter the soils in three primary ways: by irrigation with wastewater, deposition of aerosol particulates and leaching of tailings [11]. Recent studies have shown that soil and underground water in the vicinity of some copper smelters were contaminated by heavy metals [8, 12]. The greatest amounts of these heavy metals are discharged in the environment with the smelting gases in the form of airborne particles (PMx), and their concentrations decreasing as the distance from the smelter plant smokestacks increases, approximately following an exponential or negative power function.

In this study, research has been focused on spatial distribution and contamination assessment only of heavy metals in vicinity of copper smelter in Bor, Serbia, without taking into account other major pollutant- sulfur dioxide. Based on the previous studies, it had been hypothesized that atmospheric fallout of emitted heavy metals from copper smelter in Bor, was the main cause of wide-spread heavy metal contamination of topsoil in surrounding of copper smelter complex. However, according to Schulin and his associates [13], the fact that atmospheric deposition might lead to considerable soil contamination in vicinity of metal smelters, does not necessary mean that these are the main reason for high soil metal concentrations. The same authors emphasize, that spatial distribution patterns of soil pollution around the sources of heavy metals emissions are very heterogeneous. For instance, agricultural activities, natural variation in soil metal contents as well as other geochemical processes must be considered. Based on these facts, in this study special attention was directed to the soil sample locations, in manner that these locations were not exposed to fertilizers or to other agricultural measures, as well as the fact that atmospheric fallout of copper smelter emission depends on a variety factors, e.g. such are meteorological conditions and topography.

This paper has been organized in following way. In Section 2, methods which were used in this study have been described- including sampling procedures, instruments and measurements. In Section 3, the measured results of heavy metal concentration in air and soil have been analyzed by developed multicriteria methods to evaluate spatial distribution of heavy metals and identify the most critical zones of pollution in study area.

2. Materials and methods

2.1. Study area

This study was conducted in urban and rural surrounding of the copper smelter complex located in the town Bor, situated in the eastern part of Serbia. Location of the smelter is immediately beside the urban settlement of the town of Bor where more than 40,000 people live, while in the rural part in the immediate surroundings there are more than 20,000 inhabitants (see Fig. 1). The major sources of air pollution emission are two smelter smokestacks, which discharge around 200,000 tons of SO_2 into the atmosphere every year. Furthermore, per every ton of refined raw materials around 2.5 kg of dust are emitted into the atmosphere which leads to the situation that every year 5.3–19.6 kg of As, 4.86–7.99 kg of Zn, and 6.27–25.11 kg of Pb per inhabitant are emitted into the atmosphere which is many times higher compared to other industrial zones in Europe (LEAP 2003). These facts lead to a high degradation of a huge soil area around smelter, a huge volume of the soil waste and pollution of underground and surface water by heavy metals.

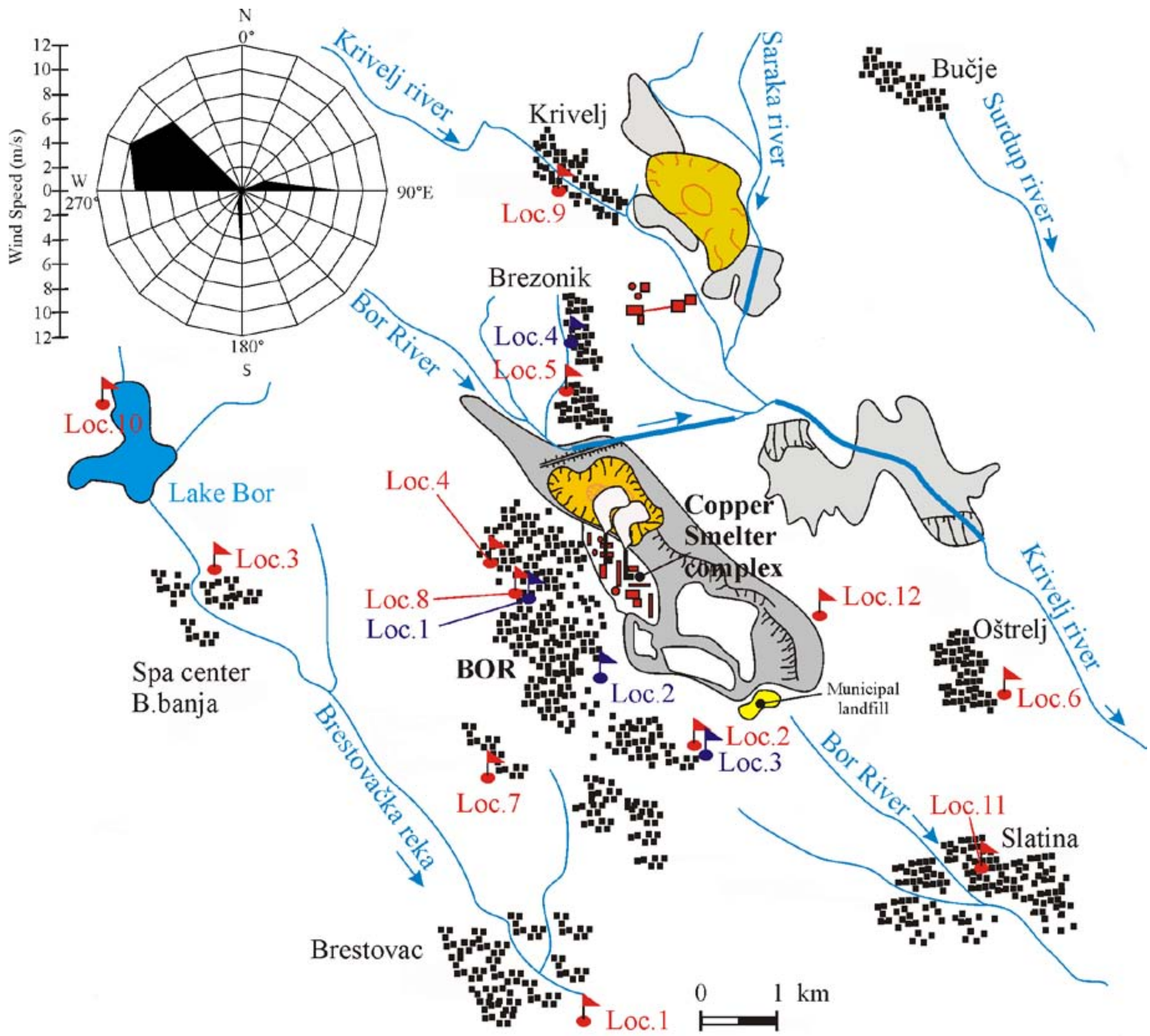

Figure 1. Study area, air measuring stations (blue markers), soil samples locations (red markers), and wind rose for the 2005-2008 period

2.2. Sample collection and analysis

The data collection was conducted in two phases, with main purpose to explore spatial distribution and variations of heavy metals in the study region (See Fig. 1). First, based on the real-time monitoring data from air monitoring system, which was installed in Bor in 2003, average annual concentrations of PM_{10} as well as heavy metals contents in PM_{10} were obtained for the 2005-2008 period. The PM_{10} sampling took place at four measuring points in vicinity of copper smelter smokestacks (blue markers in Fig.1), while contents of heavy metal and other chemical analysis were done in the laboratory of the Institute for Mining and Metallurgy in Bor.

After the first phase of air sampling, in the second phase, soil samples where taken from twelve locations indicated in Fig.1 (red markers in Fig. 1), between July and August 2008. These locations were not farmed; therefore, contamination of the ground through the use of agricultural measures was excluded. Ten samples were taken from each location. The soil samples were taken via a soil core sampler in such a way that a core of a soil was removed of radius 5 cm and depth 30 cm. A 5-cm surface layer of the core was stripped off and the rest of the sample was dried at 50 °C for 2h and its weight measured. In the next step soil, the samples were ground and homogenized until the required size was obtained and then the pH and heavy metals contents were determined.

The obtained reproducibility for the metals contents in the samples were relatively high (0.87–0.95). The pH value of the samples was realized using a pH–conductivity/°C meter, PC10 /EUTECH Instrument. For determination of the heavy metals contents in the soil, each sample was dissolved in an acidic mixture consisting of HF+HClO4, while HCl was used for filling up to the volume of the flask. The contents of Cu, Pb, Cd, Ni and Mn content were determined by atomic adsorption spectrophotometry (AAS), 33 using a Perking Elmer model 2380 instrument. The As content was determined by inductively coupled plasma atomic emission spectrophotometry (ICP–AES) employing an ARL 3410 instrument, while mercury content in the samples was determined by flameless atomic adsorption spectrophotometry–Mercury Analyzer (A– Hg) using a Perkin Elmer FIMS – 100 instrument. All chemical analyses were also performed in a certified chemical laboratory of the Institute for Mining and Metallurgy in Bor.

2.3. Methods for data analysis

The spatial distribution of heavy metals concentrations can be a useful aid to identify hot-spot area with high metal concentration [14]. Local transport and dilution of airborne pollutants can be modeled mathematically, and monitored through observations of actual concentrations. Monitored data tend to be more reliable than model estimates, but they are often unavailable [15]. There are many statistical methods used in chemometric studies. With the aim of obtaining a qualitative and quantitative contribution of different sources of pollution, researchers have been using a numerous receptor modeling techniques, for example Principal Component Analysis (PCA), followed by Cluster Analysis or Multilinear Regression (MLR) [16-18].

The relatively large amount of data generated in this research made it difficult to compare the measuring sites regarding to the level of environmental pollution for all important pollutants at the same time. In this study, this problem was overcome by using multivariate approach [19-21]. In fact, this paper deals with application of multicriteria method for decision making MCDM (PROMETHEE II) with PCA (GAIA) for grouping those location with similar pollutions problem and identifying those with a higher air pollution, as well as those with higher soil pollution.

In this study, well known MCDM method PROMETHEE/GAIA method [22-25], was used for ranking the sample locations defined in Figure 1, for two defined scenarios. Furthermore, the usage of PROMETHEE/GAIA approach has given an opportunity to compare results of two independent ranking analyses, one for air monitoring data (Scenario 1) and the other for soil samples (Scenario 2). In this way, basic assumption about distribution of heavy metals in surrounding of copper smelter plant in Bor, as well as their fate in environment, has been explored. Given this background, this paper highlights the significant advantages that can be obtained by using MCDM methods in environmental studies. However, the usage of these methods in this kind of scientific studies is quite novel.

3. Results and discusion

3.1. PM_{10} monitoring results

The analysis of PM_{10} data from 2005 to 2008, presented in Table 1, showed that the average contents of PM_{10} in the air are within the limits prescribed by EU Directives (1999/30/CE—50 μg/m^3 averagely on annual level and maximally not to be exceeded more than 35 times per calendar year or on annual level 40 μg/m^3) [26-28]. However, there are some phenomena of exceeding the limit for 15–20 days particularly in the year 2008 which points to the tendency of the increase of PM_{10} contents in the year 2008 in which maximal values were on average annual level of 44 and 78 $\mu g/m^3$at measuring points Town Park (Location 1- blue marker) and the Institute (Location 2- blue marker).

Table 1. Average annual contents of PM10 particles and contents of heavy metals in PM10 at four air measuring stations in town Bor for the 2005-2008 period.

Location		PM_{10} [$\mu g/m^3$]	Heavy metal concentration in PM_{10}				
			Pb [$\mu g/m^3$]	Cd [ng/m^3]	Cu [$\mu g/m^3$]	Ni [ng/m^3]	As [ng/m^3]
Location 1	Xmax[a]	44	0.9	14	2.4	0.2	170
	Xmin[b]	3	0.1	1	0.1	0.025	1.6
	Xavg.[c]	16	0.1425	2.25	0.6335	0.04	27.925
	DAL[d]	16	-	-	-	-	-
Location 2	Xmax	78	0.54	25	3.1	0.2	75.7
	Xmin	4	0.1	1	0.3	0.04	1.9
	Xavg.	10	0.0525	3.25	0.625	0.035	15.875
	DAL	17	-	-	-	-	-
Location 3	Xmax	20	1.5	33	2.7	27	94.2
	Xmin	5	0.05	2	0.4	0.02	7.8
	Xavg.	11	0.2175	5	0.8	0.7925	43.7
	DAL	2	-	-	-	-	-
Location 4	Xmax	28	0.1	6	0.9	0.1	48.7
	Xmin	4	0.0[f]	0[e]	0[e]	0[e]	3.8
	Xavg.	5.667	0.1	1.33	0.2	0.033	11.5
	DAL	0	-		-	-	-
Limit values according to the EU directive			5	5	-[g]	20	6

-no measurements
[a] The maximal average value on month level
[b] The minimal average value on month level
[c] The average value on annual level
[d] Days above limit
[e] Not registered concentration
[f] The concentration registered in trails
[g] Limit value for copper in PM10 is not prescribed by the EU directives (1999/30/CE; 2004/107/CE)

The main reason for such situation is outdated technology for copper production in this copper smelter plant. This technology is based on classical pyrometallurgy, with smelting in reverberatory furnaces and a relatively low degree of SO_2 gas utilization (< 50 %) for the production of sulfuric acid. The technical limitations of such technology lead to pollution of the environment with large concentrations of SO_2 and airborne particles of PM_{10} dust, as well as aero-sediments even larger than the PM_{10} particles. In that case, PM_{10} and SO_2 emissions are far over the limited values, which is a serious hazard for people's health in this region.

Another reason for increased environmental pollution in this study area is the fact that copper smelter in Bor is processing so called "dirty" concentrates. This way, available copper concentrates, besides the useful components: Cu, Ag, Au, contain harmful heavy metals, such as: As, Pb, Zn, Cd, Bi, Ni, Hg, Se, and Sb. Due to low percentage of gases purification in outdated filter stations, according to the Bor stakeholders, the gas emissions contain hundreds of tons of dust together with considerable quantities of heavy and volatile metals. In the figure 2, for five available concentrates at RTB- Company, comparison based on their quality was made. The first three concentrates (Conc. 1, Conc. 2 and Conc. 3) were obtained by the exploitation of local resources from ore deposits around the RTB – Bor Company, while the remaining two (Conc. 4 and Conc. 5) are originated from abroad.

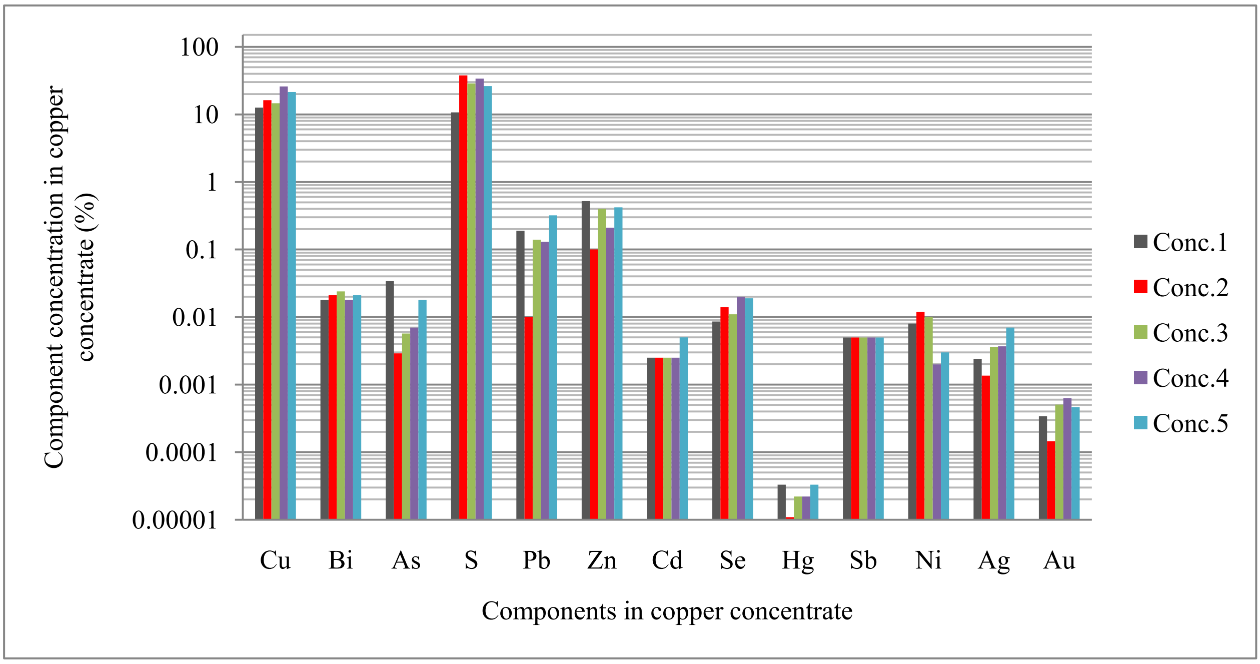

Figure. 2. Chemical composition of available concentrates at RTB- Company

PM_{10} particles were analyzed on the contents of the following heavy metals: Cu, Pb, Cd, As, Ni, Hg, and Mn The content of Mn was not registered in a single sample while the contents of mercury was registered in only a few samples on account of which it will not be specially analyzed. The results obtained by the analysis of the composition of PM_{10} for the period of 2005–2008 also were shown in the Table 1.

Obtained values of the contents of heavy metals in PM_{10} revealed extremely increased content of As due to its presence in the incoming raw material. The content of As was in all cases above the limit value of 6 ng/m^{3}and calculated on annual level is three to ten times as high at urban locations: town park, hospital, and "Jugopetrol". The values calculated on monthly average at times used to be 30 times above the limit. Bor occupies the first place in Europe according to the contents of arsenic emitted into the ambient air per inhabitant with 5.3–19.6 kg of As which has happened for the last few years with the tendency of increase [29]. It should be emphasized that World Health Organization advises that the threshold of 1.5 ng/m^3 is a risk limit for human health [30-31]. Any additional comment on the status of air in the urban area of the town of Bor would be superfluous!

The other elements Cd, Ni, Pb, and Hg are also toxic elements some of which (Pb and Cd) accumulate in the human body for the period of up to 30 years. The maximal contents of cadmium in PM_{10} during the year 2006 at measuring location 3 (blue mark), were three times as high in relation to the limit value.

It is evident that as a result of the of copper smelter operations there are much higher contents of As and Cd in the air in the studied region than prescribed by the EU directives [26-28]. With increase of the smelter plant capacity which is being announced, the concentration of PM_{10} and the contents of heavy metals will be increased which will significantly worsen air quality in the urban zone of the town of Bor and the region as a whole.

3.2. Results of soil samples analysis

The obtained results for the heavy metals contents in the samples taken from the urban zones of town site Bor and surroundings are presented in Table 2 for 12 locations in total, the positions of which are shown in Fig. 1 (red markers).

Table 2. Heavy metals concentrations in the soil samples at 12 locations in the study area of the town Bor

	Heavy metal concentrations in soil sediments							
Locations	**pH**	**Cu**	**Pb**	**Cd**	**Ni**	**Mn**	**As**	**Hg**
Unit		mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg
Location 1	7.7	530	70	2	45	1100	17	< 0.1
Location 2	7.6	1050	100	4	33	880	68	0.1
Location 3	7.5	550	60	2	33	1300	52	0.1
Location 4	7.4	2540	180	6	49	1200	260	0.3
Location 5	7.9	770	80	2	12	1200	33	0.1
Location 6	7.8	390	40	2	41	1200	15	< 0.1
Location 7	6	1000	40	< 2	37	1200	23	< 0.1
Location 8	7.2	2140	230	5	53	1100	140	0.3
Location 9	6	580	60	2	16	1200	25	0.1
Location 10	7.5	220	50	3	37	460	19	< 0.1
Location 11	7.7	930	80	3	49	900	41	0.1
Location 12	7.7	260	50	< 2	37	1100	16	0.1
Analytic method	pH-meter	AAS	AAS	AAS	AAS	AAS	ICP-AES	A-Hg
Max.value		2540	230	6	53	1300	260	0.3
Average value		913.33	86.67	2.92	36.83	1070	59.08	0.133
Min.value		220	40	< 2	12	460	15	< 0.1
Limit values according to the National legislative of the Republic of Serbia (Official Herald of the Republic of Serbia 1994)[32]		< 100	< 100	< 3	< 50	*	< 25	< 2

* Manganese limit value is not regulated with the National legislative of the Republic of Serbia

The highest contents of some heavy metals were found in the samples taken from the locations near to the town center and at the locations in south-eastern part of town (see Table 2). The wind- rose (see Fig. 1) for the period 2005 – 2008, has shown that in the annual distribution of frequency of wind direction the W-NW wind dominated (approximately 30%), the rest refer to E-SE wind (approximately 11%). This fact, led to the highest degree of air pollution in the old part of the town for E-SE wind direction (measuring station 1), as well as for W-NW wind direction, for which only eastern part of town and two villages downstream (Ostrelj and Slatina) are exposed to the air pollution deposition, noted at the sampling locations 2 and 11 (see Fig. 1). With increasing distance from the plant stacks, the soil pollution decreased and it is minimal was at a distance of 20 km (measuring point 10 – Lake Bor); however the influence of pollution was still apparent.

The heavy metals found in the analyzed soils from these sampling locations are in such concentrations that they can only be explained to be the result of atmospheric precipitations of airborne particles and aero-sediments from gases produced by the Copper Smelting Plant located in Bor. To confirm this assumption, soil samples from five locations which are more than 20 kilometers from the Copper Smelting Plant were analyzed. Three of the five samples contained copper but less than the limiting value of 100 mg/kg). The presence of As and the other investigated heavy metals was not registered at a significant level at any of the locations. The contents of the heavy metals at the investigated locations presented in Table 2 are much higher compared to these more distant locations, which corroborated the assumption that atmospheric precipitations of airborne particles and aerosediments from the Copper Smelting Plant stacks in Bor was responsible for the high levels of pollutants found in the near vicinity of the plant. When comparing the values given in Table 2 with the values at other urban regions in the surroundings of industrial zones the present results indicate that the soil pollution in the studied zone is very high [13,33].

Also, the determined values of the heavy metals contents in the surface layer cannot originate from primary mineralization of the ore deposit in this region because minerals of the heavy metals are found at depths deeper than 100 m, from where the ore deposit exploited by the Copper Smelting Plant is obtained.

3.3. PROMETHEE/GAIA ranking analysis

In order to assess the relationship between results of two developed scenarios, PROMETHEE/GAIA method was used. GAIA visual modeling method was primarily used as visualization tool for examination of the correlation between measuring locations- alternatives and pollutants- criterions.

On the basis of data presented in tables 1 and 2, two referent scenarios for ranking of polluted zones have been developed:

- **Scenario 1**: ranking four locations (blue markers in Fig. 1) on the basis of annual average values for the air monitoring data (PM_{10}, DAL, Pb, Cd, Cu, Ni, As) presented in Table 1, and
- **Scenario 2:** ranking twelve locations (red markers in Fig. 2) on the basis of average values of heavy metal (Cu, Pb, Cd, Ni, Mn, As and Hg) contents in 10 samples from each location (values in Table 2).

A number of modeling options had been chosen before PROMETHEE/GAIA method was applied on given scenarios [34-36]. These values include the impact of the criteria, namely presence of harmful pollutants at certain measuring locations with tendency of their minimizing, so the model implies ranking of the best alternatives- locations with the least presence of harmful pollutants in the air and soil in accordance with assigned set of preference functions and weights to each criterion. Linear preference function was chosen as preference function for criteria which define the contents of pollutants in the air and soil, with adopted thresholds of indifference and preference (Q and P) in the zones of 5% and 30%, respectively. For the criteria “days above limit”, which define the average number of days with pollution above the prescribed limit, V-shape preference function with preference threshold (P) of 25% was assigned.

For the purpose of defining the weight coefficients for both scenarios, it was taken into account that the pollutants, especially heavy metals, do not have the same significance, i.e., each of them has a different effect on human health and the environment, which is defined in Table 3. The weight of significance assigned to each metal was determined considering the reference dose of exposure, toxicity and damage to human health.

Table 3. Weight coefficient setting on the basis of harmfulness of present pollutants

Criteria	Weights		Influence on human health
	Scenario 1 (%)	Scenario 2 (%)	
PM_{10}- Particulate matter	20	-	Heavy metals enter the body
Number of days above PM_{10} limit	10	-	
Pb- lead	20	22.5	I class, remains in the body and is carcinogenic
Cd- cadmium	20	22.5	I class, remains in the body and is carcinogenic
Cu- copper	10	5	Harmful in the body but the body gets rid of it
Ni- nikl	10	15	II class, carcinogenic substance
As- arsenic	10	15	II class Biological halftime 3-5 days, carcinogenic
Hg- mercury	-	10	Poisonous, not carcinogenic, removed from the organism within 1 month
Mn- manganese	-	10	Influence on the nervous system
Σ	100	100	

PROMETHEE II method, by utilizing Decision Lab software package, ranked the measuring locations for both scenarios from the best to the worst in terms of pollutant presence on them. In the Fig. 3., the obtained ranking lists for both scenarios, were presented.

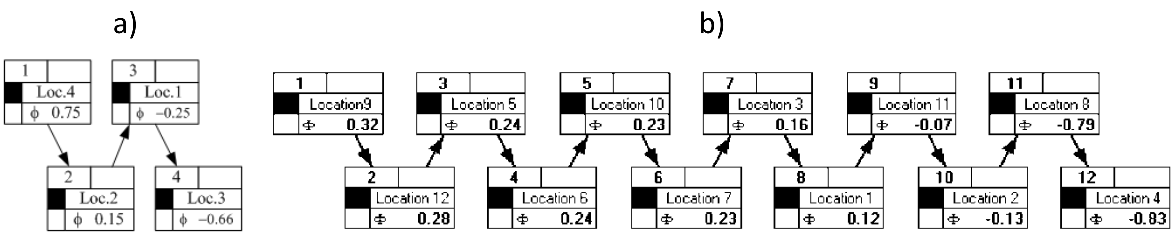

Figure. 3. PROMETHEE II complete ranking: a) ranking list for the Scenario 1, and b) ranking list for the Scenario 2

As seen in Fig. 3, the most polluted locations for Scenario 1, were: location 3 followed by location 1. This means that location exposures, of those two measuring stations to the PM_{10} and it heavy metal contents, directly depend on spatial distribution of copper smelter gasses and meteorological factors, such are wind parameters (wind speed and direction). Furthermore, the ranking results for second scenario (Scenario 2), confirmed the spatial distribution pattern of heavy metals in smelter's surroundings, that led to conclusion that that the soil pollution is caused by the temporal atmospheric distribution and fallout of heavy metal emissions from the Copper Smelting Plant in Bor, as well as meteorological and geographical conditions and the distance from the point sources. Indeed, ranking results for twelve sampling locations, based on the heavy metals contents in the soil, indicate certain correlation with the results of a similar MCDM model used for air pollution in same area, since the most polluted soil sampling locations were as follows: locations 4 and 8 (in Fig. 1 defined with red markers) placed in the old town center, as well locations 2 and 11(in Fig. 1 defined with red markers) placed near the measuring station 3 (in Fig. 1 defined with blue marker) in south-eastern part of town Bor.

On of the advantages of using PROMETHEE/GAIA method in this study was that while PROMETHEE ranked locations in both scenarios, GAIA approach provided a clear picture about correlations between pollutants and specific measuring/sampling location, in both scenarios. The

GAIA plane is defined by corresponding unit eigenvectors ***u*** and ***v***, resulting from a unicriterion net flows covariance matrix, obtained using principal components analysis (PCA). Using PCA, it is possible to define a plane having the minimal amount of information lost by projection (Δ). Another advantage of this MCDM is that GAIA incorporates a decision axis, ***pi***, which compliments the decision from the PROMETHEE ranking. When ***pi*** is long, the most preferred locations in this case are oriented in its direction and furthest from the point of interception of the principal component 1 (***u*** axis) and principal component 2 (***v*** axis) axes. Since, in this study, the "minimised" modelling option was used, pollutants which are associated with particular locations were displayed opposite those locations.

Therefore, in order to obtain clear visualization of ranking results in both scenarios, two referent GAIA planes were created (see Fig.4 and Fig. 5), respectively. The 88.62 % of the total explained variance (Δ) for the Scenario 1, as well as value (Δ) of the 88.15 % for the Scenario 2, indicate that the validity of this tool should be taken into account. Green quadratic shapes in GAIA planes represent pollutants or criterions, and blue triangles represent ranked locations. Since, in this study, the "minimised" modeling option was used for the both scenarios, pollutants which are associated with particular locations were displayed opposite those locations.

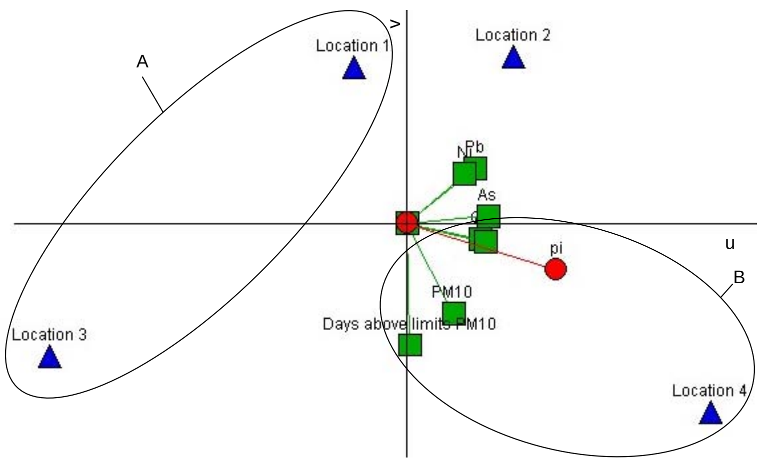

Figure 4. GAIA analysis for the Scenario 1 (Δ = 88.62%)

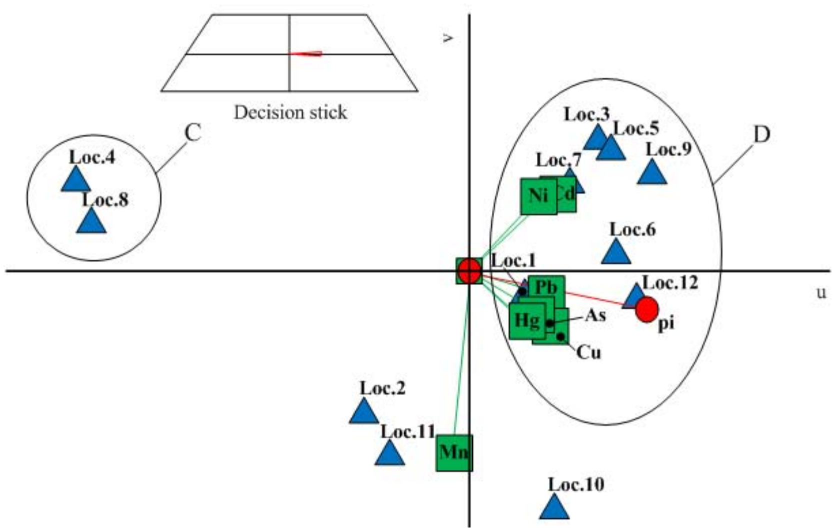

Figure 5. GAIA analysis for the Scenario 2 (Δ = 88.62%)

From the GAIA plane for defined Scenario 1, two clusters were extracted. In Cluster A (Fig. 4), air measuring locations 3 and 1, are directed opposite to all criterions in Scenario1, this means that at these locations highest level of PM_{10} and heavy metals in PM_{10} could be expected, respectively. This means that location exposures, of those two measuring stations to the PM_{10} and it heavy metal contents, directly depend on spatial distribution of copper smelter gasses and meteorological factors. And wind-rose presented in the Figure 1, support this assumption. Since the wind-rose for study period has shown that wind direction the W-NW dominated and other important wind is E-SE wind, led to the highest degree of air pollution in the old part of the town for E-SE wind direction (measuring station 1), as well for the dominant W-NW wind only eastern part of town has been exposed to the air pollution deposition, where air measuring station 3 is located. In the other hand, location 4, placed in Cluster B (Fig. 4), is best ranked location, since it is near to decision stick *pi* and the most of the criterions are directed toward this location.

The same logic that was used for previous scenario also, was used for Scenario 2, but this time only for soil samples. Within Cluster C in the Figure 5, soil samples locations 4 and 8, can be found, having the largest percentage of heavy metals in the soil, apparently not being ranked as good by any criterion in GAIA plane, and as such being oriented opposite towards the decision stick *pi*. As opposed to them, the locations grouped in Cluster D (Fig. 5) represent better solutions by a greater number of criteria. These ranking results were also determined with PROMETHEE II complete ranking.

To confirm the strong correlation between results of these scenarios, better visualization of the most polluted locations in both study cases was achieved when analysis was switched from minimization to maximization option for each criterion in both scenarios. Therefore, in both new GAIA planes (See Fig. 6 and Fig. 7), most polluted location are directed to the specific pollutant, which gives better understanding of spatial distribution pattern in this study region. Furthermore, it is clearly see that there is a strong correlation between sampling locations in both cases. For instance, soil sampling locations 4 and 8 (Fig. 7), correspond to air measuring station 1 (Fig. 6), placed in the old part of town Bor. In the other hand, ranking results of the soil sampling location 2 (Fig. 7), match with the results of air measuring station 3 (Fig. 6). The heavy metals found in the analyzed soils from these sampling locations are in such concentrations that they can only be explained as a result of atmospheric precipitations of airborne particles and aero-sediments from gases produced by the Copper Smelting Plant located in Bor, in this way the initial research assumption was confirmed.

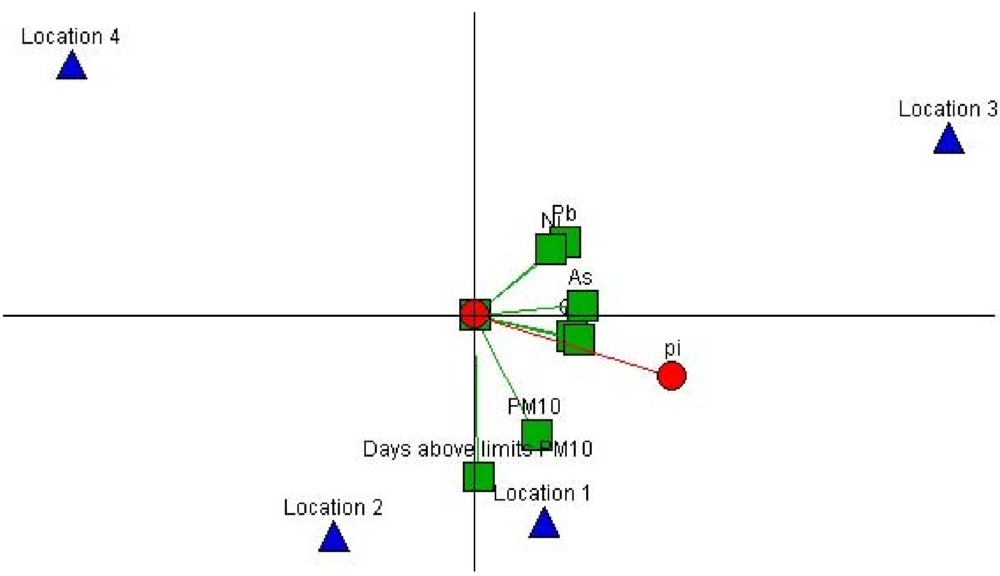

Fig. 6. Modified GAIA plane (maximization option) for the Scenario 1

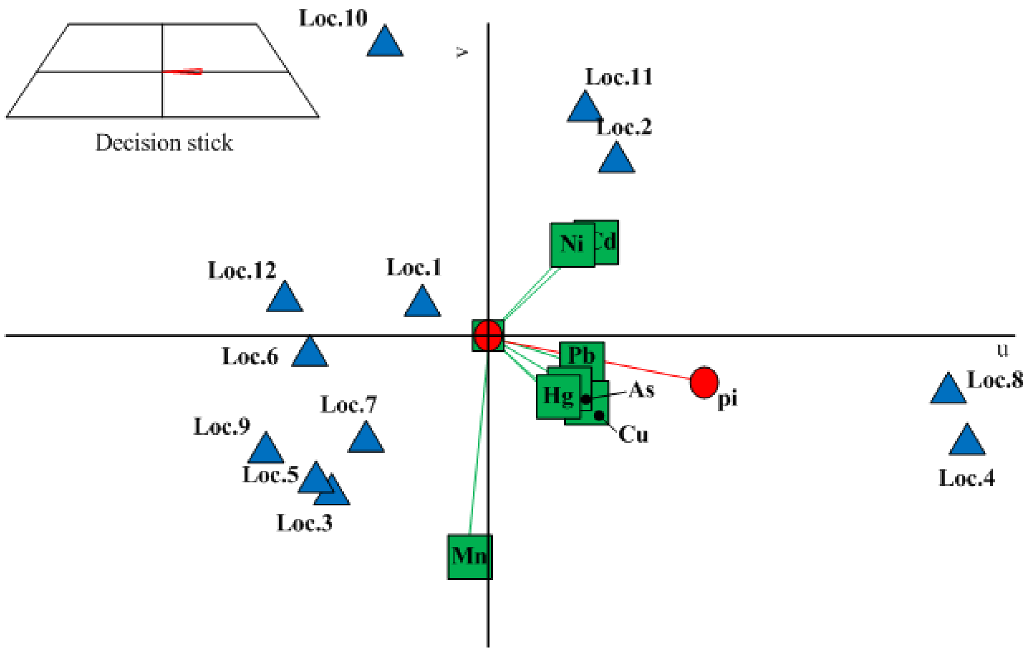

Fig. 7. Modified GAIA plane (maximization option) for the Scenario 2

4. Conclusion

This study has confirmed the spatial distribution pattern of heavy metals in smelter's surroundings, that led to conclusion that that the soil pollution is caused by the temporal atmospheric distribution and fallout of heavy metal emissions from the Copper Smelting Plant in Bor, as well as meteorological and geographical conditions and the distance from the point sources.

These facts show that it is of great importance to urgently start dismissing the sources of emission of heavy metals in PM_{10} and sulphur dioxide as well as the sediments from the air. This could be achieved by means of modernization and reconstruction of the present copper smelting factory in Bor, and this process is in progress. It is also important to start immediate remediation of the soil that has been already degraded.

After obtaining the very alarming results presented in this paper, the authors believe that the further strategy for the environmental protection of this region should include a wider methodological approach, such as the Ecological Risk Assessment (ERA) methodology []. This kind of methodology enables a detailed identification of situations dangerous for humans under conditions of this kind. This way, authors of this paper think that this study has been providing the modest contribution to the solutions of these problems which represent great scientific challenges all over the globe.

Acknowledgements

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PRACTICAL ISSUES IN REAL-WORLD IMPLEMENTATION OF THE ROHS DIRECTIVE ON ELECTRICAL CONTACT MATERIALS

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Abstract

The presented article draws attention to the importance of synchronicity between legislation and technological progress illustrated on example of implementation of RoHS directive on electrical contact materials. Significance of the communication between administration and science is pointed out as well as some common issues that may arise with an introduction of new replacement materials or product modification.
EU Directive 2002/95/EC also known as Restriction of Hazardous Substances (RoHS), restricts the use of six hazardous materials including cadmium found in electrical and electronic products and imposes that all applicable products in the EU market after July 1, 2006 must pass RoHS compliance. On the other side, for many years silver cadmium oxide (Ag-CdO) has been the preferred material for electrical contacts used in different low-tension devices of contactors type due to its outstanding functional properties.
Given that RoHS impacts the entire electronics industry and many electrical products as well as any business that sells applicable electrical or electronic products, sub-assemblies or components directly to RoHS countries, the implemented legislation creates a significant pull for the research and development of new electrical contact materials with less harmful impact on the environment. However, the directive in its original form has not yet been implemented and has undergone numerous amendments and exceptions regarding the use of cadmium. It seems that problem mostly lays in the fact that even though RoHS creates significant pull for R&D, in a given time frame, science was not able to provide adequate replacement materials and that currently available alternative materials do not always offer the same performance for electrical life as AgCdO.

1. Introduction

Recent directives approved by the European Union aim to reduce potentially hazardous substances contained in electrical and electronic equipment thus minimizing risks to health and the environment, and guaranteeing the safe reuse, recycling or ultimate disposal of equipment. One of the core documents is the EU Directive 2002/95/EC also known as Restriction of Hazardous Substances (RoHS). The directive restricts the use of six hazardous materials including cadmium found in electrical and electronic products and imposes that all applicable products in the EU market after July 1, 2006 must pass RoHS compliance [1].

Given that RoHS impacts the entire electronics industry and many electrical products as well as any business that sells applicable electrical or electronic products, sub-assemblies or components directly to RoHS countries, the implemented legislation creates a significant pull for the research and development of new electrical contact materials with less harmful impact on the environment. It also imposes fundamental challenges in material development and ongoing research in these areas that can lead to better understanding of these materials as well as aid in making them commercially viable.

On the other side, for many years silver cadmium oxide (Ag-CdO) has been the preferred material for electrical contacts used in different low-tension devices of contactors type, due to its outstanding functional properties [2,3]. Thus, finding the adequate replacement material is by no means an easy task. The main properties required for such contact materials are a high hardness to avoid erosion and an excellent electric conductivity. Physical properties that favor extinction of the electrical arc when switching off contact [4,5], good processing capabilities [6] and RoHS compliance are desirable as well. Over the years significant research efforts have been put into replacement of CdO with non toxic oxide dispersed in silver matrix, nevertheless currently available alternative materials, do not always offer the same performance for electrical life as Ag-CdO.

As a direct consequence, the RoHS directive in its original form has not yet been implemented and has undergone numerous amendments and exceptions regarding the use of cadmium, among which the latest one from 2010 extends the use of cadmium in electrical contact to by as much as 2012!

Elaborate task of finding the adequate replacement materials is made even more complex by the different requirements and motives of companies, academia and legislative administration. Therefore, apart from research and material design issues, there are quite a lot of practical, economical, legal, essentially real-world issues that should be considered. Majority of these issues are reflected in the criteria for granting exemptions from RoHS directive, which include cases when elimination or substitution is technically or scientifically impracticable, or where the negative environmental, health and/or consumer safety impacts caused by substitution are likely to outweigh the environmental, health and/or consumer safety benefits. Availability and reliability of substitutes and socio-economic impacts are taken into a count as well.

The presented article stresses the importance of synchronicity between legislation and technological progress and points out to some of the key development and testing issues concerning the real-world implementation of the RoHS directive on electrical contact materials.

2. Rohs background - motivation

The European Union with its 27 member countries and around 495 million inhabitants represents significant market for electronics and electrical industry. In 2009, it was estimated that about 10.3 million tons of electrical and electronic equipment is placed in the EU-27 market annually. Electronic waste generation was estimated to 9 million tons per year with a predicted increase up to 12.3 million by year 2020 [7].

By the end of ’90s, due to technological innovation and market expansion electronic waste was the fastest growing waste stream, with an annual growth of 3-5%. More than 90% of waste was being landfilled, incinerated or recovered without any pretreatment, thus representing considerable environmental problem and also loss of valuable resources.

For that reason RoHS directive was adopted by EU countries and similar legislations were adopted by China, Korea, Japan and some U.S. states. Objectives of RoHS are to avoid leakage of hazardous substances from waste to the environment and to prevent contamination with these substances when recycling materials.

One of the restricted hazardous materials is Cadmium, a silvery-white, relatively rare, ductile metal obtained as a byproduct of the smelting of zinc. It is widely used by the electrical switching industry in the form of Cadmium Oxide (CdO) in metal alloys (primarily silver cadmium oxide, Ag-CdO) to manufacture high quality power switching contacts.

Cadmium enters the human body either by inhaling cadmium vapors, or by consuming cadmium particles. Thus, the vast majority of human exposure to cadmium results from drinking of untreated water directly from rivers and streams where cadmium dust has been dumped, industrial exposure to cadmium fumes and dust during smelting and processing or by inhaling cadmium fumes created by incinerating garbage. Either way, the result is very slow degradation of kidney function.

3. Challenges and state of the art in contact materials development

Over the past 50 years, significant research has been performed on the performance of various metal alloys for use as separable electrical contacts. The usual challenge in developing electrical contact materials has been to overcome the drawbacks of the available contact materials and fulfill the growing interest for increasing reliability and energy efficiency in electrical and electronic systems. These challenges coupled with the regulatory drivers of focused attention on environmental issues have highlighted the need for alternative contact materials. Furthermore, “green chemistry” and “sustainable technology” concepts are forcing development in this area of industry as well. Consequently, considerable effort has been put forward in research of cadmium free electrical contact materials.

Process and product development of electrical contact materials are enabled by both industry and academia as in many other sectors. Worldwide, contact, electrical equipment and electronics manufacturers such as AMI/Doduco, Brainin, Danco, Deringer-Ney, Metalor, Naeco, General Electric, Westinghouse, Siemens as well as leading academic institutions such as Carnegie-Mellon University, University of Virginia, the University of Technology - Vienna, University of Wales, Osaka University, University of Braunschweig, University of Southampton; to name a few, conduct ongoing research into new contact materials.

The issue that arises here comes from the fact that requirements and motives of legislative administration, manufacturers and academia are quite different. Whereas the priority for researchers in industry is to enhance the company’s economic status, the drive in academia is much more complex. In the United States academic involvement in product development has been facilitated by the Bayh-Dole Act permitting a university, small business, or nonprofit institution to pursue ownership of an invention in preference to the government [8], thus the contribution of academia to product development has gained momentum [9]. One of the elegant tools for quantitative analysis and for obtaining statistics that measure the contribution of scientific publications to the advancement of knowledge within a given topic or country is bibliometrics [10,11]. In the recent years it has also been used for analysis of the relations between the publications and the patents to deduce institutional and geographical trends in knowledge dissemination and commercialization.

The bibliometric approach was used to illustrate scientific efforts and contribution in the field of electrical contact materials. The source of the data for peer-reviewed journal disclosures was the ISI Web of Science database which covers 10,000 of the highest impact journals worldwide, including Open Access journals and over 110,000 conference proceedings and 25 million cited references that are added annually. In order to emphasize the pull generated by the

RoHS directive, data used for this study were retrieved for the publications from January 2001. until May 2011.

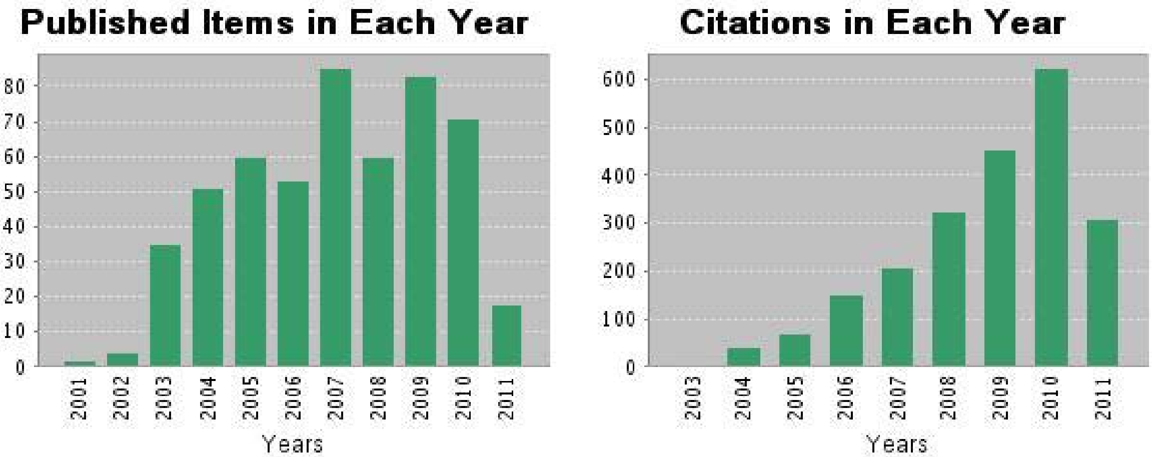

Figure 1. Peer-reviewed journal disclosures and citations

Presented graphs illustrate major increase in the number of publications and almost exponential growth of citations since 2003, demonstrating the scientific contribution to finding alternative, more environmentally friendly contact materials.

On the other side, businesses view their investments in technology in terms of the estimated return on investment, i.e. the gain in profits or market leverage to which the acquired technology will contribute. This is based on a traditional view of investment that is deeply embedded in the concepts of capitalism – you invest capital to create profit. Adopting of new technology before the old one has been paid off is not a popular course of action that is why most businesses plan their activities well ahead. Given that RoHS directive limits access to the EU market, most of the companies were eager to adjust their products to the legislation and for the most of Europe based companies it comes down to ‘‘evolve or die out’’.

However, in reality replacement of the contact material in some cases may require changing of the construction of contactor, switch, etc., which could be time and money consuming, problems with patents or licenses may arise, thus making the replacement impractical or economically unfavorable. Development and production of new products (devices) engineered to accommodate substitute materials makes sense, however it can arise all above-mentioned issues as well. Therefore, majority of businesses support continuing and accelerating research into contact materials that could be direct drop-in replacements for Ag-CdO, with the goal of reducing the use of cadmium in electrical contacts as quickly as it is technologically feasible.

As a result of research efforts there are 35 different major categories of metal alloys that are currently commercially available for use as separable electrical contacts, of which Ag-CdO is one. Furthermore, differing formulations within each major category provide hundreds of possible choices. Nevertheless, there are applications for which Ag-CdO is irreplaceable and in motor control products (sizes 00-9), transfer switching products, motor hermetic overload relays, bypass contactors, and general-purpose power switches less than 30 A (AC) or greater than 600 V (DC) at 600 A, efforts to find a suitable replacement for Ag-CdO have shown limited success [12].

The task of finding environmentally friendly alternative is made more complex by the fact that material that needs to be replaced possesses unique set of properties that makes it ideal for numerous applications.

- The cadmium in Ag-CdO electrical contacts significantly improves the ability of the contacts to extinguish electrical arc, and significantly reduces material transfer and erosion of the contacts. Hence, Ag-CdO contacts last longer i.e. require less replacement, thus reducing the overall burden on the environment and the volume of products disposed into the waste stream.
- Given that Ag-CdO contacts perform better in many applications than common alternatives and have the ability to quench arcs and resist welding they are ideal for safety-related applications where high reliability is required.
- Since products made with Ag-CdO contacts are smaller less material is needed to produce them, which not only reduces the total manufacturing energy requirement, but also further reduces the volume of product disposed in the environment.
- On the other side, products made with replacement contacts tend to fail in the dangerous welded-closed state much more often than Ag-CdO which in any safety-related application, in a case of failure, may result in a higher burden on society for the costs of personal injury and property damage.

Expert studies found in literature [13] imply that besides the type of material the type of tests that were performed in determining whether potential replacements can actually function as replacements for Ag-CdO electrical contacts are very important as well. It is suggested that in the past most research on contacts was performed in a lab and not in the actual applications. This practice may be satisfactory for many applications but in some cases it is not, as it will be illustrated on the example of “Self resetting thermal protectors” (SHTP).

The requirements for these devices are in the standards IEC 60730-1, which are applicable only to the thermal protector of many different types. When they are applied to the end product such as washing machines, dryers, dishwashers, electric blankets, etc., they are then tested to the IEC 60335-1 standard which is for the end products.

The major difference between what was tested in the lab on just the contacts and contacts in a thermal protector is that the two opposing contacts are attached to two different items. Furthermore, the contacts in lab test and in SHTP do not operate under same conditions. In an actual operation there is a possibility of reaching the conditions that would facilitate the formation of an electrical arc, which could cause the contacts to weld together. The advantage of Ag-CdO contacts in these situations is that, as previously stated, the cadmium oxide in these contacts acts as an arc quencher and extinguishes the arc. So far, none of the available substitute materials has this capability.

The matter is further complicated by the fact that each bimetal manufacturer has its own method resulting in many shapes and sizes. Hence, type of contact that might work for one manufacturer might not work for the other in a same end product.

In some areas of application technological push determines the type of contact to be used. The majority of these thermo devices used in automotive DC applications over the years did not have contacts that contained cadmium. Usually, they were made of fine silver, copper silver and a few other silver based more environmentally friendly materials. As the electrical motors used in automobiles became more sophisticated over the years and new motors were introduced, traditional contacts could no longer protect them. Again, Ag-CdO contacts proved to be very successful.

With the advances in technology over the years, silver thickness and percent of cadmium in the silver were reduced. Due to the fact that Ag-CdO contact on the bimetal works so well, in some cases it is possible to replace the opposite Ag-CdO contact with a fine silver contact.

However, so far for applications like compressor motors for refrigeration, where the motors have fault currents of 80 amperes or higher, Ag-CdO contacts are irreplaceable.

Another mode of operation for which contacts containing cadmium are irreplaceable is continuous operation or cycling. Usually the thermal protector is placed in contact with the windings of the motor. In North America, the test requirement is that the thermal protector, when the motor rotor is blocked, must be able to cycle for 18 days. At the end of the test, the motor cannot fail a dielectric breakdown test. Given that contacts that do not contain any Ag-CdO cannot contain AC arc, consequently either molten silver is plated on the bimetal or the AC arc is extinguished on the bimetal, thus changing the operating features of the bimetal. Either of these conditions would create premature failure that could lead to the apparatus either causing a fire or a potential electrical shock.

In some cases standards and legislation are lagging behind the technological progress, resulting in outdated norms and requirements [13]. During testing of thermal protectors to the 18 day test on motors, how many cycles the thermal protector will obtain depends on what current motor will draw and how much heat it will generate. So, the thermal protector may cycle only 1,000 times or as much as 25,000 cycles. Therefore, current requirement for the Ag-CdO contacts replacements of 10,000 cycles, could potentially allow devices to be installed that do not meet the industry standards. Nowadays, due to the specific location of the thermal protector in European washing machines with the new generation of universal motors, it cycles every few seconds. The present EN 60335 standard that was issued when the induction motors were used in the washing machines states that the protector only has to cycle 300 times. In the present day, 300 cycles can be obtained in a few minutes. That is not enough endurance capability to protect these motors from causing a fire, given that the washing machine could be on for an hour and if the timer failed, hours or days.

Even when an adequate and commercially viable Ag-CdO replacement is found and produced there are still a lot of issues that need to be considered. Generally speaking, electrical contacts are not just some piece of silver and most of them have three layers e.g. Ag-CdO contacts consist of the upper contact layer made of Ag-CdO, the middle copper layer and the bottom layer that is usually steel for welding the contact to another material. Since the silver contains cadmium oxide, it is difficult to impossible to bond it directly to copper. For that reason, the contact manufacturers use a bonding material of either silver nickel or fine silver. Depending on the type and conditions of application the correct bonding material has to be chosen as they can also contribute to the early failure of the contact material. Therefore, another important issue that should be considered when introducing or preferably even in a research stage of the replacement material for Ag-CdO contacts is bonding of the material to the copper holder. If the process to bond the new material to copper is already patented e.g. to exclude other contacts manufacturers from using it, it would take many years to resolve the patent issue, thus creating the supply problem.

Eventually, with all mentioned issues successfully resolved and introduction of a replacement for Ag-CdO contacts the next step would be manufacture of samples for consumers to test. However, prior to any tests, one of the first requests from the consumers will be to provide them a valid test agency approval to use these contacts. The Agency approval is issued by test houses such as VDE (Germany), BEAB (England), Demko (Denmark), UL (USA), etc. According to some studies [13] the whole approval process could take up to two years if there are no problems. After approval by the required test agency, the consumer will start his own testing. To be assured that they are not substituting a good component with a bad one, the tests could take from one up to four years. This is contingent upon manufacturers of contacts having the capability to come up with a material that is not presently in the market place.

The example of thermal protector addresses so far only a few issues regarding what it takes to make a reliable contact material. In many ways those are the challenges and problems that are encountered in development of contacts for majority of other applications.

4. Conclusion

With all being said, complexity of the task of finding an acceptable replacement of Ag-CdO contacts becomes evident. It seems that problem mostly lays in the fact that even though RoHS creates significant pull for R&D, in a given time frame, science was not able to provide adequate replacement materials; hence the currently available alternative materials do not always offer the same performance for electrical life as Ag-CdO.

Given that the goal is to replace the material with by far superior properties than any currently available substitute and which, due to its outstanding properties, has numerous safety related applications, development of new materials requires much more time than originally given by RoHS directive. Experts estimate that it may take anywhere between 5 to 10 years in order to find acceptable replacement and even more before final approval for production of new devices.

Common belief of many experts is that if anyone rushes to find a substitute material could do a great harm to the electrical and electronics industry that requires the use of reliable electrical contacts in their products. So far, the general course of action is to support of retaining the existing EU RoHS exemption allowing the use of cadmium in electrical contacts until advancements in technology provide contact materials that are “as good or better” substitutes for Ag-CdO.

Acknowledgement

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TESTING OF THE QUALITY OF INDUSTRIAL WASTEWATER IN INDUSTRIAL ZONE ZENICA

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Abstract

In the industrial zone in the northern part of the Zenica basin are concentrated metallurgical plant with a production capacity about 2 million tons of steel per year (current production is about 650,000 t / y), with the foundry production capacity of 60,000 t / y of castings for the automotive industry (current production is around 25,000 t / y) and a few plants in the field of metal processing small-scale production. All facilities and installations in the industrial zone is characterized by the use of industrial water in production processes (eg boiler water, wet dedusting and gas cleaning, cooling aggregate, slag and ash transport, laundry, etc.), which is caching from the river Bosna to a water collector. Therefore, from an industrial zone in Bosnia River discharged a large amount of industrial wastewater by three discharges outlet. Industrial wastewater varies in quantity and quality what is depending of the nature of technological processes, production and application of measures for water management and the rational use of water, reducing emissions water and wastewater treatment.
Testing of the quality of industrial wastewater discharged into the Bosna River from the industrial zone in the northern part of the valley rolls, it was found that concentrations of some measured parameters (pH, suspended matters, phenols, the degree of toxicity, etc.) exceed the prescribed limits for discharge into surface water and therefore may affect the ecological characteristics of the recipient, the Bosna River. Application of specific measures for water management is important to rationalizing water use in production processes and improved quality of wastewater discharged into the Bosna River.

Keywords: industrial wastewater, limit values, wastewater quality.

1. Introduction

In the industrial zone in the northern part of the Zenica basin are concentrated primary and secondary metallurgical plant with a production capacity about 2 million tons of steel per year (current production is about 650,000 t / y), with the foundry production capacity of 60,000 t / y of castings for the automotive industry (the current production is about 25,000 t / y) and a few plants in the field of metal processing small-scale production. All facilities and installations in the industrial zone is characterized by the use of industrial water in production processes (e.g. boiler water, wet dedusting and gas cleaning, cooling aggregate, slag and ash transport, laundry, etc.), which is caught from the River Bosna to a water collector. Therefore, the industrial zone emits a large amount of industrial wastewater, which vary in quantity and quality depending on the nature of technological processes, production and application of measures for water management and the rational use of water, reducing emissions to water and wastewater treatment. They released three major releases in the River Bosna as the final recipient of technological waste water from industrial areas, along with mining and municipal wastewater [1,2,3]. The drives are made partly of technological wastewater treatment. However, the degree of purification is not satisfactory, because the quality of the effluent does not meet the requirements for discharge into surface waters or River Bosna, prescribed in the regulations on limit values of hazardous and harmful substances for the production wastewater before their discharge in the public sewerage system or another set [4]. Because of technological wastewater from industrial zone entered a large burden of pollution in River Bosna disturbing the ecological conditions of the watercourse. According to regulations on water technology wastewater can be discharged into surface water or public sewerage system under the condition that the concentrations of hazardous and harmful substances in waste water technology does not exceed prescribed limits.

Bosna River Basin is very loaded because many industrial plants and cities discharging their wastewater without adequate treatment. This basin covers 20.4% of B&H territory where live 40, l2% of the total population from which we can see that this basin is exposed to negative influences. Unlike the basin of the River Bosna, basin River Neretva and Trebišnjica comprises 19.8% of B&H territory in which live only 9.6% of the population and therefore the quality of these watercourses preserved.

This paper presents the results of the quantitative characteristics of industrial quality wastewater industrial zone in Zenica, which are discharged into the river Bosnia by three main outfalls to determine impact on the recipient.

2. Materials and methods

In order to determine the quality of industrial wastewater, it is taken a series of samples and carried out the measurement of flow rate on the three main outfall into the River Bosnia: the main collector (GK), collector of wastewater from the rolling mill (ŽZ1) and collector of wastewater from energy and industrial landfill (ŽZ2). Simultaneous investigation of the discharge of wastewater separation of brown coal mine and two urban sewage outfalls that flow into the main sewer Ironworks and using the same discharged into the River Bosna.

Field tests are included:

- measurement volume (flow) wastewater collectors with hydrometric wing and direct volumetric method,
- measurement of temperature sewage collectors, and
- sampling of wastewater every two hours at each outlet (five measurement points) for a period of two days, on the basis of which they formed 24 hours composite samples in order to determine the characteristic parameters defining the degree of pollution and toxic wastewater (through the test with *Daphnia magna*).

Laboratory tests consisted of determining the physical-chemical parameters of wastewater quality necessary to determine the total pollution load of wastewater is expressed through the equivalent of the population (EP) as follows: pH, suspended matter, chemical oxygen demand (COD), five-day biochemical oxygen demand (BOD_5), total phosphorus and total nitrogen, nitrate, nitrite, turbidity, conductivity, m-alkalinity, evaporation residue, ash and volatile matter. In addition, the study was carried out toxicity of wastewater samples using toxicological experiment with Daphnia magna. Toxicological experiment, 48hEC50, is semi-lethal effective dose within 48 hours of completely immobilize the test organisms. Specific parameters of wastewater pollution in the daily composite samples were analyzed only phenols and mineral oils.

Physico-chemical characterization of wastewater quality were carried out using analytical methods prescribed in the regulations limit values of hazardous and harmful substances for the production wastewater before their discharge into the public sewerage system or any other receiver [4].

3. Results and discussion

The average results of physical-chemical analysis of wastewater samples which were discharged from industrial complexes in the River Bosna are shown in the following table.

Table 1. Results of wastewater monitoring

Parameters	Limit value[1)]	Main Collector (GK)	Collector rolling mills and steelworks. ŽZ1	Collector of energy plant (ŽZ2)	„RMU Zenica“	Municipal collector
Flow (m^3/s^{-1})	-	0,568	0,430	0,191	0,056	0,158
Temperature (^0C)	30	19,1	20,6	19,8	19,6	15,3
pH	6,0-9,0	8,14	**10,1**	**9,56**	7,92	7,54
Suspended matter (g/m^{-3})	35	**287**	**152**	**121**	**1537**	**196**
COD (g/m^{-3})	125	41	35	21	**230**	**195**
BOD_5 (g/m^{-3})	25	2,64	2,5	2,75	24,5	**79,5**
Total nitrogen (g/m^{-3})	10	**12,8**	2,1	2,6	5,5	**20,6**
NH_4-N (mg/l)	10	8,32	1,5	2,2	2.7	**19,2**
NO_3-N (mg/l)	10	1.7	1,2	1,4	1,4	1,5
NO_2-N (mg/l)	0,5	0,28	0,09	0,12	**0,72**	0,01
Total phosphor (g/m^{-3})	1,0	0,98	0,41	0,297	0,47	**3,15**
Fuzziness (NTU)	-	112	16	45	3221	156
Conductivity (µS/cm)	-	720	2240	1741	1040	717
m-alkalinity ($mgCaCO_3/l$)	-	232	166	376	257	283
Evoporation residue at 105°C (mg/l)	-	685	373	843	7325	774
Ash at 550°C (mg/l)	-	453	235	640	3420	334
Volatile matter at 550°C (mg/l)	-	232	138	203	3905	441
Toxcity test (%)	>50	**<50**	**<50**	>50	**<50**	**<50**
Phenols (mg/l)	0,1	**0,11**	0,03	0,09	**0,49**	**0,18**
Mineral oils (mg/l)	5,0	2,6	0,07	1,12	0,82	**8,13**

This analysis has revealed the following:

- in the main collector (GK) concentrations of suspended matter, total nitrogen and phenol were higher than the prescribed limit value. This water are toxic,
- collector in steel mills and rolling mills (ŽZ1) concentration of suspended matter, pH value and the degree of toxicity exceeded the prescribed limit,
- Wastewater from the sedimentary basin ash and slag, as well as industrial waste dump (ŽZ2) have a higher pH and suspended matters from the prescribed limit value,
- in the mine wastewater discharged into the sewer main Ironworks, measured by high content of suspended matters, and high levels of COD, phenols and toxicity, due inadequate primary treatment,

[1)] For dischargers into surface waters

- high content of suspended matters in the mine water burden of wastewater in the main sewer and water in the River Bosnia,
- urban wastewater discharged into the sewer main Ironworks, have an increased level of suspended matters, COD, BOD, total nitrogen, ammonia, total phosphorus, phenols, mineral oils and the degree of toxicity, and thus affect the overload of wastewater in the main header and final recipient – River Bosna.

The following table shows moving to EP for typical year, divided by collectors (major outlet places).

Table 2. Show trends EP

EP	1984.	2001.	2005.	2009.
Municipal sewage	23.787	26.123	21.312	25.436
„RMU Zenica“	34.444	90.809	10.939	153.055
Main sewer Ironworks (GK)	464.682	209.571	44.073	385.152
Colector of rolling mill and steelworks (ŽZ1)	16.691	2.918	6.364	48.514
Collector of energy plant and lanfill (ŽZ2)	81.997	2.013	27.974	25.753
Total	563.370	214.502	78.411	459.419
Total for Ironworks (without „RMU“ and town)	505.139	97.570	46.160	280.928

Based on the results shown in Table 2 it can be concluded as follows:

- that the earlier regime in the industrial zone was twice as "dirtier", and production wastewater were doubly burdened, because the drives are operating at full capacity (about 1.8 million tons of steel), and the technology was less advanced,
- In the meantime, it made some indoor hydro, or recirculation systems, such as in steel mills and rolling mill plants, and introduced a streamlined system for wastewater treatment (e.g. DSD), while production fell by over two times and the pollution levels dropped significantly,
- pollution load of urban wastewater is quite uniform. It has been expected,
- expressed varying pollution load of mine waste water is probably a consequence of pronounced variations in production volume and the primary treatment of wastewater,
- lower pollution load of wastewater main collector in 2009. in relation to the base 1984 year was primarily the result of small-scale production (over two times), and taking certain measures of the primary treatment of wastewater before their discharge into the River Bosna,
- variation of the pollution load of wastewater to the other two outlet places (ŽZ1 and ŽZ2) is primarily a result of variations in production volume, because the integrated production in the iron and steel is not performed during the period 1992. until 2007. year and they worked just rolling mill drives, electrical steel, energy, transport and services.

Based on the results of investigations of the quality of wastewater can be seen that it is necessary to apply measures to reduce emissions to water and improvement of existing devices for wastewater treatment. Strategic approach to effluent Ironworks in Zenica is based on:

- application of best available techniques in water management,
- integration of water management in the production process in order to reduce amont wastewater load of pollution,
- separation of the sewage system of the mine Ironworks and urban sewage,
- minimizing emissions using best available techniques,

- the design flow of wastewater with a maximum degree of recovery, and recirculation, which practically means that in normal mode operation and in compliance with the measures of good management of technological processes in the sewage system come the minimum amount of wastewater,
- reduction of waste water in a separate sewage system with built-in wastewater treatment plant at the end of the technological process in plants,
- construction of a central system for further purification of wastewater.

4. Conclusion

The quality of wastewater discharged from industrial complexes in River Bosna does not fulfill the requirements for discharge into surface water because the concentration of some measured parameters (eg, suspended matters, phenols, toxicity, etc.) exceed the limits prescribed by the regulations limit values of hazardous and noxious substances for industrial wastewater before discharging their in the public sewerage system or any other receiver. Therefore, it is necessary to take measures for providing adequate wastewater treatment prior to their release to the mentioned watercourse. According to the cited regulations any entity that discharges wastewater into surface water must fulfill the requirements for discharge into surface waters in order to preserve their natural environmental features.

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ENVIRONMENTAL ASPECTS OF PHARMACEUTICAL WASTE DISPOSAL

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Abstract

Pharmaceutical waste includes all medicines and medicinal materials, including packaging and related support materials, which have become unusable because of expired shelf life, waste, improper storage, or similar reasons. Waste management is regulated by a number of regulations that partially regulate and prescribe measures to protect the environment from its harmful effects. World Health Organization estimates that due to inadequate handling of medical and pharmaceutical waste, about 20 million people per year worldwide become infected with hepatitis B, C or HIV. Therefore, this issue should be given full consideration. The aim of this paper is to point out the necessity of proper medical and pharmaceutical waste disposal and application of relevant laws and regulations in order to significantly reduce the waste amount and the risk of environmental pollution. Mechanisms for monitoring and control activities in the field of medical waste management are very complex. Institutions that generate medical and pharmaceutical waste need to achieve a multi-disciplinary collaboration and partnerships with local governments, environmental sector and all other relevant stakeholders in order to establish adequate management of waste.

Keywords: Pharmaceutical and medical waste, environmental aspects, legal regulations

1. Introduction

Law on Environmental Protection (Official Gazette RS, No.135/04, 36/09, 72/09) provided the basis for waste management, and the Regulations on the treatment of wastes that have characteristics of hazardous substances (1995) obtained classification of hazardous waste in accordance with the Law on Ratification of The Basel Convention on the Control of Transboundary Movements of Hazardous Wastes and their Disposal, an Annex I, (1999), which defined the medical and pharmaceutical waste as:

- Y1 - Clinical wastes from medical care in hospitals, health centers and clinics
- Y2 - Waste that comes from the production and preparation of pharmaceutical products
- Y3 - Waste from pharmaceuticals, drugs and medicines
- Y4 - Waste from production, formulation and use of biocides and phyto-pharmaceuticals products

Medical waste is defined as "all waste, hazardous or non-hazardous, which is generated in the provision of health services (diagnosis, prevention, treatment and research in human and veterinary medicine)" (National guide, 2009). In other words, the medical waste means all waste generated in medical institutions (public or private), medical research centers or laboratories. According to the Regulation on medical waste management (2010), it is a heterogeneous mixture of classical garbage (municipal waste), infectious, pathoanatomic, pharmaceutical and laboratory wastes, disinfectants and packaging, as well as radioactive and hazardous chemical waste. Medical waste is any waste arising from medical, dental, veterinary, pharmaceutical or similar practice, investigation, treatment or care, where 10-25% is hazardous waste, dangerous to human health and the environment (National guide, 2008).

The marketing of medical devices is carried out in Serbia since 1995 based on the Law of the production and marketing of medicinal products (Official Gazette, No. 18/93, 24/94, 28/96, 21/99, 36/99 and 23/2002), which regulates the production and trade of medical devices for the first time. Pursuant to Article 64 Item 3 of this law was passed Regulation on the destruction of drugs, extra medications and medical devices (Official Gazette No. 16/94 and 22/94), which defined the way to destroy drugs, extra medications and medical devices and packaging. This Ordinance provides an appropriate method (physical, chemical, physical-chemical, etc.) for the destruction of drugs, depending on the characteristics of medicines so as to provide stable, non-toxic products without carcinogenic, teratogenic, mutagenic effects or effects on the ability to reproduce (fertility). From that time until now in Serbia was placed close to the 4000 sales of medical devices *(http://www.alims.gov.rs/lat/med_sredstva/medsredstva_stavljanje.php).* Today, under the new Law on Medicines and Medical Devices (2010), licensing of marketing, renewal and amendments to permit the medical devices marketing is performed by the Agency for Drugs and Medical Devices of Republic of Serbia *(http://www.alims.gov.rs/lat/med_sredstva/medsredstva_stavljanje.php)*. Drugs, starting material and other material used in the manufacturing process, as well as in developing galenic or main drugs, that have expired or found faulty in terms of the required quality, as well as medicines that were banned from the market or that are under the terms stipulated withdrawn from the market, must be destroyed according to the Law on Medicines and Medical Devices, Article 144 (2010). The procedure for destroying medical devices that is not regulated by the law governing waste management, is conducted by this law and regulations adopted to implement this law (Law on Medicines and Medical Devices, Official Gazette of RS, No. 30/2010). The manner, procedure and conditions for destruction of drugs and medical devices, starting and other materials used in the process of production and trade of medicines and medical devices are prescribed by the minister responsible for public health. Drug treatment processes and packaging must be designed to protect the environment *(http://www.eko.vojvodina.gov.rs/index.php?q=zakonska_regulativa%2C_nacionalni_propisi_i_eu_zakonodavstvo).* Nowadays, in modern industrial conditions, environmental aspects are considered the most important parts of almost every new project or work (Mihajlović et al., 2010).

2. Classification of medical and pharmaceutical waste

Medical waste is classified:

- based on the physical state (solid, liquid and gaseous),
- based on the main features (dangerous and non-hazardous).

In the total amount of medical waste generated, about 25% is hazardous waste and the rest of it is municipal waste, except that 80% of hazardous medical waste is infectious and 20% other hazardous waste. Hazardous waste is any waste which contains elements or compounds that have one of the following characteristics: infectivity, radioactivity, explosiveness, reactivity, flammability, irritability, harmful, toxic, carcinogenic, mutagenic, teratogenic, ecotoxicity, oxidizing property, the property of etching and property of releasing toxic gas during the chemical or

biological reaction, as well as all the waste from the European Catalogue of Hazardous Waste (EC, 2000).
Depending on properties, hazardous medical waste can be classified as (BC, 2003):

- infectious
- pharmaceutical
- sharps
- pathological,
- genotoxic,
- radioactive,
- pressure vessels,
- chemical and
- waste with high content of heavy metals

Hazardous medical waste is a potential risk to the environment and health, and the most significant threats (BC, 2003) are:

- infections,
- injury,
- poisoning,
- irradiation and
- Soil and groundwater pollution.

All persons who may come into contact with medical waste are exposed to potential risk to human health (BC, 2003), as follows:

- medical personnel (doctors, nurses, other medical and non-medical staff in health institutions),
- patients in and outside health care facilities and their visitors,
- employed in public utility companies that handle and transport waste
- employed in landfills, including those who search for waste and
- Population, especially children, if they play with objects that can be found in the trash outside health care facilities.

Introducing and implementing adequate procedures to minimize the risk of medical waste in the first place protect the public health and reduce environmental impact. The first step in the system of management is to identify potential risks. Possible routes of disease transmission (BC, 2003) are:

- direct contact,
- contact with vectors,
- aerobic transmissions,
- polluted water and
- polluted environment.

Many of the chemicals and pharmaceutical products used in health care may be hazardous to health (toxic, genotoxic, carcinogenic, etc.). Employed in the pharmacy, anesthesia and laboratories are exposed to risk of respiratory and skin diseases due to exposure to gases, aerosols and solvents used at work. Sporadic incidents of injuries and poisoning by chemicals and pharmaceuticals are generally caused by poor handling, so it is recommended the use of less toxic products, strict adherence to procedures for the use and implementation of adequate protective measures (National Strategy, 2008).

The following classification of biomedical and health-care waste is based on the major classification in annexes I, II, VIII and IX of the Basel Convention (BC, 1998), but specified for practical use in the health-care sector. Biomedical and health-care waste is therefore classified in the following groups:

A Health-care wastes with the same composition as household and municipal waste
- **A1** Normal household and municipal waste

B Biomedical and health-care waste requiring special attention
- **B1** Human anatomical waste (tissues, organs, body parts, blood and blood bags)
- **B2** Waste sharps (needles, syringes, scalpels, slides, ampoules, etc.)
- **B3** Pharmaceutical waste (e.g. medicines expired)
- **B4** Cytotoxic pharmaceutical wastes
- **B5** Blood and body fluid waste (materials contaminated with blood or other body fluids, soiled cotton from non-infected patients) Wastes which only require special measures to prevent the risk of infection during their management.

C Infectious wastes

Infectious health-care wastes are:
- **(a)** Discarded materials or equipment contaminated with blood and its derivatives, other body fluids or excreta from infected patients with hazardous communicable diseases (specified in section 6.1, subsection B.5 below). Contaminated waste from patients known to have blood-borne infections under going haemodialysis (e.g. dialysis equipment such as tubing and filters, disposable sheets, linen, aprons, gloves or laboratory coats contaminated with blood);
- **(b)** Laboratory waste (cultures and stocks with any viable biological agents artificially cultivated to significantly elevated numbers, including dishes and devices used to transfer, inoculate and mix cultures of infectious agents and infected animals from laboratories).

D Other hazardous wastes

Not exclusive to the medical health-care sector, e.g. solvents, chemicals, batteries, fixer solutions, etc.

E Radioactive waste from health care.

Pharmaceutical waste (B3) is waste which has become unusable for the following reasons: exceeded expiration date; expiration date exceeded after the packaging or the ready-to-use preparation prepared by the user has been opened; cannot be used for other reasons (e.g. call-back campaign). The term "pharmaceuticals" embraces a multitude of active ingredients and types of preparations. The spectrum ranges from teas through heavy-metal-containing disinfectants to highly specific medicines containing a large variety of different hazardous or non-hazardous substances. Waste management may therefore be based on a differentiated approach; for example, pharmaceutical waste could be divided into three classes and its management carried out in a class-specific manner as follows (BC, 2003):

- *Pharmaceutical wastes: Class 1*

  Include pharmaceuticals such as chamomile tea and cough syrup which pose no hazard during collection, intermediate storage and waste management. Class 1 pharmaceutical wastes are not considered hazardous wastes. They are managed jointly with municipal waste.

- *Pharmaceutical wastes: Class 2*
  Include pharmaceuticals which pose a potential hazard when used improperly by unauthorized persons. Class 2 pharmaceutical wastes are considered to be hazardous wastes. Their management takes place in an appropriate waste disposal facility.
- *Pharmaceutical wastes: Class 3*
  Include heavy-metal-containing and unidentifiable pharmaceuticals, heavy-metal-containing disinfectants, which, owing to their composition, require special management. Class 3 pharmaceutical wastes are considered to be hazardous wastes. Their management takes place in an appropriate waste disposal facility. However, owing to the fact that medicines are not normally labeled in accordance with their hazardous characteristics, the sorting of medicines into different classes, in particular classes 2 and 3, may often be too difficult in practice. Countries may therefore decide to consider all or a major part of medicines as hazardous waste or waste requiring special consideration.

3. Pharmaceutical Waste Management

On April 2010, the Government of the Republic of Serbia adopted the Strategy for Waste Management (2010), which is the basic document for evaluating the state of waste management. Based on this Strategy, the establishment and promotion of integrated waste management system are predicted, and therefore the decision-making related to management of medical and pharmaceutical waste are provided. Waste Management Strategy is adopted in every ten, and is revised every 5 years (http://www.kombeg.org.rs/Slike/CeTranIRazvojTehnologija/2010%20Maj/strategija_upravljanja_otpadom_konacno.pdf).

Management of medical and pharmaceutical waste management is a set of measures that include collecting, sorting, packaging, labeling, storage, transport, treatment and safe disposal of medical waste (Waste Management Strategy, 2010).

To reduce the generation of pharmaceutical waste, stocks of pharmaceuticals should be inspected periodically and checked for their durability (expiration date). Possibilities for returning old pharmaceuticals to the producer or handing them over to a special collection system (e.g. pharmacies) for possible subsequent use could be explored. Such a return of pharmaceuticals in their original packaging prior to or within a reasonable period after the expiration date is possible if it is ensured that the producer or collector examines possibilities for subsequent use of the pharmaceuticals and that pharmaceuticals which are no longer usable are disposed of in an environmentally sound manner. Pharmaceutical wastes which are considered to be hazardous wastes have to be collected separately in appropriate containers. Intermediate storage takes place at a location which is accessible only to trained personnel. This should be done in a manner to avoid misuse.

The precautions taken during the use of cytotoxic pharmaceuticals must also be applied on their journey outside the respective establishment, as releases of these products can have adverse environmental impacts. The management of these wastes, in covered and impermeable containers, must therefore be strictly controlled. Solid containers must be used for collection. The use of coded containers is recommended. For reasons of occupational safety, cytotoxic pharmaceutical wastes must be collected separately from pharmaceutical waste and disposed of in a hazardous waste incineration plant (BC, 2003). Marking containers must be visible with clearly declared content (Figure 1).

Figure 1 - Waste disposal and marking of pharmaceutical waste

Most commonly used technique of pharmaceutical waste disposal is high temperature destruction – incineration *(http://www.mitecosystem.com/sr/services-1-2-1.html)*. There are other methods of treatment of pharmaceutical waste (Figure 2), such as encapsulation, which is recommended when incineration is not cost-effective or when dilution in water is not recommended. Inertisation is a form of encapsulation that is used in Spain and which involves the removal of packing materials (cardboard, paper, plastic) from the drugs, so they can then be chopped and mixed with water, cement and lime to obtain a homogeneous paste. The method that EU Member States use in general, and which is consistent with the Basel Convention is returning to the manufacturer for treatment (Ilić et al, 2002.).

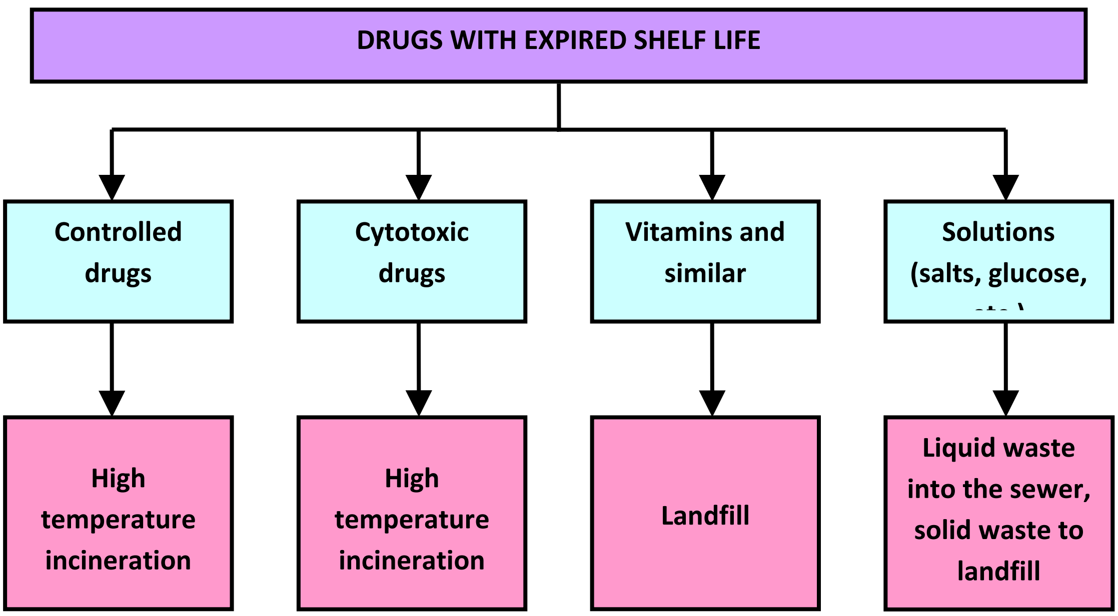

Figure 2 - Scheme disposals of drugs with expired shelf life (Source: Ilić et al, 2002).

Regulation on conditions and manner of classification, packaging and storage of raw materials (2001) prescribes the procedures for handling waste in terms of classification, labeling, and documented referral to the site immediately, recycling or destruction. According to the Regulation mentioned, the waste is classified according to origin, character and category. The origin is determined by index number from the catalog of waste that is an integral part of the Regulation. In the process of waste characterization, after determining the index number, the procedures that identify physical, chemical and biological properties of waste, determine whether waste has hazardous properties or not. Waste categorization process determines belonging to the

List of waste (green, ocher or red), which is an integral part of the Regulation (2001), designation of waste and determines its utility value. The Agency for waste recycling of the Republic of Serbia determines waste categorization *(http://www.eko.vojvodina.gov.rs/index.php?q=zakonska_regulativa%2C_nacionalni_propisi_i_eu_zakonodavstvo).*

Looking for the best solution and choice of optimal technology for the treatment of pharmaceutical waste, must be taken into account the main selection criteria, namely: economic, technological, ethical, managerial, environmental and legislative. There are also many other factors, but it is particularly important to emphasize the "principle of proximity" as recommended by the World Health Organization (2008) which states that wastes must be processed and disposed of as close as possible to where they originated.

It is generally recognized that waste management plans provide the best mechanism for improvement of environmental performance in waste management. A waste management plan can help generators to conserve resources and minimize waste through improved purchasing and reuse practices and through cost-effective, environmentally sound source separation, segregation, collection, transport, treatment and disposal of all waste streams generated within their facilities. It is recommended the plan to be in the form of an environmental management system based on the ISO 14001 series of environmental management standards (1996). Standard ISO 14001:2004 ensures that all adverse environmental impacts from organizations are identified, monitored and coordinated with federal regulations.

4. Assessment of the current situation in Serbia

By 2008, the disposal of various categories of medical and pharmaceutical waste from medical institutions in Serbia was conducted in many different ways that were not fully in comply with the requirements of the European Union (EU). In 2007 the Ministry of Health of the Republic of Serbia has launched specific activities to introduce a uniform system of medical waste management, particularly in the category of infectious medical waste. Certain categories of medical waste can be a significant threat to health of employees in health institutions. In addition to health risks that result from direct contact, medical waste can have irreversible health effects by indirect contamination of waterways and soil during the treatment and final disposal, or air pollution through emissions of highly toxic gases during incineration. It is proven that there is no method for waste treatment or disposal which completely eliminates all risks of medical and pharmaceutical waste to the population and the environment (National Guide, 2008).

Generally, depending on the type of technology for the treatment of medical waste, residues can be transferred from one stage of waste treatment to another. For example, during the incineration of medical waste, combustible waste components are converted into secondary gaseous products (CO_2, H_2O, CO and other gases) and noncombustible components remain as ashes. Under certain conditions, when waste is incinerated at low temperatures or when plastic is burned, it can lead to emissions of dioxins, furans, polychlorinated biphenyls and other toxic air pollutants. These pollutants are classified as human carcinogens and are among the persistent substances that do not break down easily in the environment and that can bioaccumulate in the food chain. Also, disposal of hazardous medical waste in an uncontrolled manner directly threatens the environment contaminating soil and groundwater. Some health facilities use the method of burning of all waste in their own existing incinerators, as the primary and only method of disposal of medical waste. Mentioned incinerators are often working in temperatures that are not adequate for the safe incineration of medical waste, so there is a tendency of their further quality control and eventual closure. Ministry of Environmental Protection conducts supervision over the work of these hospital incinerators. Only in a number of health institutions in Serbia sterilization of infectious medical waste is performed, usually in autoclaves, which are very old, but which are regularly monitored and maintained. Such practices have the institutes and departments of public health, as well as individual microbiological laboratories. After sterilization, sharps are disposed of in regular waste containers. Used needles and syringes, cotton swabs, bandages and other categories of materials, mainly infectious waste, in some health facilities are mixed with household waste instead of being segregated or sterilized first. All medical waste is then disposed of at the city landfill. Unfortunately, there is no separation of medical waste in landfills in Serbia. The existing practice of mixing medical waste with municipal waste in landfills, with an inadequate system of work, may also lead to the transmission of microorganisms through the air (through the smoke of burning waste) and rapid spread of infectious diseases. Most landfills in Serbia are not sanitary landfills, do not bury waste daily, or further treat this waste. Many landfills do not have arranged access, and they also often come up to the uncontrolled burning of waste *(http://www.komorabiohemsrbije.org.rs/pdf/vodic_medicinski_otpad,.pdf).*

Before transport, treatment or transfer of hazardous medical waste, that waste should be stored at the place provided for that purpose. Place to store medical waste, according to the Regulations on the management of medical waste, article 11 (2010), consists of a limited and separated area, room or facility provided for that purpose. Pharmaceutical waste should be stored in a room or building separate from the useful pharmaceutical products, in accordance with established requirements (2010). In order to improve the safety of human health and environmental protection the steps were taken by health facilities in Serbia for the separation and storage of medical and pharmaceutical waste in the specified containers in protected areas, till final disposal.

5. Conclusions

Given the times we live in and diseases that surround us, it is necessary to take all possible measures envisaged by the World Health Organization in order to ensure a safer and healthier living environment. For the successful conservation of the environment and the planet in general, it is necessary to comply legal regulations, especially those relating to recovery of hazardous waste, both at local and global levels and their consistent implementation by all stakeholders. By passing the Law on Waste Management (2009), Law on Packaging and Packaging Waste (2009) and Waste Management Strategy for the period 2010-2019 (2010), there has been made a significant progress towards harmonization with the EU legal heritage of the area of waste management, and the process will continue by making a series of regulations and documents for its implementation. The complete process of harmonizing national legislation with EU legal system, according to the timelines set out in the Waste Management Strategy, should be completed by the year of 2019.

Acknowledgments

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CALCULATION OF POLLUTION LOAD FROM DIFFUSE SOURCES OF A KARST FIELD

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Abstract

In order to increase crop yields, it adds nitrogen and other nutrients in the form of artificial or natural (organic, manure) fertilizers. Different types of plants in their growth take different amounts of nitrogen. The rest of nitrate nitrogen remains in the soil after harvest. Besides the absorption of the plants, nitrogen from fertilizer goes into the soil or surface runoff, assimilation microorganisms. Nitrogen in the soil encourages only fertilizer, but also from the decomposition of soil organic matter. The total area of fields in which people lived and bred cattle for specific pollution per hectare per day obtained specific value. By measuring certain parameters, we calculated the pollution load from diffuse sources of a karst field. The obtained results clearly show that the greatest threat to drinking water sources came from the fields, which are located at higher altitude.

Keywords: burden of pollution, diffuse source, nitrogen, nutrient, absorption, assimilation, organic matter,

EMS IMPLEMENTATION IN MINERAL PROCESSING PLANT -CHALLENGE FOR ITNMS SUSTAINABILITY

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Abstract

Many business firms worldwide have adopted formal environmental management systems (EMSs) as a procedure for systematically identifying environmental aspects and impacts of their operations, setting explicit goals for the performance, compliance, and continuous improvement, and managing for them throughout these operations. It can be said that an EMS, as a part of overall management system, is a change tool to improve the business that is best used to fundamentally change the organization's approach to environmental risk. In order to achieve the demands for satisfaction of stake and shareholders with quality of its products and services, the Management of ITNMS has included in its Strategy a creation of new project from quality management domain – Implementation of EMS based on standard ISO 14001. This paper presents the efforts of ITNMS's management to establish EMS in his own experimental facility where the mineral processing is basic adopted technology. It briefly describes all the reasons necessary for EMS implementation, the imperative initial steps for insuring that the appropriate EMS is taking place, and conclusion that this incorporated quality system will help ITNMS to improve its overall business.

Keywords: EMS, EIA, mineral processing plant, sustainable development

1. Introduction

Over the past decades, a huge number of companies world wide have integrated EMS into their operations, realizing all the benefits that outcomes from its implementation. In short, an EMS, which is the component of the overall management system that includes organizational procedures, environmental responsibilities, and processes, helps a company to comply with environmental law regulations, identify technical and economic benefits, and ensure that all environmental policies are adopted and followed [1]. An environmental management system EMS is a set of organizational procedures, responsibilities, processes, and necessary means to implement corporate environmental policies, and is a component of management that features organizational structure, planning activities, practices and resources for development [2]. Different authors also define an EMS as industrial tool that enables an organization to systematically control its level of environmental performance, and which helps management identify potential environmental impacts arising from its activities, set appropriate environmental objectives, establish programs to achieve corporate environmental goals, and review activities to ensure that corporate environmental policy objectives are being properly carried out [3].

We can simply say that an EMS is a change tool to improve business, but beside that, environmental performance is very important to many consumers and stakeholders. Evidence is found by noting the push on parliaments and congresses around the world to effect a culture change, or perhaps even a 2nd industrial revolution, towards *sustainable development*. Simply put, sustainable development is providing goods and services to meet the needs of current generations without compromising the ability of future generations to meet their own needs. 21st century manufacturers are looking at ways to reduce the consumption of materials and energy in production processes, and recycle their waste product into new product uses.

In the early 1990s, however, in anticipation of the 1992 “Earth Summit” in Rio de Janeiro, the Business Council for Sustainable Development proposed the development of an international voluntary standard for environmental management systems by the International Organization for Standardization. The ISO 14001 is an internationally recognized Environmental Management System (EMS) standard that was developed by the International Organization for Standardization (ISO) in response to the Rio Earth Summit. The apparent intent of introducing this standard was to offer a strategy for achieving sustainable use of the environment by businesses themselves, whether or not they were subject to effective government regulation and enforcement. This procedural standard was finalized in late 1996 as ISO 14001; other documents in the ISO 14000 series provide more detailed guidance on many EMS-related topics, such as environmental performance evaluation, life-cycle analysis, eco-labeling, and others. Environmental management systems that employ tools such as life cycle assessment and performance measures can be used to accomplish sustainable manufacturing goals and report meaningful results to all key stakeholders. The ISO 14001 EMS process-norm is internationally recognized as being effective. It is estimated that the efficiency gains brought about by ISO 14001 can help pay back the costs of implementation and certification within 3 years, and in some cases as few as 1 year.

It is important to notice that implementation of a well-crafted EMS is a key to achieving Cleaner production (CP), because it features elements that facilitate environmental improvements, and helps to coordinate the individual industrial technological and managerial processes capable of contributing to improved environmental performance [4].

2. ITNMS in EMS process formation

Institute for Technology of Nuclear and Other Mineral Row Materials (ITNMS) represent the scientific institution with the long tradition in different research fields. It was founded in 1948, and in its early beginning it was only orientated at scientific work, but now days it tends to be sort of the modern enterprise, where the results obtained in laboratories are often applied in practice. The researches conducted in different technologies (inorganic, metallurgical, mineral, environmental and chemical) are verified in the ‘plants’ for experimental production, so the products and services are later often engaged by different consumers. As Rondinelli and Berry explain [5], by implementing an EMS, a company has a greater chance of achieving positive relations with stakeholders.

Recognizing that successful integration of appropriate EMS system could lead to significant benefit through the company, the top management of ITNMS has decide to introduce this system into the existing ISO / IEC 9001:2001 quality management system. The extern demands but also the intern objectives indicated in ITNMS Strategy dating from 2004, had orientated this enterprise in creating of new project from quality management domain – Implementation of EMS based on standard ISO 14001: 2005. It was decided that first, initial steps should start at point that might have the most harmful impacts to the environment – Plant for experimental production (or Mineral Processing Plant (MPP)), in the Department of mineral processing. MPP was founded in 1994, and in its early beginning it served only for verification of laboratory obtained results. These results concerned the different adsorbents based on mineral rows, mostly zeolite types, which are applied for removing of many types of pollution. In the recent years, a lot of improved adsorbents are produced and with the growing market demands production plant was also grown. Today's capacity of this "small factory" is 880.4 kg per hour of raw material (zeolite), with different mineral preparation operations applied: ore crushing, grinding, separation/classification and physical - chemical activation of mineral grains. Although it employs only 9 persons, the profit of this part of Institute in some years was more than 35% of total monthly profit of whole enterprise. These facts induced the management of ITNMS to invest more in this plant, whose location (urban area) and possible environmental impacts make request for urgent actions.

The process of EMS orientation is present at Figure 1. It contained all the phases which prepare the conditions of Environmental Management Program (EMP) establishment. EMP practically presents the process of elimination all the dysfunctions observed in recent phases and the platform for achieving organizations objectives and targets and all further actions depend on it.

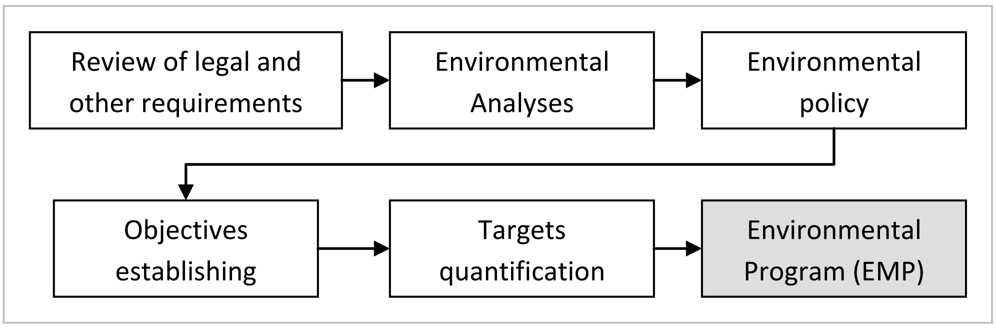

Figure 1. EMS orientation

3. Methodology

Activities of EMS preparation applied in ITNMS project had included:

1. Collecting information about experimental plant (used technology, material and energy flow, equipments, schemes, pollution sources, consumption of materials, interviews with employees, stake and shareholders opinions…);
2. Identifying of legal and other requirements and establishment of procedure for maintaining process;
3. Identifying environmental aspect and impacts of chosen activities;
4. Creating environmental analyze (contains all activities with associated aspects and impacts);
5. Determination of significant impacts (establishing the written procedure);
6. Monitoring the impacts marked as significant (written rapport);
7. Defining the Environmental Policy (supported and approved by ITNMS top management) with appropriate objectives and targets;
8. Creating proposition for Environmental Management Programme (EMP) for achieving the objectives and targets consistent with environmental policy.

The creation of Environmental Management Program is the key action part of an EMS as it identifies what activities have to be done in which time period, and what is the activity that has to be achieved, with clearly assignments of responsibilities for each activity [6].

Since a key element of a well done EMP is creating of environmental analyze, the following steps were taken in the identification of environmental aspects and the evaluation of associated environmental impacts:

1) Selecting an activity that will be observed;
2) Identifying environmental aspects of this activity;
3) Identifying environmental impacts;
4) Evaluating the significance of impacts found.

For the purpose of realisation of this project, the following tools were used:

- PDCA Methodology
- Pareto Principle
- Cause-and-Effect Diagram
- Multi-Criteria Decision Analysis (MCDA), Weighted Ranking (Sum) Model

Multi-criteria decision analysis (MCDA) is a decision making tool, which can be applied to make a comparative assessment of alternative options or measures during planning. The application of this technique, allows several criteria to be taken into account simultaneously either in a complex situation or to solve complex problems. Here will be described the use of Weighted Sum Model, one of MCDA method, simplest and well known method that serves for evaluating a number of alternatives in terms of a number of decision criteria. This method can be conducted by using a decision matrix, which is fundamentally a chart that allows a systematically identifying, analyzing, and rating of different sets of information.

The decision matrix can be created by following: identifying alternatives (also known as options or activities that need to be examined, and list these across the top of the matrix); identifying decision / selection criteria; assign weights (if some decision criteria are more important than others, review and agree on appropriate weights that are to be assigned (e.g. 1, 2, and 3); design a scoring system (well define what high, medium and low scores represent); score the alternatives (for each alternative, assign a consensus scoring for each decision criterion); sum and total the scores (multiply the score for each decision criterion by its weighting factor, and then total the scores for each alternative being considered and analyse the results).

4. Results and discussion

For the purpose of identification and determination of important environmental aspects of MPP activities by the methodology described, the following criterions were used:

- Harmonizing with legal requirements (C): criterion mostly based on agreement with environmental law regulations;
- Aspect importance (I) considering:
    - Material and energy bilans,
    - Time and frequency appereance,
    - Risk of apperance;
- Impact management (M): the possibilities for minimizing the negative impact, corrections were made or not, solutions are possible or not...

Each criterion was ranked by three scores: 5-high, 3-medium and 1- low rating mark.

The results obtained by conducting environmental analyses and rating them by the previous criterias are given in the Table 1.

Table 1. Decision matrix for evaluating activity impact importance

Activity observed	**Env. Aspect**	**Potential Impact**	**Criterion**			**Total rating mark**
			C	**I**	**M**	
Transport (eksternal)	Air	Fossil fuels consumption; Gasses emission	1	1	3	3
Transport (internal)	Air	Fossil fuels consumption; Gasses emission	1	1	1	1
	Noise	Noise generation	3	1	1	3
Unlading / Storage	Noise	Noise generation	3	3	3	27
	Air	Particle emission	1	3	1	3
Drying	Air	Energy consumption, Emision of vater vapour and disolved gasses	1	1	1	1
Production (physical activation...)	Air	Particle emission	5	3	3	45
	Noise	Noise generation	5	3	1	15
Particle removing system	Water	Water consumption; Water pollution	1	1	1	1
Chemical Activation	Water	Spill of chemicals	1	1	1	1
	Soil	Spill of chemicals	1	1	1	1
Solid waste storage	Soil	Soil pollution	1	1	3	3

Table 1 illustrates the calculations and results of a MCDA by using the decision matrix for a concrete example of assessment, obtained by application of previous criterions and detailed examination through the practice. As it can be seen from the previous results, the two most harmful activities in MPP are: physical activation of mineral rows (crushing, drilling, mealling...) with strong impact to the air and noise, by particle emission and noise generation, and unlading and storage of mineral rows in the same manner, but with the lower ranking rate. Each of the activities denoted in Table 1. had gave written results in different forms: check lists, interviews, written reports, procedures...These results are briefly described in Master these of Lopicic Z. [7].

The most important facts made from these analyses are that this plant causes serious impact to environment because of dust emission and particulate matter in ambient air, which are also known as the main pollutants in the processes of mineral raw processing and preparation. The concentration of these pollutants were 2 to 3 higher than allowed legal limit; this was shown in monitoring process that was conducted in collaboration with the certified laboratory for monitoring of this pollutants, Laboratory for environmental protection of ITNMS. It was also indicated that the pollution by noise is present at most of operations/activities, and its concentration was often over legal limits. The further activities were orientated in the direction of minimazing these negative impacts on environment, and legal requirements satisfaction.

5. Conclusion

The objectives and targets produced by briefly environmental analyses, consistent with Environmental policy adopted by highest ITNMS Management were:

1. Reduction of dust emission (this requires some modifications in system for particles removing);
2. Reduction of noise concentration to legal requirements;
3. Permanent education of employees with environmental issues and EMS
4. Improvements in process design and control for energy and cost savings by 30%.

By analysis of the data collected for this plant, it was indicated that environmental policies that had to be accepted should be implemented though pollution minimization as soon as possible. It should include strong environmental management system, advanced pollution control technologies, environmental awareness training for employees, and requirement – from company stakeholders – for increased accountability of environmental impacts.

At the end, we can summarize that the most important things were done. They included:

- Identification of legal requirements (when these legal requirements are identified, EMS should help in better understanding of the impacts on the environment and serve as guidance for developing a proactive action plan to ensure that the targets required by the law are met);
- Evaluation of hidden costs and finding alternatives for their reduction.

Acknowledgement

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GLOBAL ENVIRONMENTAL AND ECONOMIC INTERDEPENDENCE

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Abstract

Economic growth in the economy, especially in developed countries, highlights the growing international, political and ecological interdependence, and the economic growth of all countries, thus becoming a global problem.
In this context, more attention must be paid to the relationships between population, resources and environmental conditions on the one hand, and long-term sustainable economic development on the other side.

Keywords: globalization, sustainable development, economic development.

1. Introduction

The main objective of the economy in terms of natural environment is reduced to finding procedures and methods that, by manufacturing processes, would provide the most efficient ways of processing of natural resources and services to meet specific human needs.

The contrast of the objectives of economy and ecology in terms of utilizing the environment and its resources is emphasized by contrast of environmental principles and measures to protect the natural environment and use the market as a basic mechanism allocation of social resources.

In that context, the requirements imposed on free access and use of resources through a process of limited competition, which includes market mechanisms for allocation, and control and limited use of the natural environment and its resources.

The contrast of the economy and ecology, it comes down to finding and applying the mechanism for allocation of social resources, including natural, through implementation of its core functions to the maximization of the efficiency of allocations, and providing maximum protection of the ecological balance

2. Economic and ecological independence

Towards linking economic and environmental independence I would like underline the basic types of economic instruments for environmental protection:[2]

- Fees (which must be collected for the emission in the environment, based on the principle of quality)
- Financial assistance - in the form of grants, loans, etc.

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- Exchange (market) emissions permits-used utility instruments should contribute to the establishment of ecological standards, and also the potential for cost savings
- Systems for deposits and return on assets-mainly regulated programs for regulating waste.

3. Ecological and economic efficiency

When it comes to mutual dependence, should make distinction between ecological and economic efficiency.

The central issue for the evaluation for the environmental effects of market mechanisms are their environmental impact and how the same is achieved the required reduction in emissions or environmental damage.

Eco-effectiveness is crucial in the evaluation of all environmental and political measures. Especially in the process of assessing costs and benefits of applied measures such as emission fees or make up, where eco-efficiency depends on the reaction of the pollutants to market changes.

On the other hand, the reason for the application of economic instruments in environmental policy lies in the fact that there is a low level of economic costs that should be incorporated in policies to reduce the level of pollution.

4. The impacts of the global economy on the development priorities

Today the world is in the front of the major challenge in the field of globalization in terms of global effects, the influence of state regulatory systems and so on.

Small countries, especially transition economies such as Macedonia, are facing a huge challenge where necessary specifically to define the packets of specific intervention measures through finical, economical and tax measures.

On the other hand the global economic crisis includes the Macedonian economy with classic scenario: monetary restriction due to the decline of FDI; the collapse of credit which has the effect of falling domestic demand and ultimately falling economic activity.
Intervention package of economic policy should include:[3]

- Intervention measures to encourage economic growth;
- Social measures;
- Infrastructure measures.

To realize all these economic activities is necessary to have adequate support from the companies through which they themselves with their management will contribute to creating a society and sustainable development.

Directing attention to social aspects and environmental aspects in the development of the private sector is becoming integral part of sustainable development.

Successful managers around the world begin to realize that the financial, social aspects and environmental aspects are equally important elements.

[3] Mirowski, P (1989) More Heat Than Light - Economics as a social physics: Physics as nature's economics. Cambridge UK, Cambridge University Press.

Now the challenge is to learn from past experiences and use most of the potential of privatization to achieve better and lasting results to improve environmental conditions and sustainable development.

Evaluation of Economic Instruments in Central and Eastern Europe (especially for that in transition) has some difficulties in comparison with applications in OECD countries:[4]

- Most fees for emission and collection of products designed with the operation of the Parallel System licensing;
- Economic and industrial restructuring, and the associated period of recession, have also influenced the emission and ecological quality, making evaluation of the effectiveness of environmental policy is very difficult;
- We should not ignore the impact of inflation, which is present in almost all countries.

5. Conclusion

Economy considers the relationship to nature as a rational exploitation of resources, thus an active attitude.

Therefore, ecology is not aimed at maximizing any gains.

Moreover, we could say that ecology aims minimize losses, which the environment caused by the exponential expansion of human economic activities.

Economic and ecological independence indicate the necessity of mutual conflict relation, which does not mean that they lack integration points, especially in developing models consider of economic and socio-ecological development.

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THE POSSIBILITY ADVANTAGE OF GEOTHERMAL WATERS OF SIJARINSKA SPA

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Abstract

Geothermal water of Sijarinska Spa was having a significant energy potential. Well B-4 in Sijarinska Spa is able to exploit to 30L/s of water temperature 75^{o}C. This worked there are structure and tendency to create deposits in the pipe installation. Investigation of the composition was performed by standard physical and chemical methods. Was determined by the saturation index (L.I.) and Ryzner stability index (R.I.) and measure of the tendency to create deposits. The results indikate that the value of the L.I. and R.I. for geothermal water of Sijarinska spa (well B-4) were 1.45 and 4.6, respectively. The obtained values show that the geothermal water of B-4 is more favorable for use in pipe installations, since it indikate bigest tendency to create deposits. The not decrease of deposits, not come to aggressive effects in material of pipe installations.

Keywords: geothermal water, deposits, deposits creations, L.I., R.I.

DEVELOPMENT OF THE PROGRAM FOR ENVIRONMENTAL PROTECTION AND SUSTAINABLE DEVELOPMENT IN SERBIA WITHIN ACCESSION PROCESS TO THE EU

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Abstract

European Strategy for Sustainable Development is based on the coordinated development of common policies which deal with economic, social and environmental dimension with sustainable development as its essential purpose. One of the elements in accession process to the EU is development of the National Environment Programme, within the contemporary perception of environmental protection issues in the Republic of Serbia, which should provide a legal and institutional basis for numerous projects in the Stabilization and Association Process and the use of funds from budget and pre-accession programs.

Keywords: environmental protection, sustainable development, accession to the EU, Serbia

1. European Strategy for Sustainable Development

Until the sixties of the twentieth century no one country in Europe did not have a clearly defined policy on environmental issues. Not until the United Nations Conference on Environment, public became aware of links between environment and economic development.

EU activities in the field of environmental protection is based on the principles of prevention, on the principle that damage was caused to the environment to the greatest extent possible be stopped at its source, and that the basic principle of polluter pays damages.

European Environment Agency is body that monitors and collects information on all matters related to environmental protection and provide to Member States technical, scientific and economic information linked to environmental protection.

EU Programe in the field of environmental protection has as its primary goal the sustainable development. This means that short-term economic benefits to the detriment of the environment must be replaced with a sustainable model of economic and social development, which will form the basis for greater efficiency and competiveness.

European Strategy for Sustainable Development is based on the coordinated development of common policies to deal with economic, social and environmental dimension with sustainable development as its essential purpose. On the basis, it establishes a set of key objectives to limit climate change and increased use of clean energy, respond to threats to human health, manage natural resources more efficiently and improve the transportation system.[1]

Based on the strategy, EU adopts action programs that define the main objectives that should be achieved in the field of environmental protection, as well as activities that should be accomplished to achieve them. The Sixth Action Programme has four priority areas:[2]

1. Climate change - the main objective, until 2020., is to reduce the emissions of greenhouse gases between 20 and 40% (starting from the basics of1990), so that will be undertaken structural change and stronger measures for saving energy, especially in transport and energy, and strengthen research and technological development.

2. Nature and biodiversity - preservation and restoration of the structure and functioning of natural systems and halt the loss of biodiversity through the adoption of environmental legislation, rounding network Nature 2000 (conservation of natural habitats of rare plants and animals), new initiatives for the conservation of marine resources and adopt strategies for the conservation of arable land.

3. Environment and health - the preservation of environmental quality that does not violate human health, so as to establish a system for risk management of chemicals, a strategy to reduce the risk of pesticita, protection of water quality, noise and air quality.

4. Management of natural resources and waste - the main goal is to separate the use of sources of economic growth, particularly by allowing the increased efficiency of use, taxation of their use, increasing recycling and reducing waste.

At each spring summit of heads of the States to assess the success of the implementation of the European strategy for sustainable development and observe its major problems (launched in 1998, the Cardiff Process).

2. EU program for environment – LIFE +

The LIFE programme is the EU’s funding instrument for the environment. The general objective of LIFE is to contribute to the implementation, updating and development of EU environmental policy and legislation by co-financing pilot or demonstration projects with European added value. Western Balkan countries can use LIFE program for third countries. Budget program for the period 2007-2013 is over 2 billion €.[3]

Users of the program: all levels of government, public and private organizations and institutions and research centers involved in environmental protection programs. Program Administrator: European Commission and the Directorate General for Environment.

LIFE + program consists of the following components:[3]

1. Nature and Biodiversity - supports projects that contribute to the implementation of the EU's Birds and Habitats Directives, the Natura 2000 network and that contribute to the EU's goal of halting the loss of biodiversity. The maximum rate of co-financing can be up to 75% for priority species and habitats, bur is usually 50%. This component includes the following topics:

- Coasts, seas & fisheries
- Forests
- Grasslands, scrubland & bogs
- Rivers & lakes
- Wetlands
- Animal & plant species

2. Environment Policy and Governance - supports technological projects that offer significant environmental benefits. This part of LIFE+ also helps projects that improve the implementation of EU environmental legislation, that build the environmental policy knowledge base, and that develop environmental information sources through monitoring. Projects can be co-funded to the

level of 50%. This component involves the development of innovative techniques and methods for the protection and improvement of environment, especially in the following areas:

- Air
- Energy & climate
- Environmental management
- Industry & production
- Urban environment & quality of life,
- Soil, land-use & agriculture
- Waste
- Water

3. Information and communication - projects related to communication and awareness raising campaigns on environment protection, nature protection
and biodiversity conservation issues and projects relating to the prevention of forest fires and actions for implementing, updating and developing European environmental policy and legislation.

3. National Environment Programe

One of the elements in accession process to the EU is development of the National Environment Programme, which should provide a legal and institutional basis for numerous projects in the Stabilisation and Association Process and the use of funds from budget and pre-accession programs.[4]

National Environment Strategy represent the most important, comprehensive, intersectoral, strategic framework in the field of environmental protection, which provides planning and management in this area over the next ten years and should be implemented by the Action plan.

Environmental protection program include:[4]

- description and assessment of the state of the environment;
- the basic objectives and criteria for enforcement of environmental protection in general, by sectors and by geographical areas with priority measures;
- most favorable conditions for the application of economic, technical, technological, economic and other measures for sustainable
- development and environmental management;
- long-term and short-term measures for prevention, mitigation and control of pollution;
- holders, the manner and schedule of implementation;
- financing plan.

Starting from the concept of sustainable development, the program provides a solution of key national environmental issues that are consistent with the economic and social development.

Sustainable Development stands for meeting the needs of present generations without jeopardizing the ability of futures generations to meet their own needs – in other words, a better quality of life for everyone, now and for generations to come. It offers a vision of progress that integrates immediate and longer-term objectives, local and global action, and regards social, economic and environmental issues as inseparable and interdependent components of human progress.[1]

It is estimated that total investment will rise from around 48 million euros in 2010. to 725 million euros in 2019. (Table 1.1). Temporal distribution of investment shows that during the short-term implementation period covered by the Action Plan (2010-2014.) gradually increasing investment. The reason for this is that the short-term implementation phase focuses on building an effective legal, financial, and systems of monitoring and reporting on environmental protection and thus includes many activities that are not capital intensive. Nature of the investment expenditure during this period, mostly related to black spots and existing projects in development. A significant increase in investment in the field of environment envisaged in the medium term implementation (2014-2019).[4]

The program includes activities that are directly associated with improvement of the environment, but also includes sectoral activities that benefit the environment, although their main purpose is protection of the environment (eg transport infrastructure, drinking water treatment).

Table 1.1 Total annual investment for the implementation of the program (including indirect costs) toward sub-sectors from 2010 - 2019.

	2010	2011	2012	2013	2014	2015	2016	2017	2018	2019	total
Waste	10	36	52	70	138	128	133	139	144	150	1000
Energetics	4	2	54	47	51	141	192	243	227	244	1205
Mining	2	2	0,3	10	12	3	2	2	2	2	37,3
Industry	2	18	30	20	15	18	21	25	28	31	208
Chemicals	0,5	4	6	6	8	5	5	5	5	5	49,5
Transport	0,1	1	15	12	12	68	79	94	107	127	515,1
Agriculture	1	12	14	15	15	11	12	13	15	16	124
Land	0,1	2	2	2	2	3	3	3	3	3	23,1
Air	0,6	5	7	3	3	3	3	3	3	3	33,6
Water	25	40	50	60	80	108	115	121	127	134	860
Nature	2	2	3	1	4	3	3	3	4	4	29
Noise	0,3	0,5	1	0,9	0,9	1	2	3	4	5	18,6
Radiation	0,4	1	1	1	3	18	18	18	1	1	62,4
Total	48	125,5	235,3	247,9	343,9	510	588	672	670	725	4165,6

Source: National Environment Protection Programme

Instrument for Pre-Accession Assistance (IPA) replaces a series of EU programmes and financial instruments for candidate countries or potential candidate countries, namely PHARE, PHARE CBC, ISPA, SAPARD, CARDS and the financial instrument for Turkey.[5]

The IPA is made up of five different components:[5]

1. Assistance for transition and institution building;
2. Cross-border cooperation;
3. Regional development;
4. Human resources;
5. Rural development.

The fact is that 30 percent of regulations that Serbia have to adopt in the Stabilisation and Association Process to the EU relates to environment and in this sense was made great progress since the last year.[6]

Serbia as potential candidate for the EU may use only the first two components,so for now the money is used for projects related to air quality, hazardous waste management, chemicals and technical assistance projects that are important for negotiations on European integration. [6]

From IPA 2007 were approved three projects worth a total of 4 million euros and from IPA 2008 were approved three projects worth a total of 5 million euros.[7]

When Serbia receive status of candidate country, should use the so called third, fourth and fifth component of IPA funds, which are intended for waste management, wastewater management, and the biggest investment will be the construction of facilities for wastewater. [7]

4. Instead conclusion

Environmental awareness is a required basis for further sustainable development of environmental protection. With knowledge and skills provides base to move into larger systems, broader aims and more sophisticated understanding of the relationship prevailing in the environment. Protection and improvement of the environment is important global problem of modern society. Its solution initiates, among other things, to find ways for the rational and complex use of natural resources and improving international cooperation in scientific research.

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POSSIBILITIES FOR IMPLEMENTATION OF POLLUTION PREVENTION TECHNIQUES IN COMPANIES WITH LOWER CAPACITIES THEN THOSE SET BY IPPC DIRECTIVE

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Abstract

IPPC Directive directs industrial enterprises in the implementation of "best available techniques - BAT", encouraging the use of techniques that prevent and produce less waste, use less hazardous materials and substances, reducing the use of raw materials and energy consumption, and increase recovery and reuse of materials within the production process, which is the essence of cleaner production. According to legislation in Bosnia and Herzegovina, the subject of integrated environmental permitting in accordance with IPPC philosophy and requirements are installation with significantly lower than those capacities set by Annex 1 of the IPPC directive.

Bosnia and Herzegovina has, through adopted a set of environmental laws in 2003 year, accepted the modern principles of environmental protection, including the principle of "prevention" and regulated the procedure for issuing environmental permits in the spirit of the IPPC Directive.

Unlike the EU, the requirements for the application of integrated prevention and control were put in front companies with significantly smaller capacity than those prescribed by the directive, thus paving the way for a comprehensive sustainable industrial development, but also a number of challenges in implementing the concept. The paper presents results of research into the possibility of application of preventive techniques in manufacturing plants with smaller capacity than those specified by the IPPC Directive. The research has been done on sample of 10 manufacturing plants of different characteristics in terms of types of production processes and capacities, the company's size and mode of production, ownership status and the status of the transition. The specific objective of this research is to explore the possibility and economic feasibility of applying preventive techniques in industrial plants in Bosnia and Herzegovina.

Keyword: pollution prevention, cleaner production

PERSPECTIVE OF WASTE TYRES UTILIZATION IN KAKANJ CEMENT PLANT

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Abstract

Problem of waste tyres disposal in Bosnia and Herzegovina is very actual, especially because of the annual tyre production which varies between 12.000   15.000 tonnes. The largest quantity of waste tyres in Bosnia and Herzegovina is improperly managed with great negative impact on the environment. International experiences in waste tyre management are mostly connected to their use as alternative fuel in cement industry. Energy costs in cement production process are 30-40% of total production costs. This fact justifies utilization of waste tyres in cement kilns from economical and ecological aspect.

One of the most perspective systems for waste tyres utilization in Bosnia and Herzegovina is Kakanj cement plant which is a member of Heidelberg Cement Group one of the biggest construction materials producers in the world, with big experience in waste tyre usage.

All necessary preconditions for use of waste tyres in Kakanj cement plant already exist; good communication connections with big centres in Bosnia and Herzegovina, continuous tyre supply etc. The main advantage of waste tyre utilization in cement kilns is their heating value, as well as incorporation of tyre components in clinker without affecting its quality but significantly reducing consumption of virgin materials. This process does not generate waste and does not have negative impact on environmental components: water, air and soil, under condition that necessary reconstructions in kiln preheater system are properly done.

THE ROLE OF BIOFILMS IN BIOLEACHING OF MINERAL SULFIDES

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Abstract

This work represents a review of the research efforts that have contributed to a better understanding of the phenomena connected with the biofilm formation at a sulfide surface and its role in bioleaching of sulfides. The important questions relating to the biofilm formed on the sulfide surfaces, particularly on copper, nickel, cobalt and zinc sufides, considered here are: (1) *the structure of biofilms* (composition, interface sulfide-biofilm-electrolyte/bacteria, and reactions involved in a biofilm), (2) *the mechanisms of the biofilm formation*, and (3) *the effects of biofilm on leaching behavior of a sulfide*.

Keywords: sulfide, leaching, bacterial leaching, attachment of bacteria.

1. Introduction

Biohydrometallurgy has become an important economical alternative for treatment specific minerals. Biohydrometallurgy is, in fact, a natural process that uses microorganisms (in particular, bacteria) to enhance the dissolution of metals from mineral ores (mostly from sulphides), thus making them more amenable to dissolution in aqueous solutions. Among the available mining technologies, the attractiveness of this technology is largely due to its low operational costs, lower environmental impacts and its simplicity in operation.

Biohydrometallurgy is an interdisciplinary field that involves at least four disciplines: hydrometallurgy, mineral processing, chemistry and microbiology.[1] It consists of two related microbial processes: (1) bacterial leaching (or bioleaching) and (2) biooxidation.[2] The former refers to an extraction of metals from solid ores into solution, that is enhanced by the metabolism of certain microorganisms such as bacteria, archaea and eukaryota. The bioleaching of sulfides encompasses electrochemical and chemical reactions of the mineral with the leach solution and the extra-cellular polysaccharide layers on the microorganisms.[3] The latter – biooxidation – is an oxidation process caused by the activity of microorganisms where the valuable metals remains in the solid phase.

It has been known for a long time that the bioleaching of sulphide minerals is based on a primary acidic or oxidative ferric reaction with the sulphide surface, which can be represented by the reaction written as follows:[4]

$$MS_x + Fe^{3+} \rightarrow Me^{x+} + Fe^{2+} + S(?) \quad (1)$$

which, apart from the dissolution of the metal sulphide ions, produce Fe^{2+} ion and some primary sulphur compound (?). The ferric iron and sulphur compound formed in this reaction represent the substrate required for microbial growth according to the following reactions:

$$4Fe^{2+} + O_2 + 4H^+ \rightarrow 4Fe^{3+} + 2H_2O \quad (2)$$

and

$$S(?) + O_2 \rightarrow SO_4^{2-}, \quad (3)$$

respectively.

The Fe^{3+}/Fe^{2+} turnover may occur within the extracellular poly-saccharide (EPS) layer excreted by the microorganisms attached to the mineral surface. The primary sulfur product in bioleaching process depends on which sulphide mineral is being leached and is subsequently either chemically or biologically transformed to either elemental sulfur or sulfate. In adition, this reaction of the sulfur product might also take place in the EPS layer.

The mechanism proposed above describes very well the bioleaching of pyrite, Fe_2S, molybdenite, MoS, and tungstentite, WS. The Fe^{3+} species react with the iron in the pyrite leading to dissolution of ferrous iron, whereas water molecules react with the sulphur to produce thiosulphate as the main dissolved sulphur particles (Reaction 1). These sulphur species are further oxidized by ferric iron, thus producing sulphates (Reaction 2). Finally, the Fe^{2+} ions are converted to the Fe^{3+} by *Thiobacillus ferrooxidans* or *Leptospirillum ferrooxidans*.

Bioleaching is, therefore, commercially used in operations to process ores of copper, nickel, cobalt, zinc and uranium, while biooxidation is used in gold processing and coal desuphurization. Recently, a significant commercial interest has been appeared in the exploitation of moderate thermophiles and thermophiles for bioleaching.

Activity of microorganisms is not only limited to the attack on sulphide minerals, uranium ores, refractory ores, and coal. In fact, the microorganisms can also corrode (dissolve) and destroy the ferrous and non-ferrous metals, through a process called microbiologically induced corrosion. Microbial biofilms of varied composition and thickness develop on all surfaces in contact with aqueous environments, a process known as biofouling. Biofouling and microbiologically induced corrosion of metal surfaces are due to biological and electrochemical processes mediated by microorganisms adsorbed to the metal surface or embedded in biofilms. Biofilm formation and metallic corrosion have traditionally been analyzed as separate, independent processes that occur simultaneously or sequentially on metal surfaces.

2. Bacterial attachment

Microorganisms can be classified as either protists or monera. Protists are eucaryotic, meaning that they have a true nucleus and include protozoa, algae, and fungi. Monera are procaryotic, lacking a true nucleus, and include bacteria and blue-green bacteria.[5] Bacteria have received the most attention because of their presence and activities within biofilms formed on a dissolving ore surface. The attachment of bacteria to the mineral surface is sometimes considered as the process of importance in bacterial leaching of sulphides, such as pyrite or sphalerite. .

However, many factors affect the attachment of bacteria to substrata and the subsequent growth within the film: (1) composition of metal surface,[6] (2) roughness,[7] (3) presence inorganic passivating films (hydrated oxides, hydroxides),[8] (4) presence or absence of cracks and crevices,[9] and (5) the electrolyte properties (pH, ionic strength, inorganic ions, presence of C, P, and N).[10,11]

In natural environments, the process of biofilm formation occurs continuously. The process includes a series of events: (1) adsorption of organic molecules to the substratum surface, (2) bacterial adhesion, (3) cell growth and cell reproduction and (4) extracellular polymer formation to build up the biofilm matrix. A variety of mechanisms exists to describe bacterial adhesion at surfaces.

In order to develop and optimize the bioleaching process, it is necessary to understand the mechanisms and kinetics of the microbial attack of sulphides. Although the bioleacing of minerals sulphides has been studied for a long time, there is still a lack of knowledge regarding the generally accepted mechanism and the kinetics – for instance, clearly defined rate equations which could be used to predict the performance of the bioreactors used for bioleaching. In this paper, the research on the chemistry and electrochemistry of the ferric bioleaching of sulphide minerals in terms of the biofilm role will be presented and reviewed.

3. Biofilm structure

A biofilm is a gelatinous structure, at least 95% water, made of a matrix of extracellular polymeric substances (EPS) of polysaccharidic nature, bacterial cells, and diverse inorganic detritus.[5] The results[11,12] obtained using the confocal scanning laser (CSL) microscopy show that more of volume of bacterial biofilms is occupied by the matrix (±75 to 95%) than by bacterial cells (±5 to 25%). The cells may be concentrated either in the lower or upper areas of these biofilms. Biofilms lead to an important modification of the metal-solution interface and the aqueous environment. Reactions between metabolites produced by bacteria and metals take place underneath biofilms or within the film. Thus, biofilm formation creates conditions that are crucial to either the acceleration or inhibition of dissolution.

There are different shapes of bacteria: spherical, filamentous, rod shaped, or helical. In most cases, rod shaped bacteria attach first on a metal surface.[6] The range in size of bacteria is more often from 0.2 microns wide to 1-10 microns long. Bacteria can tolerate a wide range of environmental conditions, for instance, temperatures from less than 0 up to 99 ^{o}C, or pH from 0 to 12. The review written by H.L. Ehrlich[14] contains data about environmental conditions for some microorganisms, including various kinds of bacteria, fungi, algae, and protozoa.

Bacteria as a class of microorganisms can be categorized according to their requirements for oxygen (obligate aerobes and obligate anaerobes) and their nutritional requirements (heterotrophic, autotrophic, and phototrophic). Aerobes require oxygen for survival, while anaerobes cannot tolerate oxygen. However, between these bacteria strains exist the microaerophilic bacteria that require low oxygen concentrations as well as the facultative anaerobic bacteria, which prefer aerobic conditions but can live under anaerobic conditions. Heterotrophic bacteria produce energy from a wide range of organic molecules, while autotrophs oxidize inorganic compounds, elements or ions (e.g., NH_3, H_2, NO_2^-, SO_4^-, Fe^{2+}, Mn^{2+}) as source of energy. Phototrophic microorganisms can use light as a source of energy.

Within different strata of biofilms, conditions are present for existence of different types of bacteria.[15] A series of oxidative reactions may occur due to oxygen diffusion into the biofilm, while another series of reductive reactions may occur, depending on what electron acceptors are available in the environment and on the metal surface. According to W.A. Hamilton *et al*.,[16] bacteria within the biofilm act symbiotically to produce conditions more favorable for the growth of each species. However, sometimes this is not possible. For instance, when sulphates are present in solution, the sulphate reducing bacteria (SRB) predominate because of the ability of some species to produce the enzyme *hydrogenase*, that can reduce the hydrogen concentration to such a low level that other bacteria cannot compete. On the other hand, in systems with low concentrations of sulfate (e.g., some freshwater systems) the SRB activity, more often expressed as the sulfate reduction or sulfide production rate, significantly decreases. Diffusion of sulfate into the biofilm becomes limiting for the activity of SRB when sulfate concentrations are below 0.5 to 1.0 mM, depending on the biofilm thickness.

According to Costerton,[18] two properties of the bacterial cell significantly determine its life in the biofilm matrix: reproduction by binary fission and phenotypic plasticity. These properties cause inherent discontinuity into bacterial biofilms. The bacterial reproduction by asexual binary fission is very sensitive to positive changes in environment, even for a short time (e.g., a few minutes). Thus, when a nutrient suddenly enters the solution, the dormant bacteria resuscitate and adhere quickly to this source of "food," eventually forming biofilm of macroscopic dimensions.[18,19] At the cellular level within a biofilm, a bacterium cell that finds itself at nutrient-limited area (marked as "A" in Figure 1) continues to live as a single cell, while another identical cell that finds itself at more beneficial area ("B", in Figure 1) produces a microcolony. As can be seen in Figure 1, the cell supplied with an essential organic substrate (part "B") by its proximity to a neighboring microcolony of cooperative organisms, forms a functional consortium within the biofilm. A driving force of this process is the nutrient gradient.

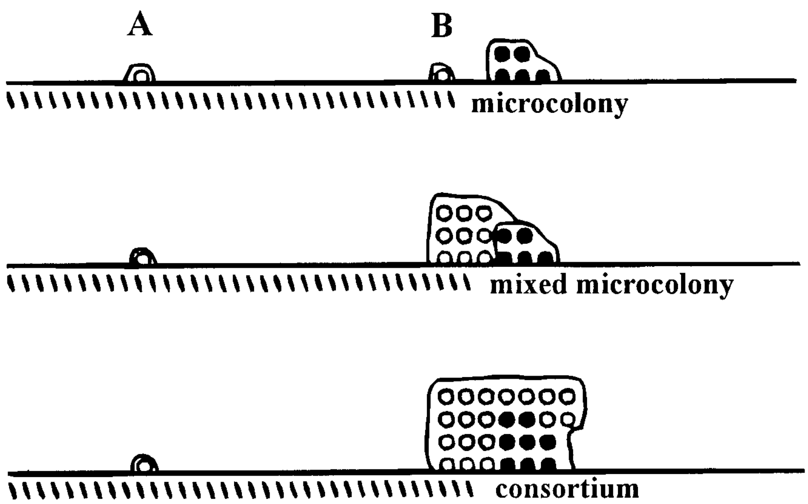

Figure 1. Schematic representation of the different responses of two identical, newly adherent cells that find themselves in (A) a nutrient-poor surface area and (B) a surface supplied with nutrient by a microcolony of a physiologically cooperative organism. The progeny of the cell at B eventually form a mixed microcolony, and then a functional consortium, with the cooperative organism. (Reprinted with permission from ref. 18.)

Phenotypic plasticity, another property of bacteria pointed out by Costerton,[18] can be defined as the bacterial cell response to changed environmental conditions. In addition, adaptation of certain type of bacteria in contact with the other different bacterial strains occurs much faster than those present in the genotype.

4. Interface solid surface – biofilm-electrolyte

The relationship between bacterial attachment to the metal and dissolution of such surfaces is not fully understood. However, the formation of a dense mass of adhered bacterial cells may cause the development of concentration (electrochemical) cells due to differential aeration of oxygen. If an organism plays a significant role in the dissolution process, it should be closely associated with the corroding surface.[20] In the related phenomena (bioleaching minerals by bacteria, caries formation, and aerobic or anaerobic wastewater treatment) attachment bacteria to the solid phase appears to be common.

Despite qualitative evidence[21-24] that surfaces have a significant effect on the bacterial metabolism, the experimental observations are not always in agreement; nor is there a general explanation given for this influence. The experimental inconsistency can be attributed to the great variations in experimental set-up with respect to the kind of the solid phases, the microorganisms, the substrates, sterility, and so on. Yet, interactions between the metal surface and a bacterium may be explained according to the mechanism proposed by M.C.M van Loosdrecht *et al*.[25] (Figure 2).

The first step in these interactions is transport of cells to a surface that can occur as diffusion, convection, or active movement. In diffusion transport, bacteria exhibit a non-negligible Brownian motion (average displacement, 40 μm h^{-1}), which can be seen under a microscope. Diffusion transport is much slower than transport by convective flow or transport by motile cells. Convective transport of bacteria is a result of liquid flow. The final part of the convective route, under certain circumstances, is diffusion controlled.[26] While moving, once a motile bacterium is close to a surface, it may encounter a surface by chance or chemotactically respond to any concentration gradient that may exist in the interfacial region.[25]

The second stage, initial adhesion, is mainly a physicochemical process. It can be reversible or irreversible. Reversible adhesion is defined as deposition to a surface in which the bacteria continue to exhibit Brownian motion and can be readily removed from the surface by moderate shear or the bacterium's own mobility. On the other hand, irreversibly adhered bacteria exhibit no Brownian motion and cannot be removed except by a strong shear force.

Third stage is attachment. When the bacterium is deposited on the solid surface, special cell surfaces (e.g., fibrils or polymers) may form strong bonds between cell and solid surface. Polysaccharides have been shown to be essential for the development of surface films, but not for the initial adhesion of bacteria.[27]

Last in the sequence is surface colonization. When firmly attached cells begin growing and newly formed cells remain attached to each other, microcolonies or biofilms may develop. In the case of growth of reversibly adhered bacteria, some of the new cells will be released into the medium. Finally, it is important to point out that the last two processes (attachment and colonization) are very sensitive to the type of organism and therefore they are more specific than the first two.

The bacterial colonization at a surface depends also on the presence of different species (e.g., certain nutrients) at the interface. Although the concentrations of a nutrient in the bulk and at the surface might be very different, in a state of equilibrium its chemical potential is the same in both positions. The positive influence of the surface on bacterial activity, including corrosive action, has often been attributed to the accumulation of nutrients at the surface. Furthermore, the geometry of the interaction between cells and surface is important. The average length of bacteria is 1 - 2 μm, and they have thin cell walls of 20 to 100 nm thickness. Reversibly adhering bacteria are positioned at a distance of approximately 5 nm from the surface.[28] The thickness of an adsorbed layer of substrates, nutrients, anions, cations, etc., usually does not exceed a few nanometers, which means that only a very small part of the bacterial surface (less than 0.1%) is in direct contact with adsorbed substances. Therefore, depending on the conditions, adsorption and desorption may influence bacterial activities positively, negatively, or not at all.

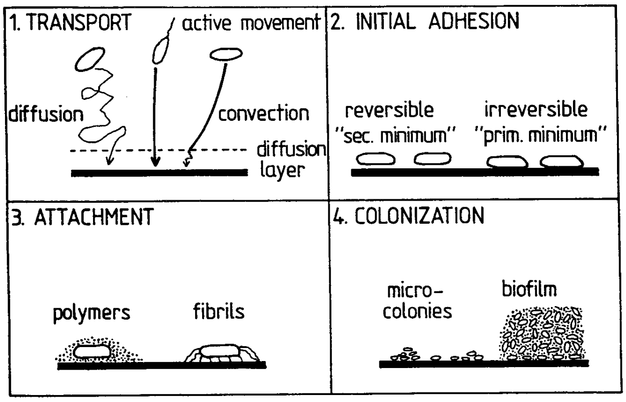

Figure 2. *Schematic presentation of the sequencing steps in the colonization of surfaces by microorganisms. (Reprinted with permission from ref. 25.)*

The mechanism described above considers the existence of the bacterial suspension as a living colloidal system. Consequently, the initial steps of adhesion are, in a first approximation, described by colloidal chemical theories such as the DLVO theory (reviewed by H.J. Butt *et al*.[29]), named after Derjaguin and Landau,[30] and Verwey and Overbeek.[31] They separately proposed that many interactions between small particles in aqueous solution could be explained by the interplay between two forces: the van Walls force (usually attractive) and the electrostatic double-layer force (usually repulsive). The electrostatic double-layer force arises because of surface charges at interfaces. The surface charge is balanced by dissolved particles which are attracted back to the surface by the electric field, but spread away from the surface to increase entropy. When the approaching surface charges have the same sign, the concentrations of ions between the surfaces always increases and results in a repulsive force.

G.E. Jr. Brown *et al*.[15] pointed out that the double layer of interest to chemists for modeling metal/aqueous solution interfaces is of the order of 0.4 nm and the overlying solvent region of interest may extend to 2 to 3 nm, while a single microbial cell layer is approximately 500 nm, 100-200 times thicker. This accompanied with the fact that single cells on the surface may extend from 1000 to 2000 nm in length, demands that bacterial layers and biofilms should be seriously considered in terms of interfacial chemistry. B.J. Little *et al*.[6] have also suggested that microorganisms are more complex than typical colloids as they are capable of independent locomotion, growth in different shapes, and production of extracellular polymeric materials that aid in anchoring the microbe to the surface. In addition, the theory based on the colloidal nature of microorganisms is not useful in understanding the adhesion of wild strains of bacteria in natural environments. According to J.R. Lawrence *et al*.,[12] this is because bacteria in natural environment are not regular spheres and rods, but are "hairy" cells whose actual surfaces are composed of carbohydrate (glycocalyx) and protein (pili and flagella) appendages, and because bacteria are capable of "sensing" the surface and responding by phenotypic change and by specific behaviors.

As long as 1913, many studies reported that the presence of a solid phase can influence a diversity of bacterial processes, for example, nitrogen fixation, alcohol oxidation, nitrification, and denitrification.[25] Although attachment to the mineral surface mediated by exopolymeric compounds was widely studied (e.g., leaching of sulphides), the nature of these compounds and their interactions with the mineral sulphide surfaces have received only limited attention.[32] The organic layer seems to be a kind of reaction space where all dissolution reactions occur, and a very thin exopolymer layer (perhaps from 10 up to 100 nm) is decisive in adhesion process. Cells of *T. ferrooxidans*, for instance, from which the extracellular polymers had been removed by centrifugation, needed several hours before attachment to pyrite to become detectable, whereas untreated cells started to adhere within the first hour.[33]

On the other hand, there are examples in the literature showing extracellular polysaccharide synthesis upon attachment of free-living cells to a surface.[34,35] For instance, P. Vandevivere *et al*.[34] reported that exopolymer production by attached cells (in continuous-flow sand-packed columns) was greater than that of free-living counterparts. When surface-grown cells were resuspended in fresh medium, exopolymer production decreased to the level of the unattached cells.

On the basis of available literature, one can say that there is a general agreement that surfaces do affect bacterial metabolism. These influences may be direct and indirect. To the former group belong changes in microbial activities directly resulting from the presence of a surface, e.g., changes in the structure and permeability of the membranes as an immediate consequence of the presence of a nearby surface. Indirect influences denote changes in cell activity due to: (1) changes in the composition of the medium, (2) the specific geometry and heterogeneity of the space near an adhered cell, and (3) the fact that the cells remain in a particular place when they colonize a surface. [25] Some of examples for indirect influences are changes in substrate availability, pH buffering, water activity, and so on.

5. Bacterial attachment and bioleaching

Biofilms are able to change significantly in the environment surrounding the ore surface to facilitate the dissolution or metal. These changes can be expressed in a number of ways. Characklis,[35] for instance, made the following classification of various effects of the biofilm on the interface and, consequently, on dissolution:

1. Influence of microbial activity on the substratum; in this respect, the influence is higher if the biofilm is patchy,
2. Influence of microbial metabolites on the substratum,
3. Alteration of the passage of charged entities through the polymer matrix of the biofilm,
4. Modification of the degree of conductivity of the polymer matrix,
5. Chelation of metal ions by the polymer matrix,
6. Drastic modification of the resistance to biocides (biocides are anti-microbial substances able to kill the microorganisms or inhibit their growth and reproductive cycle), and
7. Destabilization of corrosion inhibitors.

Microorganisms within the biofilm are capable of maintaining a solution that is significantly different from that of the bulk medium in terms of dissolved oxygen (DO), pH, or metabolic products. When these differences occur in the horizontal[36] dimension relative to the electrode surface, they can create active electrochemical cells due to the discontinuity formed in biofilm structure. On the other hand, the discontinuity in the vertical[36] dimension usually takes the form of gradients of nutrients and ions, influenced by the combined action of mass transfer into the biofilm and of microbial utilization within the biofilm. Here again, the amount of dissolved oxygen is the most important factor determining the conditions of an interface at which dissolution process occurs either aerobic or anaerobic.

The structural discontinuities within the biofilm and the obligate interdependencies characteristic of consortia represent another effect of dissolving biofilms. The degree of chemical solution modification near the biofilms is directly related to the biofilm substrate uptake rate. Experimental methods for determining biofilm reaction kinetics depend on two types of analyses: (1) chemical analysis of bulk water and (2) chemical measurements inside the biofilm using microsensors. According to Z. Lewandowski,[37] the second type of analysis is much better since the biofilms systems are diffusion limited, and chemical conditions near and inside biofilms can vary considerably over a distance of only a few micrometers. The kinetic parameters determined using microsensors (reaction rate, diffusivity, and half-saturation coefficient), evaluated at different locations, may be useful in understanding structural discontinuities within the biofilms.

6. Conclusion

The scientific study of biofilms and the identification of their major impacts on dissolution behavior of sulphides exposed to acidic environments require an interdisciplinary approach. The basic information on the interactions between the three components of the bioleaching process (mineral surface-electrolyte-microorganisms) comes from scientific disciplines such as electrochemistry, microbiology, and studies of microbial adhesion and biofilms. The latter aspect has become an intensive research area due to recent developments in microscopy techniques and chemical analysis of the biofilms by microsensors. These advances open new possibilities for reaching a better understanding of the complex bioleaching processes.

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WATER QUALITY TRENDS OF THE DANUBE RIVER IN SERBIA

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Abstract

This paper presents the results of the water quality of the Danube River in order to define the development tendency of water quality changes in watercourse in Serbia. Water quality is determined by the method of Serbian Water Quality Index (SWQI), using fund data of the Hydro-meteorological service of the Republic of Serbia for the period 2005 - 2009. Research shows that the average quality index was SWQI = 81 for the observed five-year period and to match the descriptive indicator of "good" water. Variations of the time series values of SWQI water quality index are expressed by a trend line which shows the average trend of water quality for a longer period of time. There was a growing trend of water quality stream of the Danube River in Serbia on the basis of these results.

Keywords: SWQI, water quality trends, the Danube River

1. Introduction

The Danube River is 2781 km long and has a basin of 817000 km^2. It connects the western and eastern Europe. The European blue highway through Serbia runs a length of 588 km and catchment area is 102,350 km2. On its course through Serbia, the Danube extends from the tri-border area of Serbia, Hungary and Croatia to the mouth of Timok, where the borders of Serbia, Bulgaria and Romania. Passes through vivid Vojvodina plain and national parks "Fruska worse" and "Iron Gate". In addition to natural wealth, there are numerous cultural and historical values that are dotted along its shores. The main tributaries of the Danube River in Serbia are the Tisza, the Sava, the Tamiš, the Morava, the Nera and the Timok [1].

Special attention must be given to the evaluation of the river Danube water quality, pollution problems and protection having in mind that it is one of the most valuable natural water resources in Serbia. Research analysis of the Danube River water quality is based on Data Fund of the RHMZ of Serbia for the period from 2005. to 2009. year in order to define the development tendency of water quality changes in watercourse in Serbia. The investigation includes sixteen hydrological measuring stations at given distances from the river mouth: 1. Bezdan – entry point – 1425.59 km; 2. Apatin – 1401 km; 3. Bogojevo – 1367.4 km; 4. Bačka Palanka – 1298.6 km; 5. Novi Sad – 1254.98 km; 6. Slankamen – 1215.5 km; 7. Čenta – 1189 km; 8. Zemun – 1174 km; 9. Pančevo – 1154.6 km; 10. Smederevo – 1116.0 km; 11. Banatska Palanka – 1076.6 km; 12. Veliko Gradište – 1059.2 km; 13. Dobra – 1021 km; 14. Tekija – 956.2 km; 15. Brza Palanka – 883.8 km; 16. Radujevac – exit point - 852 km [2].

The selected parameters show physical, chemical and microbiological characteristics of the water and all together they give a summary of the River Danube water quality by calculated value of SWQI index number.

2. Methodology

The Agency for Environmental Protection has developed an indicator of the environment for the area of water that is intended for reporting to the public, experts and decision makers (local government, state agencies). The indicator is based on the method of *Water Quality Index* (Scottish Development Department, Engineering Division, Edinburgh, 1976) according to which the ten parameters of physical-chemical and microbiological quality of aggregate in the composite indicator of surface water quality [3].

The method of *Water Quality Index* (WQI) of ten selected parameters (oxygen saturation, BOD5, ammonium ions, *pH* value, total nitrogen, orthophosphate, suspended matter, temperature, electrical conductivity and E. Coli) have the quality (q_i) represent the characteristics of surface waters by reducing them to an index number. The share of each of the ten parameters on the overall water quality has the same relative importance, because each of them won their weight (w_i) and the number of points to share in jeopardizing quality. Summing up the product $(q_i * w_i)$ get the index of 100 as the ideal sum of share the quality of all parameters. In the case of missing data on the quality of a parameter value measured arithmetic *WQI* corrected by multiplying the index with a value of $1/x$, where x is the arithmetic sum of the measured weight of available parameters [4].

The classification system of surface water quality description according to the Serbian Water Quality Index (SWQI) method represents a method for the evaluation of quality for a group of selected parameters, which means that by implementation of this method an overall evaluation of the surface water quality can be obtained.

SWQI indicators of the surface water quality were obtained by comparing the quality parameters according to Serbian classification with those of the original *WQ*I method. The adopted descriptive classification criteria of the descriptive quality indicators and the determination of the surface water class according to the calculated SWQI value are given in Table 1.

Table 1 Classification of surface waters according to the WQI method

WQI		**WQI**	**WQI**	**WQI**
85 - 84		74 - 69	56 - 44	51 - 35
100 - 90	89 - 84	83 -72	71 - 39	38-0
Excellent	***Very good***	***Good***	***Bad***	***Very bad***
Serbian Water Quality Index (SWQI)				

Indicators of the quality of surface waters are classified compatibility with existing classification according to their purpose and degree of purity:

- Excellent - water that in the natural state of the filtration and disinfection, can be used to supply water to settlements in the food industry, and surface water and the cultivation of precious fish species;
- Very good and good - the water in its natural state can be used for swimming and recreation of citizens for water, for breeding of other fish species (cyprinids), or that

the modern methods of treatment can be used to supply drinking water to villages and the food industry;
- Poor - water that can be used for irrigation, and after the modern methods of treatment and in industry, except food;
- Very poor - have the quality of water that adversely affects the environment, and can only be used after the use of special methods of treatment.

The numerical value of the water quality index is calculated by the software package: "Calculate your SWQI" of the Agency for Environmental Protection of Republic of Serbia [5].

3. Results and Disscusion

Water quality is determined by the method of Serbian Water Quality Index (SWQI), using fund data of the Hydro-meteorological service of the Republic of Serbia (RHMS) for the period 2005 - 2009. Main input parameters-data on water quality resulting from sampling performed generally once per month for relevant parameters, are used according to Serbian Water Quality Index methodology. Data gouped on a sampling site basis, averaged on a yearly level, resulting with a median SWQI of each sampling station are employed to create a synthesized quality indicator.

The regularity of the changes of the Danube water quality is obtained by the analysis of the given SWQI values in Table 2 for the period 2005-2009.

Table 2 - SWQI for the River Danube water quality for the period 2005-2009

Parameter (Unit)	**2005**	**2006**	**2007**	**2008**	**2009**
Temperature (°C)	13.4	13.5	14.4	14	14.2
pH	8.1	8.0	7.9	8.0	8.1
Conductivity (µS/cm)	392.8	439.7	395.4	401.0	394.1
Oxygen saturation (%)	92.1	97.2	93.9	92.8	95.8
BOD-5 (mg/l)	2.6	2.8	2.5	2.6	2.3
Suspended matter (mg/l)	34.7	25.9	24.5	28.9	23.1
Total Nitrogen (mg/l)	1.569	1.662	1.384	1.391	1.326
Orthophosphates (mg/l)	0.054	0.093	0.089	0.066	0.080
Ammonium (mg/l)	0.17	0.17	0.10	0.11	0.10
E. Coli (per 100ml)	6888	9918	5972	4629	6957
SWQI	**79**	**79**	**83**	**81**	**85**
Average SWQI	**81**				

The calculated SWQI value for each measuring point in period of 2005 – 2009 shows that the Danube quality along its course was in the range from 79 to 85, which corresponds to descriptive indicator "*good* " water. The lowest SWQI values were obtained in 2005 and 2006, while the highest SWQI value was in 2009. The average quality index for the observed five-year period is SWQI = 81. Poboljšanju kvaliteta vode doprinela je stagnacija industrijskih centara lociranih u slivu reke Dunav .

Graphically, the variations of SWQI values empirical series are expressed by a trend line which shows the average trend of water quality for a longer period of time. In Figure 2 given is the empirical series of SWQI values and linear fit with average quality trend of 81.4 and absolute growth for averge +1.4 SWQI index points for the quality of the River Danube water every year for the analyzed period.

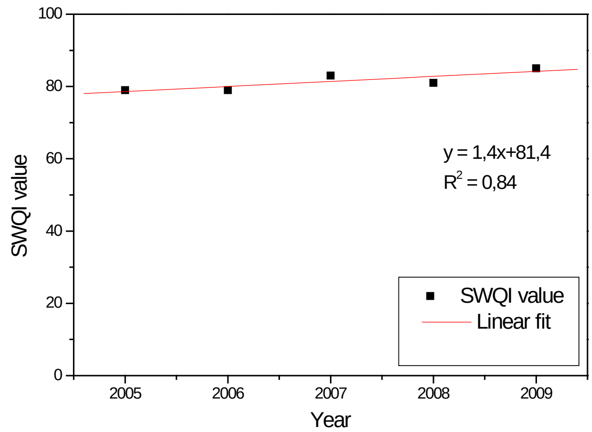

Figure 2 - Linear trend of the River Danube water quality expressed by SWQI method

The Danube quality determined by a median of an arranged series od SWQI average values at the measuring points in Serbia over a five-year period shows a quality growth.

4. Conclusions

The presented investigations show that by use of SWQI method a comprehensive evaluation of the Danube water quality can be obtained. Determination of water quality, using a single index number, is the simpler approach of comparing the measured individual indicators of water quality parameters with reference values. Variations of the time series values of SWQI water quality index show growing trend of the Danube River water quality in Serbia for a longer period of time.

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RANKING THE MOST CONTAMINATED PARTS OF RIVER TIMOK FROM ZAJEČAR TO ITS CONFLUENCE WITH THE DANUBE USING PROMETHEE/GAIA METHOD

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Abstract

This paper presents the results of multi criteria ranking of the most contaminated parts of river Timok from Zaječar to its confluence with the Danube, using PROMETHEE/GAIA method. Multi criteria ranking was done based on the content of useful and harmful parameters measured at nine measuring locations on the river Timok, from September to November 2010, within the project *The causes of water contamination and analysis of Timok basin from Zajecar to its confluence with the Danube*, which was financed by Ministry of Agriculture, Forestry and Water Management.

Keywords: river Timok, water contamination, multi criteria decision making, PROMETHEE/GAIA method

1. Intorduction

Timok is a river that flows through East Serbia and for the last 15 km forms the border between Serbia and Bulgaria. The river's mouth represents the northernmost point of Bulgaria, and is only 28 m above sea level, which makes it the lowest point of Serbia. It is a very branchy system of many shorter rivers, a large number of them have the same name (Timok) only clarified with adjectives. River Timok, also called Great Timok is created by merging White and Black Timok in Zaječar. Timok flows through the municipalities of Zaječar, Bor and Negotin. Timok runs through Zaječar and beyond, near the villages Veliki Izvor, Vražogrnac, Halovo, Šipikovo, Tamnič and others, it flows to the municipality of Negotin. In its middle course Timok has no major tributaries, but several smaller streams. The municipal and industrial wastewater empties into the river Timok.

According to water quality and considering the basic legal parameters, water of Timok basin belongs to all classes of water. Only the source parts of streams with a low flow in the most mountainous parts of the basin, where practically there is no settlement, belong to first class water. Other rivers and streams mostly belong to the second and third class of water [1], while Bor's river, as highly contaminated, cannot be categorized. During the low water levels and reduced flow in the summer, when there is not enough water to dilute the municipal and industrial waste water, water of second and third category become water of fourth category. This had far-reaching adverse effects on aquatic biosystem, the coast and water users along the coasts of Timok and rivers from which it emerged. Due to a high level of pollution from industrial waste water from Mining and Smelting Complex in Bor, Bor's river belongs to lifeless river flows.

For many years, the Institute of Public Health "Timok'', studied two dozen water samples per month from Timok basin. The analysis from that time showed high contamination of Bor's river by ions of heavy metals (Cu^{2+}, Zn^{2+}, Fe^{2+}, Pb^{2+}, Cd^{2+}, As^{3+} / As^{5+}, Sb^{3+}, ...) and suspended solids containing sulfides of these metals, which have been admitted to Timok. Furthermore, Bor's river is characteristic by reduced pH activity as a consequence of the presence of free sulfuric acid in the mine water, which through Krivelj river gets in Bor's river, and then in Timok.

In the last 15 years, the Institute of public health ''Timok'' stopped this monitoring, so the sampling and analysis are done only temporarily, for the needs and on demand of some polluters, which discharge their waste water in Timok basin. These investigations, through several samples a year, show that every investigated river from Timok basin (White Timok, Svrljig Timok, Bor's river, rivers in Brestovac and Lubnica) and Timok itself, doesn't belong to its class, defined by the rules on the categorization of water streams in Serbia. The parameters which are the most above prescribed limited concentrations are: ammonium ion, particulate solids, MPN, HPK, detergents, and for Bor's river heavy metals eather like ions or minerals (carbonates, hydroxides, sulfides), that can precipitate and become latent contaminants from the form of sediments, passing spontaneously in asoluble form.[2,3] The biggest polluters of this water are: RTB Bor [4], with its industrial and mine water, and water utilities from Bor, Knjaževac, Minićevo, Spa in Gamzigrad and Zaječar, which are discharged without any treatment in Bor's river or in Svrljiški, White and Black Timok. Beside them, there are numerous small, but not negligible contaminants, along the flow of these tributaries to Timok, so the current true state of the water quality of Timok basin can be determined only by re-introducing a monitoring process. Recent data of the water quality of Bor's river and its tributaries indicate that the pollution of heavy metals, sulfate ions and suspended particles are still present. During the last few years, the Republic Hydrometeorological Service (RHMS) performed monthly quality control of Timok's water, at two locations and also the water quality control of White and Black Timok before their merger.

Since the last few years, there was no analysis of water samples from Timok, at the profile downstream of Čokonjar to the mouth of Danube, the current water quality of Timok at this profile couldn't be determined. Therefore, project: *The causes of water contamination and analysis of Timok basin from Zajecar to its confluence with the Danube*, financed by the Ministry of Agriculture, Forestry and Water Management, enabled monitoring and analyzing the water quality of Timok at nine points. Based on the results of this monitoring significant information about the condition and quality of Timok was revealed.

Industrial waste water has a multiple negative impact on the environment, including water quality of Timok. The negative impact is even greater if we have in mind that the coast of Timok contains a large number of illegal dumps.

This effect is particularly pronounced in small tributaries, which often receive more waste water than its own water amount. Municipal landfills of smaller settlements are generally not safe, not sanitary ordered and mostly left to the impact of storm water, creating leachate that contaminates the surrounding soil. Municipal waste landfill of Zajecar is located near the village Halovo, on the banks of Timok. The landfill is not sanitary provided and is one of the serious environmental and urban problems and potential polluters of Timok's water.

Bearing in mind that this is about a waste water and materials different in composition, physico-chemical properties and different amounts, their effect on water quality in Timok basin is very different. Regarding this, the impact of waste water and deposited material on eco-system of Timok basin is expressed through three main segments of environment, through:

- pollution of surface and ground water, often active sources of drinking water;
- air pollution, and delivery of materials under the effects of wind;

- pollution of surrounding land and the seizure of land, useful for agriculture and urban needs.

Water sampling was done at measuring points that are shown in Figure 1. These are the following measuring points: M1 - Black Timok before the merger with White Timok (Zajecar), M2 - White Timok before the merger with Black Timok (Zajecar) M3 - Timok after the merger of White and Black Timok (Zajecar) M4 – Bor's river before flow into Timok (Vražogrnac) M5 - Timok before flow of Bor's river and landfill Halovo (Vražogrnac) M6 - Timok downstream of the landfill Halovo (Halovo) M7 - Timok at the village Tamnič (Tamnič); M8 - Timok after the flow of Sikolska river (Mokranje) and M9 - Timok before flowing into Danube (Srbovo).

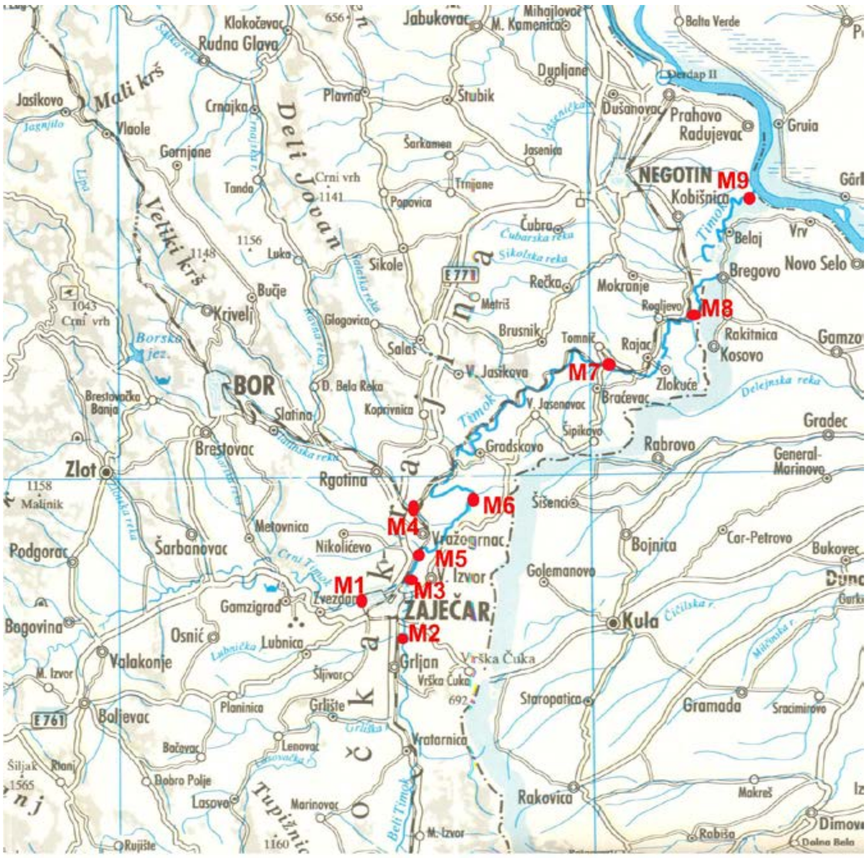

Figure 1 Measuring points at which samples of water and sediment were taken

The aim of this study was to use multi-criteria PROMETHEE / GAIA method, for ranking measuring points based on several criteria, simultaneously, taking into account the content of useful and harmful substances present in water samples.

2. Method used for data analysis

The method of Multi-Criteria Decision Making (MCDM) was chosen for ranking measuring points.[5] PROMETHEE method was used for ranking the measuring points, simultaneously taking into account the content of useful and harmful water constituents, where GAIA plane was used for graphical interpretation of PROMETHEE method. [6]

When applying this method it is necessary to define the appropriate preference function and assign weight factors to each criterion. Preference function is defined as a certain option ranked relative to each other, and the deviation between two parallel alternatives is translated into a single parameter that is related to the level of preference. The level of preference represents a growing preference function of deviation. If the deviation is small it is related to a weak preference, otherwise, if the deviation is large it represents a strong preference of the reference alternative. In PROMETHEE method the preference function can have six forms: Usual, U - shape, V-shape, Level, Linear, and Gaussian. Each form depends on two thresholds (Q, P). Indifference threshold (Q) is the largest deviation that decision maker considers irrelevant, while the preference threshold (P) represents the smallest deviation which is considered decisive for a decision maker, where P must not be less than Q. Gauss's threshold(s) represents the average value of thresholds of P and Q [5-10].

PROMETHEE method is based on a determination of positive (Φ^+) and negative flow (Φ^-) for each alternative considering ranking relations, in accordance with the obtained weights for each criterion. A positive flow of preferences shows how some alternative dominates over other alternatives, or if the positive flow has higher value ($\Phi^+ \rightarrow 1$) the alternative is more important. Negative flow of preferences shows how some alternative is preferred by other alternatives. The alternative is more significant if the value of negative flow is less ($\Phi^- \rightarrow 0$). Calculation of net-flow (ϕ) is used for complete ranking (PROMETHEE II). Net flow (ϕ) represents the difference between positive and negative flow of preferences: $\phi = \Phi^+ - \Phi^-$. An alternative that has the highest value of net flow is the best-ranked. [11]

3. The results of applied PROMETHEE/GAIA method

For multi-criteria ranking of measuring points by the quality of samples, water samples collected from nine measuring sites at Timok basin from Zajecar to the mouth of Danube, were correlated. $O_{2,r}$ was taken as useful parameter in multi-criteria analysis, while NH_4^+, NO_2^-, suspended solids, Cu^{2+}, Zn^{2+}, Pb^{2+}, Fe^{2+}/Fe^{3+}, Mn^{2+} and As^{3+}/As^{5+} were taken as harmful parameters. Table 1 presents the results of physico-chemical analysis of water samples by measuring points, whose ranking was done.

Considering that the data shown in Table 1 are quantitative, the selected preference function is a linear function, for all defined criteria, with indifference and preference thresholds (Q and P) in zones 5% and 30%, respectively.

Table 1. Physico-chemical composition of water samples ranked by measuring points

Alternative	**NH_4^+**	**NO_2^-**	**S.M.**	**$O_{2,r}$**	**Cu_2^+**	**Zn_2^+**	**Pb_2^+**	**Fe**	**Mn**	**As**
Max/min	Min	Min	Min	Max	Min	Min	Min	Min	Min	Min
Preference function	Linear	Linear	Linear	Linear	Linear	Linear	Linear	Linear	Linear	Linear
Indifference treshold (Q)	5 %	5 %	5 %	5 %	5 %	5 %	5 %	5 %	5 %	5 %
Preference treshold (P)	30 %	30 %	30 %	30 %	30 %	30 %	30 %	30 %	30 %	30 %
Measuring point	mg/l	mg/l	mg/l	mg/l	mg/l	mg/l	mg/l	mg/l	mg/l	mg/l
M1	1,560	0,043	7,467	0,733	0,005	0,049	0,018	0,074	0,012	0,002
M2	0,273	0,013	1,733	0,967	0,007	0,049	0,018	0,140	0,016	0,002
M3	0,783	0,100	20,533	0,233	0,004	0,049	0,018	0,069	0,028	0,002
M4	4,523	0,012	221,267	0,667	0,149	0,454	0,088	3,360	0,549	0,103
M5	0,747	0,123	14,200	0,133	0,006	0,049	0,018	0,115	0,106	0,003
M6	0,570	0,102	24,333	0,867	0,044	0,167	0,025	0,133	0,717	0,048
M7	0,607	0,301	9,000	1,200	0,122	0,052	0,019	0,371	0,402	0,002
M8	0,320	0,014	3,200	1,467	0,049	0,049	0,018	0,173	0,170	0,002
M9	0,320	0,079	8,800	1,567	0,080	0,049	0,018	0,346	0,213	0,002

The fact that all parameters don't have the same significance, or the same impact on water quality, was used for defining weight criteria (Table 2).

Table 2. Assigned weight coefficients

Element	Weight
NH_4^+	5.0%
NO_2^-	5.0%
S.M.	10.0%
$O_{2,r}$	10.0%
Cu_2^+	15.0%
Zn_2^+	10.0%
Pb_2^+	10.0%
Fe	15.0%
Mn	10.0%
As	10.0%
Σ=	100%

PROMETHEE ranking was done for defined scenario with the help of software package Decision Lab 2000. Based on data in Tables 1 and 2 the values of positive (Φ^+) and negative (Φ^-) flows were determined (Table 3).

Table 3. Preference net-flows for Scenario

Alternative	**Scenario**		
	Φ^+	**Φ^-**	**Φ**
M1	0,5458	0,1563	0,3895
M2	0,5842	0,1014	0,4828
M3	0,4833	0,2395	0,2438
M4	0,0905	0,8530	-0,7625
M5	0,4083	0,3667	0,0416
M6	0,1288	0,8132	-0,6844
M7	0,3111	0,3854	-0,0744
M8	0,4959	0,2096	0,2863
M9	0,3799	0,3026	0,0773

PROMETHEE II has performed complete ranking of measuring points from the best to the worst option for given criteria, for defined scenario (Figure 2). The results show that the least polluted measuring point is under number 2, while the most polluted measuring point is under the number 4.

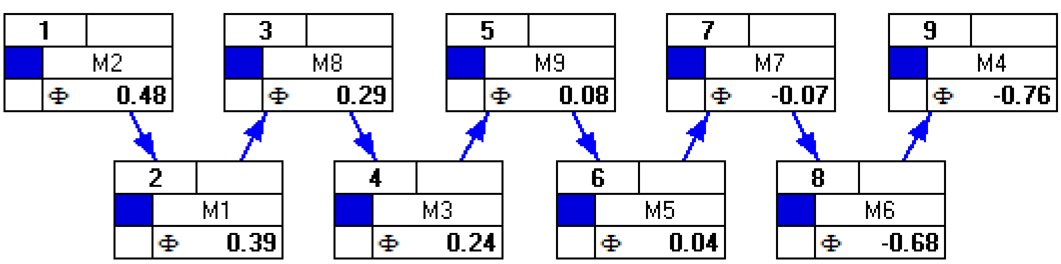

Figure 2. PROMETHEE II complete ranking of alternatives

To determine the robustness of preferential relations, an analysis of stability intervals was done, as shown in Table 4. This analysis enabled determination of stability intervals for each criterion, and those intervals define limitations within the values of weight coefficients of the given criterions, which could vary and jet not to have any influence to the result of PROMETHEE II ranking, but the change of weight could be made only by one criterion, while other relative weights remain the same. Based on relatively wide stability intervals, it can be concluded, that the final hierarchy of ranking doesn't change even when the weight coefficients vary within wide boundaries oflimitations.

Table 4. Stability weight intervals

Element	Weight	Scenario	
		min	max
NH_4^+	0.05	0,3642	12,7781
NO_2^-	0.05	1,0683	11,4383
S.M.	0.10	6,7897	31,5924
$O_{2,r}$	0.10	6,9384	18,1066
Cu^{2+}	0.15	3,2626	18,4671
Zn^{2+}	0.10	0,0000	Infinity
Pb^{2+}	0.10	0,0000	Infinity
Fe^{2+}/Fe^{3*}	0.15	2,2865	19,4325
Mn^{2+}	0.10	0,0000	17,7290
As^{3+}/As^{5+}	0.10	5,9191	23,2545

The GAIA plane was used in order to determine discriminating power of each criterion, aspects of correspondence and conflicts as well as the quality of each alternative by each criterion. Alternatives are presented by triangles and criteria by axes with square ends. Eccentric position of square of the criterion represents the volume of influence of that criterion, while correspondence between some criteria is defined by approximately the same direction of the axe of those criteria. Thus, for a defined scenario (Figure 3), it is possible to determine the agreement between the observed parameters. Furthermore, the alternative positions (triangles) determine the strength or weakness of alternative in relation to criteria. If it is in a direction of the axe of some criteria, the alternative is better by such criteria. Alternatives: 2, 1, 8, 3, 9 and 5 (Cluster A), for defined Scenario, are the best options because they are in a direction of pole decision *pi*, which defines compromising solution regarding weight criteria, while alternatives 4, 6 and 7 (Cluster B) represent the worst options, and these are the most polluted measuring points.

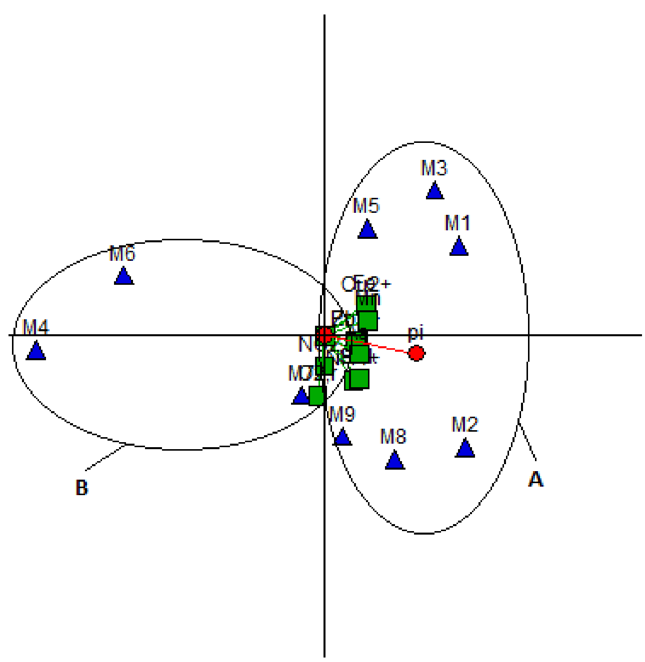

Figure 3. GAIA plane defined for Scenario

5. Conclusion

Multi-criteria ranking of measuring points, by the content of useful and harmful water constituents enabled determination of the least and most polluted places in Timok basin from Zajecar to the mouth of Danube. Results of application of PROMETHEE method can be further used as a starting point for implementation of adequate measures of rehabilitation of main pollutants in order to improve the quality of Timok.

Acknowledgement

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CONTROLLING THE REACTION FLOW OF THE BAUXITE LEACHING PROCESS IN THE BAYER INDUSTRIAL PROCESS

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Abstract

This paper presents the results of defining the mathematical model which can be used to predict the leaching degree of Al_2O_3 based on the parameters of the process in the Bayer technology of alumina production. Model describes the dependence of leaching degree of Al_2O_3 in bauxite from the most influential input parameters in industrial conditions of conducting the leaching process, which enables better control over one of the most crucial steps in the Bayer technology workflow. Mathematical model is defined using the stepwise MLRA method, with $R^2 = 0.764$ and significant statistical reliability – VIF < 2 and p < 0.05, on the one - year statistical sample. Validation of the acquired model was performed using the data from the following year, collected from the process conducted under industrial conditions, rendering the same statistical reliability, with $R^2 = 0.759$.

Keywords: Prediction; MLRA; Stepwise; Leaching; Bayer process

1. Introduction

Bayer's process of alumina extraction from bauxite is the dominant process for obtaining alumina for more than 100 years. Today, more than 90% of alumina production in the world is achieved by this process, despite the fact that alternative processes have been developed in the meantime.[1, 2]

Bayer process involves the leaching of bauxite with concentrated sodium aluminate solution at temperatures between 100^0 C and 250^0 C, depending on the mineralogical form of the aluminum in bauxite. Trihydrate bauxite type – gibbsite can be dissolved in caustic solution in the temperature range 100 – 180 ^{0}C. Monohydrate bauxite forms (boehmite and diaspore) are dissolved in the temperature ranges: 130 - 180 ^{0} C and 200 -250^0 C, respectively.[3] This process includes reactions with soluble silica compounds and titanium dioxide under certain conditions. [4]

Process parameters influencing the leaching rate and the degree of Al_2O_3 recovery are: mineralogical and chemical composition of the bauxite, granulation size distribution, caustic modules of the starting solution and its Na_2O (caustic) content, temperature of the leaching process, stirring speed and duration of the process.[5] The process of bauxite leaching, under industrial conditions of the Bayer technology for alumina production, is highly complex. The ability to predict the recovery of Al_2O_3 during leaching, as the result of modeling the input parameters of the process, presents a large advantage for management of the process. [4]

This paper presents the modeling of the leaching process of bauxite based on the results obtained under the industrial conditions, in order to predict the leaching degree of Al_2O_3 (process output) depending on the parameters of the process (process input). Obtained model presents a great advantage based on its ability to predict the accurate output of the investigated process.

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2. Experimental data

The database used in this work was created on the basis of data collected from the industrial production in the alumina factory Birač in Zvornik (Bosnia and Herzegovina), whose capacity is 600,000 t of alumina per year. The created database contains the chemical composition of bauxite: Al_2O_3, SiO_2, Fe_2O_3, TiO_2, CaO, roasting loss, H_2O; composition of the aluminate solution at the beginning of leaching process: Al_2O_3, Na_2O, caustic module at the beginning and the end of leaching, the chemical composition of autoclave residue: Al_2O_3, Na_2O_t, SiO_2, TiO_2, CaO, and the solution composition at the end of leaching process: Na_2O_k and Al_2O_3. A complete set of data for all of the leaching process indicators had been measured daily during 2008. and 2009. and used to create a database consisting of 659 series of data taken under consistent operating conditions of the factory.

The "Al_2O_3 leaching recovery" – Y term refers to the alumina recovery in the tube digestion process and was calculated using the following equation:

$$Y\ (Al_2O_3\ \text{leaching recovery}) = (1 - Al_2O_{3(am)} \cdot Fe_2O_{3(b)} / Al_2O_{3(b)} \cdot Fe_2O_{3(am)}) \cdot 100\ (\%) \qquad (1)$$

Where:
$Al_2O_{3\,(b)}$, $Fe_2O_{3(b)}$ - the contents of components in bauxite (%)
$Al_2O_{3(am)}$, $Fe_2O_{3\,(am)}$ - component contents in the autoclave residue (%).

Using the formula (1) to calculate the leaching degree of Al_2O_3 by the use of "inert'' Fe_2O_3 provides satisfactory results in industrial practice, with an accuracy of over 99%, which is why it is used in this study.

For the modeling of the dependence of Al_2O_3 leaching degree from bauxite - Y (process output) using established database, following technological parameters of the leaching process (process inputs) were used:

- X_1 - concentration of Na_2O_k in the leaching solution (g/l)
- X_2 - caustic ratio of the solution at the beginning of the leaching process
- X_3 - the moisture content of the bauxite (%)
- X_4 - The Al_2O_3 content in the bauxite (%)
- X_5 - The SiO_2 content in the bauxite (%)
- X_6 - The Fe_2O_3 content in the bauxite (%)
- X_7 - The TiO_2 content in the bauxite (%)
- X_8 - The CaO content in the bauxite (%)
- X_9 - roasting loss (%) and
- X_{10} - caustic ratio of the solution at the end of the leaching process.

During the studied period the database was generated from data measured during the industrial production in the factory Birač in Zvornik, where factory work was stable. At that time, as well as in the future period, processed bauxite mainly originated from the Vlasenica ore deposit (Bosnia and Herzegovina) which is of the bemite type. Leaching temperature throughout the whole period was constant and amounted to 245^o C, while pressure in autoclaves "reactors" amounted to 35 bar. Granulation of the bauxite in all cases after hydrocyclonic classification was 100% - 74 µm, and the ratio S : L = 1 : 5. Rotational speed of the mixers in the autoclaves was 31 rpm. In Table 1 the experimental results are presented in the form of descriptive statistics that were used for statistical modeling of process output-input dependence, i.e. Y = f (X_1 - X_{10}). A set of 300 data relates to the operation of the factory in 2008.

Table 1. Descriptive statistics for the input (X_1 - X_{10}) and the output (Y) of the bauxite leaching process in industrial process conditions for a set of 300 samples for 2008.

	N	Range	Minimum	Maximum	Mean		Std. Deviation	Variance
	Statistic	Statistic	Statistic	Statistic	Statistic	Std. Error	Statistic	Statistic
X_1	300	60.107	159.75	219.857	209.878	0.448	7.764	60.273
X_2	300	1.701	2.075	3.776	3.089	0.012	0.215	0.046
X_3	300	6.29	8.11	14.4	11.291	0.081	1.397	1.95
X_4	300	3.54	50.13	53.67	51.734	0.045	0.775	0.6
X_5	300	2.88	4.88	7.76	6.091	0.028	0.482	0.233
X_6	300	3.64	23	26.64	24.846	0.039	0.669	0.447
X_7	300	0.44	2.41	2.85	2.583	0.004	0.067	0.005
X_8	300	2.68	0.43	3.11	1.331	0.021	0.358	0.128
X_9	300	3.17	11.4	14.57	12.795	0.03	0.527	0.278
X_{10}	300	0.284	1.355	1.639	1.404	0.001	0.025	0.001
Y	300	7.658	81.713	89.371	85.273	0.078	1.343	1.803
Valid N (listwise)	300	60.107	159.75	219.857	209.878	0.448	7.764	60.273

The values of standard deviations in Table 1 show that there is a normal Gaussian distribution with certain parameters. On this basis it can be concluded that this dataset is suitable for statistical analysis with multilinear regression analysis (MLRA) technique. [5,6] If the satisfactory degree of fitting is not achieved then the methods of nonlinear regression analysis (NLRA) are used, including methods of artificial neural networks (ANNs). [7,8,9]

3. Statistical analysis

Forced-entry method was used to rank the influence of all predictors X_1 - X_{10} on the dependent variable Y, which in principle gives the possibility to define MLR dependence Y = f(X_1 - X_{10}), Table 2. The results indicate that the values of the variance inflation factor (VIF) are greater than two, indicating the existence of a larger share of collinearity among certain predictors. Also, the values of statistical significance ($p>0.05$) indicate that the method Forced – entry, in this case, does not provide statistically valid results.

Table 2. MLRA values for a set of 300 samples, using the Forced-entry method

Model		Unstandardized Coefficients		Stand. Coeff.	t	Sig.	Correlations			Collinearity Statistics	
		B	Std. Error	Beta			Zero-order	Partial	Part	Tolerance	VIF
1	(Constant)	46.440	17.063		2.722	0.007					
	X_1	-0.002	0.007	-0.012	-0.304	0.761	0.040	-0.018	-0.011	0.833	1.200
	X_2	0.421	0.310	0.068	1.357	0.176	0.441	0.080	0.051	0.561	1.782
	X_3	0.165	0.051	0.172	3.220	0.001	0.512	0.186	0.120	0.487	2.055
	X_4	0.446	0.182	0.257	2.451	0.015	0.527	0.143	0.091	0.126	7.934
	X_5	-0.980	0.214	-0.352	-4.575	0.000	-0.637	-0.260	-0.171	0.235	4.253
	X_6	0.070	0.194	0.035	0.359	0.720	-0.328	0.021	0.013	0.150	6.689
	X_7	0.863	0.826	0.043	1.045	0.297	0.304	0.061	0.039	0.816	1.226
	X_8	0.179	0.226	0.048	0.790	0.430	0.010	0.046	0.029	0.381	2.624
	X_9	0.627	0.215	0.246	2.913	0.004	0.341	0.169	0.109	0.195	5.133
	X_{10}	4.832	2.385	0.089	2.260	0.044	0.396	0.118	0.076	0.717	1.395

a. Dependent Variable: Y (%)

Since the Forced-entry method did not give a satisfactory result because it takes into consideration the impact of all predictors, it is useful to eliminate the impact of those predictors whose effect on output - Y is negligible. This fact requires the use of stepwise regression analysis method, which solves the problem of collinearity by basing the order of entry of predictors on a mathematical criterion of significance of impact of individual predictors.[9] Acquired results of the stepwise method are shown in Table 3. Now the values of VIF are less than two, and the statistical significance is $p<0.05$, indicating a satisfactory statistical reliability of results.

Table 3. MLRA values for a set of 300 samples, using the Stepwise method

Model	Unstandardized Coefficients		Stand. Coeff.	t	Sig.	Correlations			Collinearity Statistics	
	B	Std. Error	Beta			Zero-order	Partial	Part	Tolerance	VIF
1 (Constant)	96.076	0.760		126.456	0.000					
X_5	-1.774	0.124	-0.637	-14.264	0.000	-0.637	-0.637	-0.637	1.000	1.000
2 (Constant)	90.442	0.956		94.618	0.000					
X_5	-1.481	0.117	-0.532	-12.644	0.000	-0.637	-0.592	-0.508	0.912	1.096
X_3	0.341	0.040	0.355	8.432	0.000	0.512	0.439	0.339	0.912	1.096
3 (Constant)	102.689	2.489		41.262	0.000					
X_5	-1.540	0.113	-0.553	-13.662	0.000	-0.637	-0.622	-0.526	0.903	1.107
X_3	0.258	0.042	0.269	6.186	0.000	0.512	0.338	0.238	0.784	1.275
X_6	-0.441	0.083	-0.220	-5.292	0.000	-0.328	-0.294	-0.204	0.860	1.163
4 (Constant)	91.747	4.258		21.549	0.000					
X_5	-1.496	0.112	-0.537	-13.365	0.000	-0.637	-0.614	-0.507	0.889	1.124
X_3	0.218	0.043	0.226	5.045	0.000	0.512	0.282	0.191	0.714	1.401
X_6	-0.400	0.083	-0.199	-4.813	0.000	-0.328	-0.270	-0.182	0.839	1.193
X_{10}	7.206	2.292	0.133	3.144	0.002	0.396	0.180	0.119	0.803	1.246

a. Dependent Variable: Y (%)

Redundant predictors were eliminated through the four step iteration, and the dependence of output – Y of the most important predictors: X_3, X_5, X_6 and X_{10} is defined by the following dependence:

$$Y = 91.747 + 0.218X_3 - 1.496X_5 - 0.400X_6 + 7.206X_{10} \qquad (2)$$

Fig.1 shows dependence of Y measured = f (Y-calculated) with the coefficient of determination $R^2 = 0.560$.

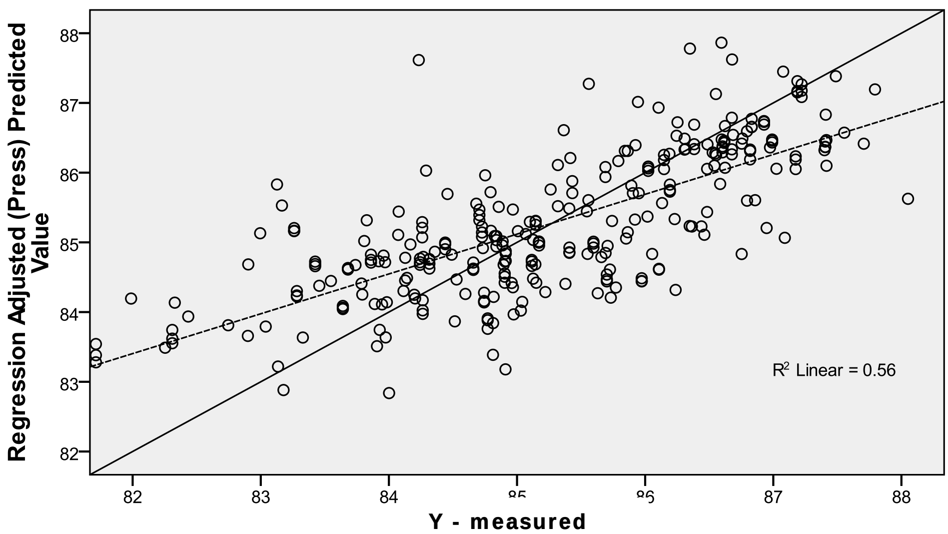
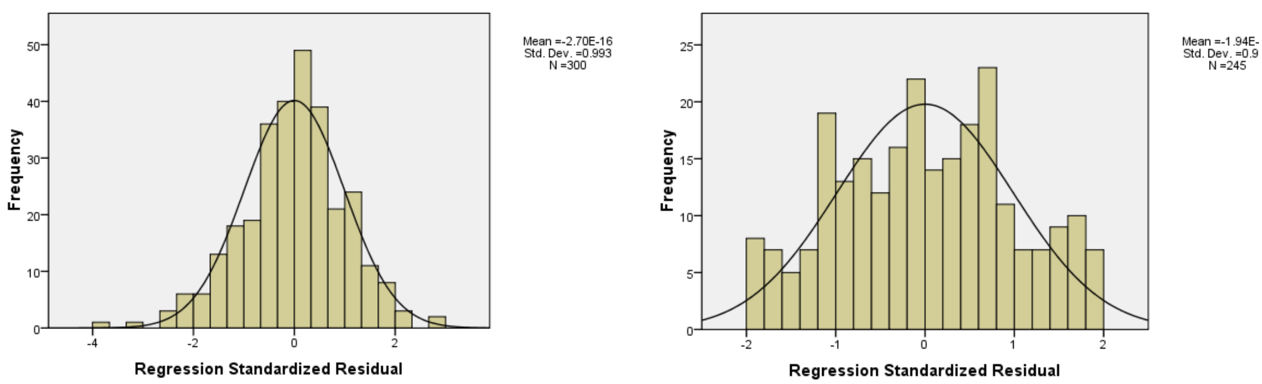


Figure 1 - Linear regression analysis of utilization of Al_2O_3 by equation (2) for the statistical sample of 300 elements

Since the value of $R^2 = 0.560$ is determined by the distribution of errors above 4σ, Fig.2.a, in the further statistical analysis of this empirical data set, reduction of the statistical sample was carried out by truncating the values which go beyond the 4σ boundaries. After ten iterations, 55 elements were discarded and the initial set was reduced to a set of 245 elements with distribution error within 4σ boundaries, and undisturbed statistical reliability Fig.2.b.



(a) (b)

Figure 2 - The distribution of errors for the initial statistical sample - 300 (a) and for the reduced statistical sample – 245 (b)

With the reduced statistical sample of 245 elements within the error limits of 4σ, MLRA was performed with the stepwise method, and the results are shown in Table 4.

Table 4. Results for the MLRA for reduced sample of 245 elements, using the Stepwise method.

Model		Unstandard. Coeff.		Stand. Coeff.			Correlations			Collin. Stat.	
		B	Std. Error	Beta	t	Sig.	Zero-order	Partial	Part	Tolerance	VIF
1	(Constant)	96.212	0.712		135.103	0.000					
	X_5	-1.776	0.117	-0.696	-15.120	0.000	-0.696	-0.696	-0.696	1.000	1.000
2	(Constant)	90.717	0.740		122.557	0.000					
	X_5	-1.544	0.096	-0.605	-16.036	0.000	-0.696	-0.718	-0.592	0.957	1.045
	X_3	0.359	0.031	0.440	11.664	0.000	0.565	0.600	0.431	0.957	1.045
3	(Constant)	102.005	1.856		54.958	0.000					
	X_5	-1.576	0.089	-0.618	-17.699	0.000	-0.696	-0.752	-0.603	0.954	1.048
	X_3	0.278	0.031	0.341	8.983	0.000	0.565	0.501	0.306	0.805	1.241
	X_6	-0.409	0.063	-0.243	-6.541	0.000	-0.398	-0.388	-0.223	0.841	1.190
4	(Constant)	105.367	1.892		55.682	0.000					
	X_5	-1.626	0.085	-0.637	-19.022	0.000	-0.696	-0.775	-0.618	0.941	1.062
	X_3	0.245	0.030	0.300	8.085	0.000	0.565	0.463	0.263	0.766	1.305
	X_6	-0.487	0.062	-0.289	-7.900	0.000	-0.398	-0.454	-0.257	0.788	1.270
	X_8	-0.551	0.110	-0.170	-5.014	0.000	-0.104	-0.308	-0.163	0.916	1.091
5	(Constant)	93.638	2.996		31.259	0.000					
	X_5	-1.553	0.083	-0.609	-18.711	0.000	-0.696	-0.771	-0.581	0.911	1.098
	X_3	0.193	0.031	0.237	6.271	0.000	0.565	0.376	0.195	0.676	1.478
	X_6	-0.447	0.059	-0.265	-7.512	0.000	-0.398	-0.437	-0.233	0.773	1.294
	X_8	-0.548	0.105	-0.169	-5.214	0.000	-0.104	-0.320	-0.162	0.916	1.091
	X_{10}	7.740	1.576	0.175	4.910	0.000	0.507	0.303	0.152	0.757	1.320
6	(Constant)	92.847	2.963		31.334	0.000					
	X_5	-1.521	0.082	-0.596	-18.442	0.000	-0.696	-0.767	-0.564	0.895	1.118
	X_3	0.154	0.033	0.189	4.664	0.000	0.565	0.289	0.143	0.567	1.764
	X_6	-0.424	0.059	-0.252	-7.175	0.000	-0.398	-0.422	-0.219	0.759	1.318
	X_8	-0.518	0.104	-0.160	-4.979	0.000	-0.104	-0.307	-0.152	0.907	1.102
	X_{10}	6.755	1.590	0.153	4.249	0.000	0.507	0.266	0.130	0.723	1.384
	X_2	0.587	0.203	0.114	2.891	0.004	0.533	0.184	0.088	0.600	1.667

Obtained results presented in Table 4 show statistical correctness in all cases because $VIF<2$ and $p<0.05$. It should be noted that the number of predictors in this case compared to the previous (sample of 300 elements) increased from 4 to 6, with an increase in R^2 from 0.560 to 0.764. MLRA gives the following form of linear dependence of $Y = f(X_i)$:

$$Y = 92.847 - 0.587X_2 + 0.154X_3 - 1.521X_5 - 0.424X_6 - 0.518.X_8 + 6.755X_{10} \quad (3)$$

Fig.3. shows the dependence of the measured and calculated values for Y given by the equation (3) for reduced statistical sample of 245 elements.

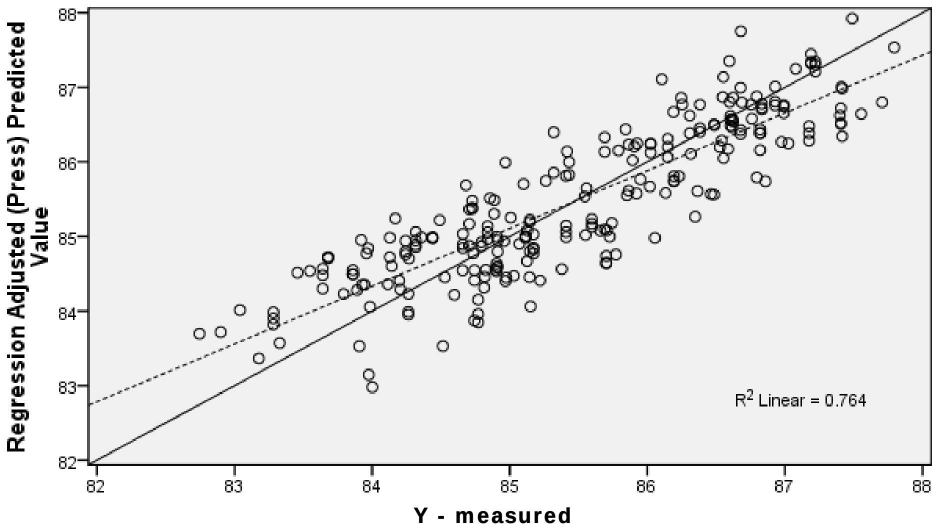


Figure 3 - Y (calculated) = f(Y - measured) for a reduced statistical sample of 245 elements

Model defined in this way, given by the equation (3), has a satisfactory value ofR^2 = 0.746, and it can be useful for the prediction of the leaching degree of Al_2O_3 if values of the predictors are known: caustic module of the initial aluminate solution, the moisture content of bauxite, the content of SiO_2 in the bauxite, the content of Fe_2O_3 in the bauxite, the CaO content in the bauxite and caustic ratio at the end of the leaching process. Parameters which have positive influence on the degree of leaching of Al_2O_3 from the bauxite are: caustic module of aluminate solution at the end of the leaching process and the moisture content of bauxite, while following parameters have negative influence (in descending order): SiO_2 content in the bauxite, caustic module of aluminate solution at the beginning of the process, CaO content in the bauxite and content of Fe_2O_3 in the bauxite.

Validation of the mathematical model given by the equation (3) was carried out through its application to data obtained in regular production during the following 2009. using the statistical set of 330 measurements. The results of defined model validation are shown in Fig.4 with a value of R^2 = 0.759 which is very close to the value determined in the phase of defining the model (training phase) which was 0.764.

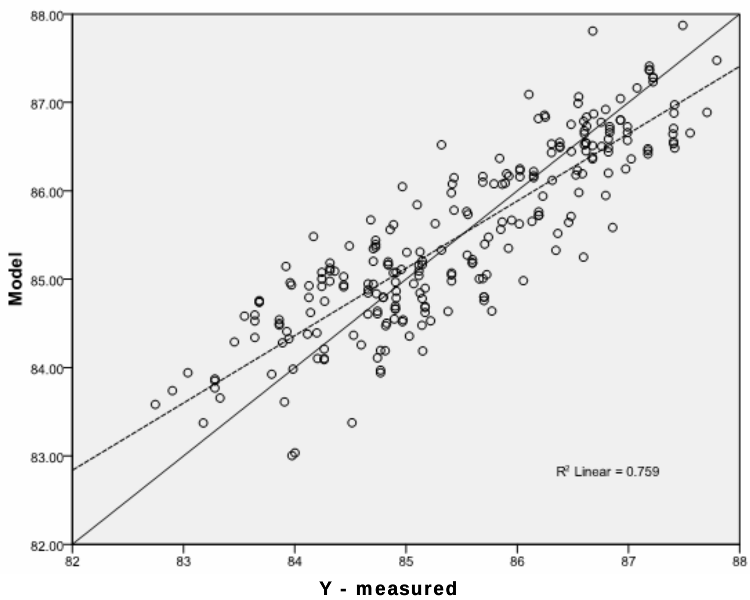


Figure 4. Validation of the model (3) on a sample of 330 measurements in regular industrial production in 2009.

The results of defined linear model validation for the prediction of the degree of leaching of Al_2O_3 from the bauxite, in industrial conditions of the Bayer process, in alumina plant BIRAČ in Zvornik, consistently describes 75.9% of the Y variation, depending on the mentioned predictors - the inputs of the process.

4. Conclusion

Stepwise MLRA method was used to define a mathematical model for the dependence of the leaching degree of Al_2O_3 from the bauxite in industrial conditions of Bayer alumina process for the conditions in the alumina factory Birač in Zvornik. Defined linear dependence of the degree of leaching of Al_2O_3 from: caustic ratio of the aluminate solution at the beginning and end of the leaching process, the SiO_2, Fe_2O_3, CaO and moisture contents in the bauxite, having a value of R^2 = 0.764 in the stage of defining the model and 0.759 in the model validation phase, indicates the satisfactory degree of fitting of the obtained results.

Further research, aiming to increase the value of R^2, should be focused on applying some of the non-linear regression methods, among which special attention should be paid to the possibility for utilizing the artificial neural networks (ANNs) which, in similar systems, provide much larger values for R^2.[10,11]

Acknowledgements

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EXAMPLES OF LCA METHODOLOGY IMPLEMENTATION IN STEEL INDUSTRY

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Abstract

Steel industry kept pace with actual trends for environmental protection in many ways – through different technological improvements considering environment protection, important share of recycling in the steel production, design of so called eco-steels, materials designed according to recent environmental directives and legislatives, etc. In the frame of steel production monitoring, LCA methodology is very important to obtain an accurate environmental picture of a process, due to the fact that the process should be evaluated over its entire life cycle. A number of tools and methodologies have been developed in recent years to assess the potential environmental impacts associated with a product, process or activity during its entire life cycle. The examples of Life Cycle Assessment (LCA) use by large steel industrial companies as potentially helpful tool for improving the production processes, efficiency of resource utilization and significantly reduction of waste generation and emissions are presented in this paper.

Keywords: steel industry, Life Cycle Assessment (LCA), environmental protection

1. Preface

At the beginning of the 21st Century it is thought to be very hard for the world economy to continue developing. Iron and steel are two of the most popular materials on the Earth and will remain so in future. Therefore, the development of such materials into an eco-material will greatly affect both issues - resources and environment. In producing iron and steel, a lot of resources such as electricity, water, fossil fuels, iron ore, limestone, refractories and metallic elements like molybdenum, cobalt, vanadium, niobium, nickel, chromium, zinc, aluminum, manganese and silicon are consumed, and further technological progress and development is required to save resources and energy from a viewpoint of ongoing depletion of resources [1].

Steel production is an energy- and CO_2 - intesive activity, as much of the production process takes place at high temperatures. Besides, iron ore is converted in metallic iron by using carbon as reducing agent. As global warming due to CO_2-emissions is considered one of today's main environmental problems, publications about the environmental impact of steel production mainly focus on reduction of energy use. For example, ArchelorMittal Gent decreased its energy use from 25 GJ/ton hot rolled coil in 1980 to 17,9 GJ/ton in 2005. The reduction of specific energy demand is the result of important process-integrated measures such as the switch from ingot casting to continuous casting (realised during 1989-1996), the reduction of material losses in the various production steps, as well as of good company management practices. Next to CO_2, large industrial steelworks also emit pollutants that may have other environmental impacts [2].

Steel, as a construction material, provides many beneficial and essential services to society. However the processes linked to the production, transportation, use, maintenance, deconstruction, reuse, recycling and ultimate disposal of steel construction products contribute to the global environmental pressures being exerted on our planet. It is essential to understand how, where and why these environmental impacts occur and to quantify them. This will allow strategies to be implemented so that steel can continue to provide benefits to society but at a reduced or acceptable environmental cost. LCA is increasingly gaining acceptance as the most useful and relevant decision-support tool when assessing the environmental impacts of the built environment [3].

To obtain an accurate environmental picture of a process, it is essential that the process will be evaluated over its entire life cycle. A number of tools and methodologies have been developed in recent years to assess the potential environmental impacts associated with a product, process or activity during its entire life cycle. Life Cycle Assessment (LCA) is one such tool, and is sometimes referred to as “cradle-to-grave” analysis.

2. Life cycle assessment method – implementation in steel industry

LCA is an environmental assessment method for evaluation of impacts that a product, process or technology has on the environment over the entire period of its life – from the extraction of the raw material through the manufacturing, packaging and marketing processes, the use, re-use and product or technology maintenance, to its eventual recycling or disposal as waste at the end of its useful life. LCA can assist steel plants in the environmental management. LCA is a method of the evaluation of environmental aspects and potential impacts associated with all stages of the life of product, process and technology. The LCA method consists of four phases defined by the Society of Environmental Toxicology and Chemistry (SETAC) and more recently by the International Standards Organization (ISO):

1. **Goal Definition and Scoping** lays out the rationalization for conducting the LCA and its general intent, as well as specifying the product systems and data categories to be studied.
2. **Life-Cycle Inventory** (LCI) involves the quantification of raw material and fuel inputs, and solid, liquid, and gaseous emissions and effluents.
3. **Life-Cycle Impact Assessment** (LCIA) characterizes the environmental burdens identified in the LCI and assesses their effects on human and ecological health, as well as other abiotic effects, such as smog formation and global warming.
4. **Improvement Assessment or Interpretation of Results** uses findings from the analysis to identify and evaluate opportunities for reducing life-cycle environmental impacts of a product, process, or activity, or to reach conclusions and provide recommendations.

LCA evaluates the life-cycle environmental impacts from each of five major life-cycle stages: raw materials extraction/acquisition, materials processing, product manufacture, product use, and final disposition/end-of-life. Figure 1. shows the steel life cycle.

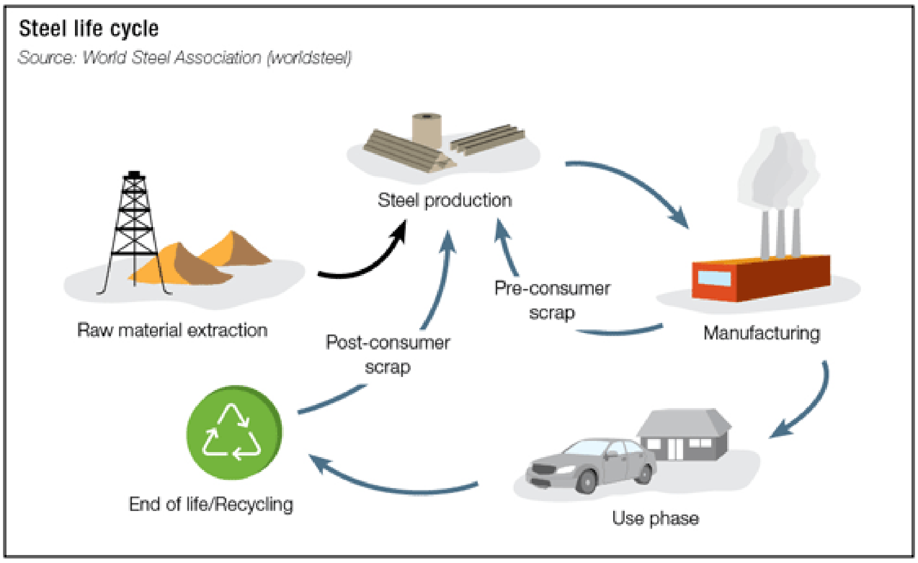

Figure 1. Steel life cycle

World Steel Association leads perform of LCA analyses in the metallurgical sector. Life Cycle Assessment (LCA) is undertaken as the most holistic approach for evaluation environmental impact and selecting new technologies to reduce emissions for iron and steel industry.

3. Examples of LCA implementation in steel industry

LCA methodology is being used by large industrial companies as potentially helpfull tool for improving the production processes, efficiency of resource utilization and significant reduce of waste generation and emissions.

3.1.Nippon Steel Corporation

Steel can contribute to the environment from the standpoints of steel manufacture and products in the following four main stages:

1. steel manufacture (from raw materials to finshed steel products)
2. fabrication and assembly of final products using steel
3. use of final products
4. scrapping or recycling for reuse.

The first stage is concerned with the steel manufacturing process itself. It is essential to establish steel production processes with small energy and low environmental loads, or eco-processes. The steel industry is a large energy consumer. Two successive oil crisis in the 1980's prompted the Japanese steel industry to implement positive energy-saving measures. Japanese steel production is one of the most energy-efficient processes in the world now [4].

The second stage is concerned with the contribution to the manufacturing processes of customers using steel. The user can improve or reduce its environmental load by using a given type of steel. For example, the use of appropriate steel helps the customer to enhance manufacturing efficiency in its fabrication process, eliminate some of its fabrication steps, or simplify its fabrication process itself.

The third stage is concerned with contribution to the environment when end products made by using steel are actually used. For example, better steel products contribute to the fuel mileage improvement of automobiles and the efficiency enhancement of motors.

In the fourth stage, the used products are scrapped or recycled for reuse. In this stage, steel scraps are returned to the steel industry, normally. In the stages after the second stage, steel products contribute to the environment when they are utilized as commercial products by customers and end users. These steel products can be called environmentally conscious steel products or eco-steel products [5].

3.2. LCA of automobiles and steel

In considering the LCA of automobiles, the energy consumption concerned can be roughly divided into two areas: one for the manufacturing of the vehicles; and the other for driving them. For the lifetime energy consumption for passenger cars, energy for motion accounts for 75-80%, while the percentage for material energy is only 15-20%. It is evident from this that priority should be given to the development of materials to reduce the vehicle weight for the purpose of energy consumption for producing motion rather than pursuing reduction of the energy consumption for manufacturing materials. The ratio of each material for passenger cars 2000cc class, in terms of weight, accounts for 75% of all the materials for passenger cars. Although steel products, used to ensure safety of automobiles, cannot be reduced, if the strength of hightensile steel can be improved, the weight of the steel products used can be decreased, thereby enabling contribution to improving fuel economy for producing motion [6,7].

As for the relationship between vehicle weight and fuel economy of Japanese, a 10% decrease in the vehicle weight corresponds to a 10-12% improvement in fuel economy. Present passenger cars have achieved some 5% decrease in weight by the use of high-tensile steel, compared with those in and around 1970. Furthermore, in the future, nearly 10% reduction in weight is expected by increasing the use ratio of high-tensile steel.

As refining technologies improve and advance, steel products become purer, resulting in the improvement of corrosion resistance. It is well known, for instance, that ferritic stainless steel corrosion resistance is improved sharply when its carbon plus nitrogen content is reduced to 100 ppm or less. Recently, this knowledge has been applied in Japan. In addition, recently surface-treated steel sheets for automobiles that remain corrosion resistant for 10 years of service have been developed.

3.3. LCA between a steel-framed house and a conventional wooden structure

The iron and steel industry has just launched a drive to promote steel-framed houses. At a recent academic meeting, the results of a study carried out at a correlative iron-making course at Tokyo University on the comparison of the carbon dioxide emission in terms of LCA between a steel-framed house and a conventional wooden structure were reported. Metaphorically, steel products are masses of energy. This means that the emission of carbon dioxide in building a steel-framed house is greater than that of a wooden house. However, when viewed by the method of disposal at the end of their service life the wooden house is burned and produces carbon dioxide, while the CO2 emission from the steel-framed house can be held to one-quarter of the wooden house's as the waste steels are scrapped and recycled. Furthermore, when the longer service life of the steel framed house is taken into account, the results obtained show that the total carbon dioxide emission from the steel-framed house is reduced to as low as some 20% of that of the wooden house.

3.4. CSIRO Minerals

A Life Cycle Assessment (LCA) of stainless steel production, including that of the nickel, ferronickel, ferrochromium and iron feedstocks was carried out using inventory data derived from the literature. The environmental impact categories considered in the study were Global Warming Potential (GWP), Acidification Potential (AP) and total (or full cycle) energy consumption. The effects of different sources of electricity (black coal, natural gas and hydroelectricity) were also examined in the study.

While other environmental impact categories are also important in LCA studies, the data necessary to evaluate these impact categories are often not available in the literature. In the case of toxicity impact categories (human toxicity and eco-toxicity), there are also concerns that even when such data are available, they do not truly reflect what occurs in the environment [8].

The functional unit for the study was 1 kg of refined stainless steel, with all impacts being expressed per kg of refined stainless steel.

The following processing routes were considered in the LCA study:

- iron and steel production by the integrated steel route (Blast Furnace and Basic Oxygen Furnace)
- nickel metal production by flash smelting and Sherritt-Gordon refining
- ferrochromium and ferronickel production by the rotary kiln/arc furnace process
- stainless steel production by the electric arc furnace/argon-oxygen decarburization (EAF-AOD) process

The feedstocks to each process and their compositions as used in the LCA study are given in Table 1.

Table 1. Processes and feedstocks included in LCA study

Metal	Feedstock		Process
Iron/steel	Iron ore	(64% Fe)	Blast furnace & Basic Oxygen furnace
Nickel	Sulphide ore	(2.3% Ni)	Flash smelting & Sherritt-Gordon refining
Ferrochromium	Chromite ore	(27.0% Cr, 17.4% Fe)	Pelletising/sintering/pre-reduction/ submerged arc furnace
Ferronickel	Laterite ore	(2.4% Ni, 13.4% Fe)	Rotary kiln / electric furnace
Stainless steel	Pig iron	(94% Fe, 4.4% C)	Electric arc furnace / argon oxygen decarburization
	Ferrochromium	(55% Cr, 30% Fe)	
	Ferronickel	(23% Ni, 69% Fe)	
	Nickel	(100% Ni)	

Stainless steels are typically produced by a two-stage process. Raw materials (including scrap) are melted together in an electric arc furnace, with the composition of the molten metal used corresponding approximately to that of the desired steel product, apart from the carbon content. The molten metal is then transferred to a refining vessel (most commonly an argon-oxygen decarburization (AOD) vessel) which reduces the impurities (especially the carbon content) to the low levels required in the final product.

A schematic flowsheet of stainless steel production by the electric furnace- argon/oxygen decarburization (EAF-AOD) process is shown in Figure 2. The compositions of the various metal inputs into this process given in Table 1 were used to estimate the required amounts of the various metal inputs to produce 304 stainless steel (which accounts for more than 50% of all stainless steels produced) with a composition of 68.6% Fe, 19.0% Cr, 9.3% Ni and 0.08% C.

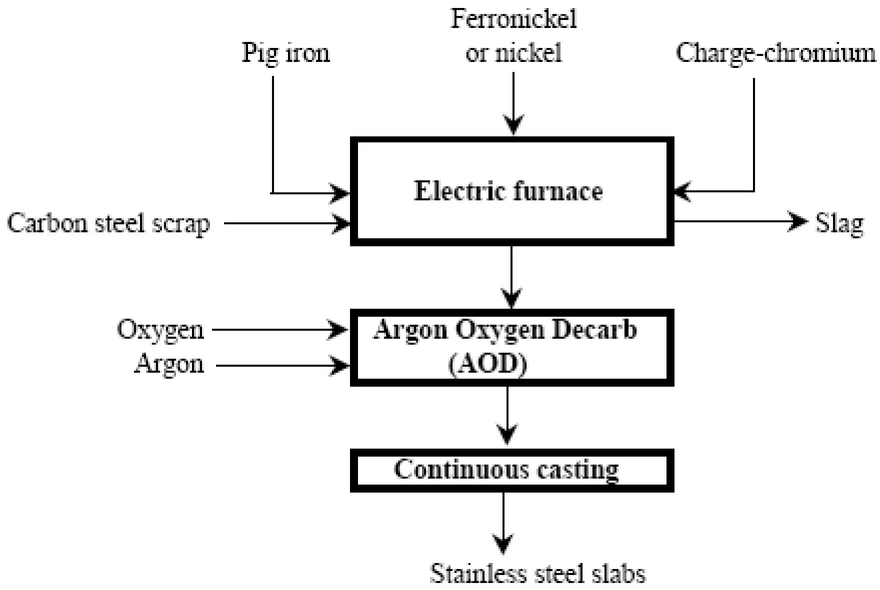

Figure 2. Schematic flowsheet of stainless steel production

Individual LCA spreadsheet models of the various metal production processes outlined in Table 1 were set up using the CSIRO Minerals in-house LCA software LCA-PRO (Excel-based). The relevant inventory data were incorporated into the respective models and the results generated by the models are summarised in Table 2.

Table 2. LCA results for stainless steel production

Environmental impact	Feedstock materials for stainless steel production				304 Stainless steel	
	Iron	Nickel	Ferrochrome	Ferronickel	From nickel	From ferronickel
Total energy (MJ/kg)	22	114	56	110	49	75
Gaseous emissions						
CO_2 (kg/kg)	2.0	11.1	5.1	8.9	4.8	6.6
CO (g/kg)	1.9	2.9	5.4	5.6	3.4	4.7
N_2O (g/kg)	0.02	0.05	0.06	0.07	0.04	0.06
CH_4 (g/kg)	2.6	16.6	6.2	18.4	6.0	10.8
NOx (g/kg)	12.6	44.6	29.6	70.6	24.8	44.1
NMVOC ** (g/kg)	0.20	2.7	0.17	1.6	0.4	0.8
SO_2 (kg/kg)	0.007	0.107	0.018	0.026	0.022	0.020
GWP (kg CO_2e/kg)	2.1	11.4	5.3	9.3	4.9	6.8
AP (kg SO_2e/kg)	0.015	0.138	0.039	0.075	0.039	0.051

** Non-Methane Volatile Organic Compounds

The results of the LCA showed that when ferronickel is used as the nickel source, the total energy consumption for stainless steel production is approximately 50% higher than when nickel metal is used as the nickel source (75 MJ/kg cf. 49 MJ/kg). This result comes about largely because the Fe units in ferronickel have a much higher energy intensity than do the Fe units in pig iron, and the greater the use of the former at the expense of the latter, the greater is the total energy consumption.

The results also showed that the production of ferronickel made by far the largest contribution (59%) to the total energy consumption for stainless steel production when this feedstock is used as the nickel source, but when nickel metal is used as the nickel source the contributions of the various stages are more evenly distributed. It was also observed that the electricity consumption of the electric furnaces used in the production of ferronickel, ferrochromium and stainless steel contributed approximately 50% to the total energy consumed in stainless steel production. Given the relatively low efficiencies associated with electrical power generation, significant reductions in the total energy of stainless steel production could be anticipated if more direct use of thermal energy was made in the ferronickel, ferrochromium and/or stainless steel smelting stages, for example by utilising bath smelting processes.

The energy intensity of stainless steel production relative to the production of a number of other metals is shown in Figure 3. where the results from this LCA study are compared with the results from previous LCA studies by the authors [9-11].

It can be seen from this figure that the energy intensity of stainless steel is comparable with that for copper and zinc, lower than that for aluminium and nickel, but higher than that for steel and lead. Toxicity concerns often associated with copper and lead and the generally shorter life span of steel compared to stainless steel due to its lower corrosion resistance, means that when all three factors (energy intensity, toxicity and lifespan) are considered together, stainless steel is probably the most suitable candidate of all the metals shown in Figure 2. for meeting sustainable development goals.

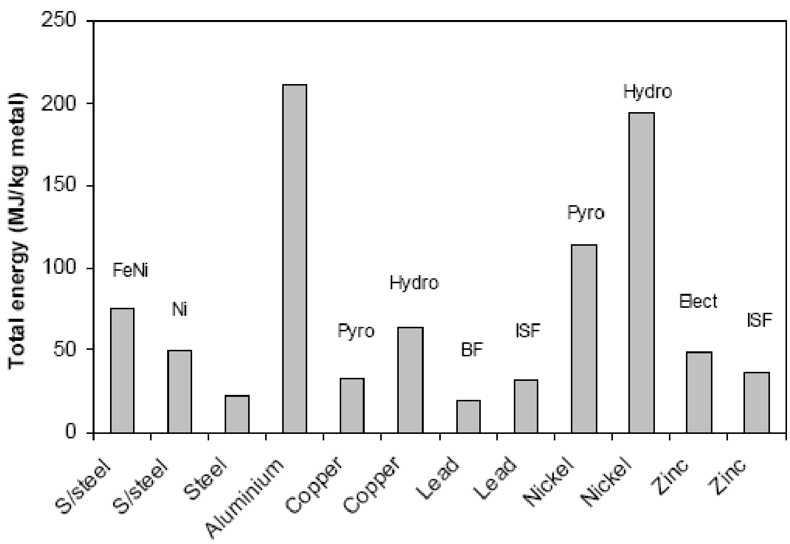

Figure 3. Total energy consumption for stainless steel production compared to other metals

The energy intensity of the pyrometallurgical processes in Figure 3. can potentially be reduced in a number of ways, including:

- eliminating the need to reheat the feed materials into the process
- recovering the thermal energy contained in the slag products and utilising this energy within the process.

Using the stainless steel LCA model in conjunction with process simulation software, it was estimated that 1,4 MJ/kg stainless steel (400 kWh/t) would be saved by removing the need to reheat the feed materials shown in Figure 2. This saving constitutes two-thirds of the electricity input, with the total energy consumption and GWP being reduced by approximately 6% to 71 MJ/kg and 6,4 CO_2 e/kg respectively (with ferronickel feedstock), bearing in mind the electricity generation efficiency of 35% [12]

If the energy intensity of stainless steel production relative to the other metals in Figure 3. could be reduced even further, it would enhance stainless steel's attractiveness from a sustainable development viewpoint. As mentioned earlier, this may be possible by more direct use of thermal energy in the smelting stages used to produce the various metallic feedstocks. Work is currently in progress at CSIRO Minerals to investigate the use of bath smelting processes for more direct routes to stainless steel.

3.5. ArcelorMittal Gent

ArcelorMittal Gent with a production capacity of 5 $\cdot 10^6$ ton of steel per year, it is one of the major production sites of the ArcelorMittal Group, which is the largest steel producer in the world. ArcelorMittal Gent represents a fully integrated steelwork, meaning that every step of the production process, from the supply of raw materials to the production of finished products such as coated steel sheets and laser-welded blanks, takes place on site.

By using LCA method, a detailed evaluation of the evolution of the environmental impact of the ArcelorMittal Gent site was done.

In order to evaluate the evolution of the environmental impact of ArcelorMittal Gent over the period 1995–2005, six partial ecoefficiency indicators or ''eco-intensities'' taking into account the evolution in production were proposed.

For the impact category acidification, the eco-efficiency improved between 1995 and 2005 with 45% as a result of improved production efficiency and by a number of process-integrated measures.

The impact of emissions contributing to photo-oxidant formation was 4% lower in 2005 than in 1995, despite a relative increase in own sinter production (which is the main source of photo-oxidants).

The partial eco-efficiency indicator for emissions to air contributing to human toxicity decreased with 52% between 1998 and 2005 (1998 was chosen as reference year for this theme, since for 1995 and 1996 there exists no accurate emission data for some pollutants). This decrease is the result of both process-integrated and end-of-pipe measures leading to a significant reduction of PAH- and PCDD/F-emissions.

The emissions to water only accounted for less than 0,3% of the total impact (of all the emissions to air and water) in the impact category human toxicity. The partial eco-efficiency indicator for freshwater aquatic ecotoxicity (only emissions to air) decreased with 9% between 1998 and 2005.

The impact of the pollutants in the discharged wastewater is in the same order of magnitude as the impact of the emissions to the air. In some years the impact was negative because the concentration of heavy metals e.g. vanadium and nickel in wastewater discharged in the canal was lower than the concentration in the canal water used.

NO_x is the major contributor to eutrophication; its emission decreased with 11% from 1995 to 2005 as a result of improved production efficiency and because of the switch to certain types of anthracite as fuel in the sinter plant.

As for ecotoxicity, the concentration of eutrophying pollutants is lower in the wastewater than in the canal water. The (negative) impact of N- and P-containing substances in the wastewater is 10 times lower than the impact of NO_x-emission to air. ArcelorMittal's water use per ton of liquid steel produced decreased by 33% as a result of the realisation of an intelligent recycling system.

The extraction of non-phreatic groundwater was stopped in 2002. For the impact categories acidification, human toxicity (emissions to air) and water use, ArcelorMittal Gent succeeded in an absolute decoupling of environmental impact and steel production.

For photo-oxidant formation, freshwater aquatic ecotoxicity and eutrophication, the decoupling of environmental impact and steel production was relative [13-15]

4. CONCLUSIONS

The technology of ferrous metals is well established. The use of iron and steel, in particular, is considerable and widespread. However, the processing of these materials is resource intensive and generates considerable pollutants, despite continual development. To maintain the use of these popular and versatile materials in the future will necessitate an increased attention to reductions in the consumption of natural resources and power, and greater sensitivity to the environment.

As human civilization advances, it is inevitable that iron and steel will increase in quantity on the global scale. Therefore, in production and application processes of such materials, their eco-material-oriented. i.e. to take ecology into consideration development is a serious issue that is indispensable for the world economy to continue growing. This involves a lot of engineering and industrial issues and requires rapid development in the future. Furthermore, by releasing the implementation results of LCA correctly and having consumers utilize it, consumers can chose more eco-friendly products and whether a company's product development is eventually considered environmentally friendly can be evaluated. LCA has been a topic of growing interest to the steel industry. Several steel companies and associations have already independently carried out LCA studies, each different in purpose, system boundary and methodology, and some of the examples are shown in this paper. The challenges posed by a competitive market are forcing steel makers to switch over to cleaner production by adopting the best practices at each stage in the life cycle of steel making. This shift may be gradual but is unmistakable. Heavy investment programmes, top management support, employee education and training are all contributing towards enhanced environmental performance. It is hoped that in the coming years, the use of new and innovative management tools such as LCA will be increased.

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CORPORATE SOCIAL RESPONSIBILITY AS AN IMPORTANT PART OF ENVIRONMENTAL MANAGEMENT

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Abstract

Technical and technological progress at the end of XX and at beginning of XXI century was accompanied by demands for increased productivity and quality of products and services. Increase the physical volume of production in response to the growing needs of consumers and society, on the other hand, caused a various environmental problems. Development and raising awareness about the necessity of implementation of environmental management and basic environmental standards in business, is the way that emerging problems of the entire human society can successfully be solved. In making many business decisions, modern managers need to analyze not only economic, but also the environment dimension in the determination of cost-effectiveness of a particular job. In addition to responsibility for the successful operations of the company led by managers also have some social responsibility. CSR is a process in which companies wish to harmonize their relations with all sorts of social actors who may have an impact on their business.

Keywords: progress, changes, environment, ecology, CSR.

1. Introduction

Global world environment at the end of XX and at beginning of XXI century, is characterized by the scientifical-technological progress, which is escorted by constant and dynamical changes in the socio-economic processes. Technical and technological achievements were accompanied by demands for increased productivity and quality of products and services. In that times, business companies were focused on achieving growth in the volume of production whose result was the increase in profits. Therefore, imperative task manager has been achieving so colled „economy of scale", so the success of the company was measured by the quantity produced and sold products and services. On the other hand, these phenomena and processes in the global economy and society, have influenced the changes in the environmental sphere and to specific environmental problems are gradually gaining multiply growing, global dimension. Increase the physical volume of production in response to the growing needs of consumers and society, caused a disturbance of the environment by increasing pollution of the environment.

However, rapid economic growth and irrational use of natural resources 70th of the last century have influenced the emergence of global structural crisis in energy and raw materials. Disproportion in the development of individual countries and regions, caused shortages of certain products on the world market, which is its immediate consequence the sudden jump in the prices of scarce products, growth, unemployment and the decline in income - only confirmed the necessity of practical implementation of environmental management as a new management concept of management in everyday life companies.

2. Environmental management

Dynamic and complex changes are caused by technological, economic, political and social factors and there are constant of the time. During the XX century, changes have become significantly faster and more complex. Accelerate the pace of change is related to the increase in the frequency of change and the increase in the rate of diffusion changes. As such, the changes are permanent and challenges for management for the purpose of training and development of appropriate approaches that will successfully manage change.

Change in requirements environments, caused changes in the very businesses, primarily through perceived the necessity of acquiring and implementing new, first of all ecological knowledge in all organizational functional areas. The production and technological revolution, the whole society is being called management revolution that is, as Drucker points out, the third change in the dynamics of the application of knowledge, where science is applied directly to the science - knowledge is applied to knowledge. Management revolution emphasizes the importance of the intellectual capital and the necessity of its implementation as a precondition for the creation of value and effective organizational management. While it is important to point out that: ”(a) knowledge is the basis for the modern business enterprise and was efficiently and effectively through management, and that (b) the human factor in their dual participation in the management process...only able to generate, use and valorize the knowledge.” [1]

With the emergence of the first environmental problems 70th of the last century, and who have acquired a global character, gradually developed the awareness of the necessity of implementation of a new systematic and strategic approach to managing the problems in the field of ecology. "Awakening of ecological consciousness" influenced the decision-Business Charter of Sustainable Development 1991st year in which the environmental management marked a key determinant for sustainable development and the priority task of the modern enterprise. This Charter was proclaimed that ecology and environment protection must be integrated into the management of the company and that its promotion must be a continuous process, to ensure that employees are required to motivate and educate environmentally, that we must make a constant assessment of environmental consequences of any new processes and products, the company must assume responsibility for the behavior of their subcontractors and suppliers, that the company must be open to dialogue on environmental risks and engaged in joint efforts to promote environmental awareness and regularly informing all interested parties. A year later, 1992. in Rio de Janeru held The First International Environmental Summit which adopted Agenda 21. Starting from the Business Charter of Sustainable Development to elaborate further principles for strengthening the role of business entities in the environment. The Agenda 21 explicitly defined category of environmental management as one of the priorities of each business entity. [2]

Environmental management is a new concept for solving environmental problems, and it "includes organizational structure, processes, procedures, resources for the implementation of environmental policy and accountability in the region."[3] Model environmental management system shows the five phases of the cycle repeated:

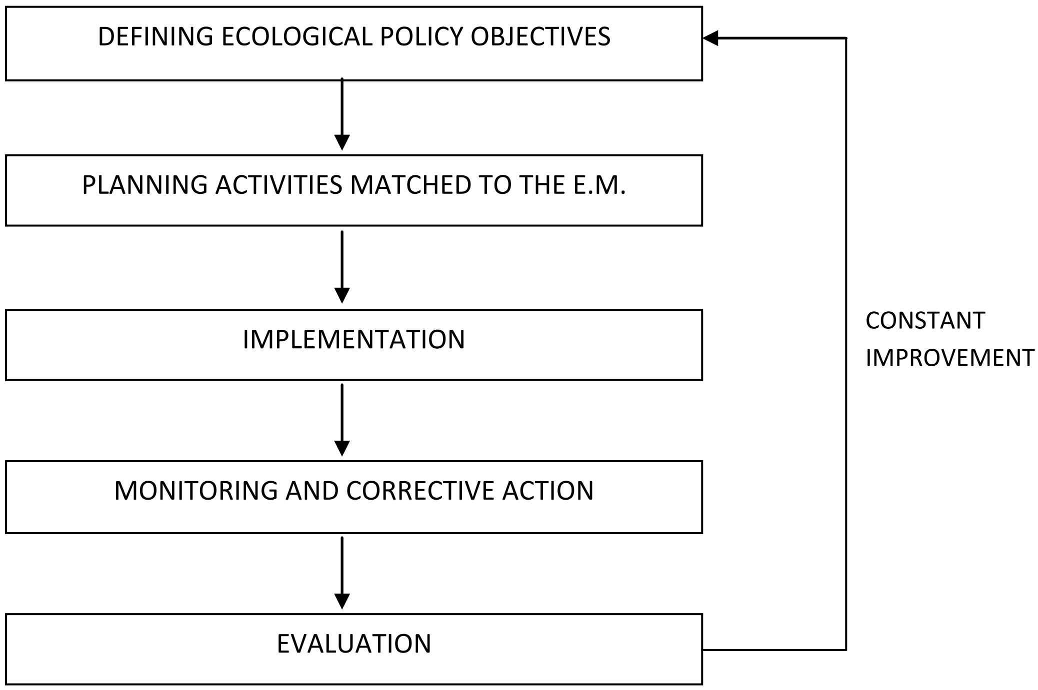

Figure 1. Model environmental management system [3]

Environmental management is the process by which environmental health is regulated. It does not involve managing the environment itself, but it is the process of taking steps and behaviors to have a positive effect on the environment. Environmental management involves the wise use of activity and resources to have an impact on the world. [4]

"Environmental management is entirely anthropocentric concept of business management, making it significantly different from all other management approaches. Also, it is not just standard science, skills, effective and efficient conduct and achieving the goals the right way, but true knowledge and practice to achieve real goals, then those related to human survival and quality of his life. Environmental management, according to professor Vujic, is already involved into each business practices and sustainable management and so turns into a sort of global management. In no area of application management is not confirmed anywhere so strong and convincing performance of the dominance of the principle of the effectiveness under the principle of efficiency, or the inability to a lack of effectiveness (bad, so inhuman and unecological selected targets) compensate even the highest efficiency. In that sense, environmental management can (and must, in the future) become kind of a management infrastructure and pilot test performance each management practices, without exception." [5]

"Conservation is a state of harmony between men and land. Environmental management is the practice of creating this harmony. It involves management of both the living and non-living components-all components of nature." [6]

Regardless of the different ways in which the authors define the concept of environmental management, the common denominator in all of them, is the unanimous view that the main task of environmental management of a comprehensive understanding of changes in the environment and creating the preconditions for the successful adjustment of enterprises to these changes. The essence of the application of environmental management is to ensure the necessary conditions for the effective planning and operation of companies with the factors in the environment.

3. Corporative social responsibility

Companies that want to work successfully in contemporary business society must respect the presumption of sustainable development and environmental standards in planning their business activities and defining the goals.

Modern managers must be able to recognize and understand the basic trends of changes to their management of the enterprise was successful. Adaptation becomes a condition of growth and development of modern enterprises, and above all, its survival. The existence of the company in today's market environment, is thus determined, its ability to adapt to their environment and/or adapt to the environment itself, with the necessary existence of some kind of feed-back between enterprises and the environment. At the beginning of the creation of environmental management, basic moves are undertaken in the direction of remedy and mitigate the problems caused by different types of pollution and environmental disruption. Acting manager was reactive to the changing external environment. Knowledge, skills and experience as the main elements of "classical" management skills are increasingly measured not only the ability of managers to effectively do their jobs, but their ability to recognize the strategic goals of treir organization and strive to achieve them. In this respect we follow the development of preventive measures for organizational actions to reduce environmental pollution, which are a consequence of applying the concept of environmental management in enterprises. In fact, some measures such as installation of treatment represented a significant corrective action on the emergence of environmental management, but they are now superseded by preventive measures, precisely as a result of the development of environmental awareness, ecological education and management. [7]

Recognition of basic environmental requirements and to integrate environmental objectives into specific business objectives of the company, must not be an exception and an example of only the best companies and the company today, but it represents a kind of imperative for all participants in the global market.

In making many business decisions, modern managers need to analyze not only economic, but also the ecological and environmental dimension in the determination of cost-effectiveness of a particular job. In addition to responsibility for the successful operations of the company led by managers also have some social responsibility.

“Corporate social responsibility is assumed the involvement of the business entity in the social and community development programs in the field of health, environment, sports, culture, assisting vulnerable people, implementation of health (clean) technology, prudent use of resources, training employees on environmental protection, public reporting on success and its consequences, funding research projects of a wider social significance that are not strictly related to the activity of the company. Therefore, the socially responsible companies overcome once the primary target acquisition and distribution of profits by integrating into the process of solving social problems." [8]

Differences in business ethics can lead companies to take very different positions or views on what their responsibility is toward their stakeholders. The way a company announces business problems or admits its mistakes provides strong clues about its stance on social responsibility. In carrying out organizational activities managers must take into account the impact of internal and stakeholder interests or insiders, but the external stakeholder's called outsiders.

Certo and Peter listed four specific areas of social responsibility of managers:

1. concern for consumers,
2. concern for employees,
3. concern for the environment,
4. concern for society in whole." [9]

"Social responsibility refers to the task or duty manager to make decisions that respect, protect, strengthen and promote the welfare of the stakeholders of the organization and society as a whole. Corporate social responsibility is a moral responsibility to the stakeholders that influence the activities of the organization." [10]

CSR is a process in which companies wish to harmonize their relations with all sorts of social actors who may have an impact on their business.

According to Hitt et. al. „corporate social responsibility is concerned with the obligation corporations have to constituencies and the nature and extent of those obligations. Companies have a wide variety of constituencies including current shareholders, customers, employees, specific communities, society at large, governments, and so on." [11]

„A company's stance on social responsibility is the way its managers and employees view treir duty or obligation to make decisions that protect, enhance, and promote the welfare and well-being of stakeholders and society as a whole". [12]

Table 1. Forms of Socially Responsible Behavior [13]

Managers are being socially responsible and showing their support for their stakeholders wnen they:

- Provide severance payments to help laid-off workers make ends meet until they can find another job.
- Provide workers with opportunities to enhance their skills and acquire additional education so that they can remain productive and do not become obsolete because of changes in technology.
- Alow employees to take time off when they need to and provide health care and pension benefits for employees.
- Contribute to charities or supoort various civic-minded activities in the cities or towns in which they are located. (Target and Levi Strauss both contribute 5% of their profits to suppotr schools, charities, the arts, and other good works.)
- Decide to keep open a factory whose closure would devastate the local community.
- Decide to keep a company's operations in the United states to protect the jobs of American workers rather than move abroad.
- Decide to spend money to improve a new factory so that it will not pollute the environment.
- Decline to invest in countries that have poor human rights records.
- Choose to help poor countries develop an economic base to improve living standards.

4. Environmental standards

In order to reduce the harmful effects of production processes on the environment, and in response to the social responsibility of companies, are defined and specific environmental standards ISO 14000 which must adhere to managers.

„The ISO 14000 Standards are a set of environmental standards designed by the International Organization for Standardization 1994. to assure that businesses are environmentally responsible. The ISO 14000 Standards were created to help meet the objective of "sustainable development" outlined at the United Nations Conference on Environment and Development in Rio De Janeiro in 1992. The ISO 14000 Standards include guidelines for waste disposal, use of natural resources, pollution control and environmental responsibility. The ISO 14000 Standards also include sets of tests and measures that help organizations and businesses measure the impact they are having on the environment. ISO 14001 is the corner stone standard of the ISO 14000 series. It specifies a framework of control for an Environmental Management System against which an organization can be certified by a third party.

ISO 14001 was first published in 1996 and specifies the actual requirements for an environmental management system. It applies to those environmental aspects which the organization has control and over which it can be expected to have an influence.

Other standards in the series are actually guidelines, many to help you achieve registration to ISO 14001. These include the following:

- ✓ ISO 14004 provides guidance on the development and implementation of environmental management systems,
- ✓ ISO 14010 provides general principles of environmental auditing (now superseded by ISO 19011),
- ✓ ISO 14011 provides specific guidance on audit an environmental management system (now superseded by ISO 19011),
- ✓ ISO 14012 provides guidance on qualification criteria for environmental auditors and lead uditors (now superseded by ISO 19011),
- ✓ ISO 14013/5 provides audit program review and assessment material,
- ✓ ISO 14020+ labeling issues,
- ✓ ISO 14030+ provides guidance on performance targets and monitoring within an Environmental Management System,
- ✓ ISO 14040+ covers life cycle issues.

Of all these, ISO14001 is not only the most well known, but is the only ISO 14000 standard against which it is currently possible to be certified by an external certification authority." [14]

5. Conclusion

Rapid economic growth and irrational use of natural resources 70th of the last century, caused a disturbance of the environment by increasing pollution of the entire human environment. These processes, at the other hand, only confirmed the necessity of practical implementation of environmental management as a new management concept for solving different environmental problems. The essence of the application of environmental management is to ensure the necessary conditions for the effective planning and operation of companies with the factors in the environment.

In making many business decisions, modern managers need to analyze not only economic, but also the environmental and ecological dimension in the determination of cost-effectiveness of a particular job. In order to harmonize their relations with all sorts of social actors who may have an impact on their business, companies apply the concept of social responsibility in their everyday business life.

So, we can conclude that corporate social responsibility, as an important part of environmental management, is one of the basic precondition for success in the contemporary business environment.

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THE IMPORTANCE OF DEFINING THE OPTIMAL STRATEGIES FOR SUSTAINABLE TOURISM DEVELOPMENT

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Abstract

The present generation must be the bearers of economic development, but not at the expense of future generations. It directs us to the rational use of nature in creating the efficiency of economic activities, such as tourism. The importance of nature conservation and its sustainable exploitation, in this case requires a strategic approach. To succeed it is essential to define and implement the optimal strategy for sustainable tourism development. The sustainability strategy of nature in the context of economic exploitation should be based on convergent method. Itself this method is based on uniformity and moderation. Uniformity and moderation are the basic principles in defining the best strategy for sustainable development. The best strategy is not considered that it is theoretically possible, and as such would give the best results, but one that is practically feasible and also provides economic prosperity, while still saving the natural environment, and also refines it.

Keywords: environment, development, sustainable tourism, strategy

RELATIONS BETWEEN SOME PARAMETERS OF TWO IMMERSED STREAMS AND SPRINGS AT A LOWER ALTITUDE

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Abstract

Earlier injecting diluted fluorescent colors proven connection is two water streams Immersed with spring water that occurs at a lower altitude. In order to monitor the possible impact of two streams Immersed in the quality of drinking water in the aquifer, which occurs at a lower altitude measured some parameters. Comparing the mutual relations of the measured parameters can be determined concerning the influence of one or another Immersed in the stream source. Based on the results obtained it is possible to accurately determine the extent and size of the buffer zone of origin.

Keywords: fluorescent color Immersed stream, water source, the measured parameters, source protection zones.

DETERMINATION OF O_3 AND ITS PRECURSORS, MEASURED IN BELGRADE URBAN AREA

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Abstract

In this study we investigate temporal variation of ozone and its precursors and the impact of precursor on O_3 variations. Ozone, NOx, NO, NO_2, SO_2 and CO were measured simultaneously during October 2010, at 5 measuring stations in Belgrade, Serbia. Two statistical model, PCA (Principal Component Analysis) and multicriteria ranking (PROMETHEE/GAIA) were applied to collected data set with the aim to identify city areas with similar air pollution behavior. The results indicate that the most polluted stations are those which are exposed to traffic pollution. The weekend effect was also investigated and analysis suggests that NOx, NO and NO_2 concentrations are lower during weekend than weekday. By contrast concentrations of O_3 are higher during weekend than weekday.

Keywords: Urban ozone, PCA, Multicriteria ranking, weekend effect

1. Introduction

In order to monitor and predict changes in ozone concentrations in a future period, it is necessary to understand the nature of the ozone, as well as the conditions leading to its creation. Ozone is unique among pollutants, because it is a secondary pollutant and is created through multiple chemical reactions of primary pollutants in the atmosphere, particularly nitrogen oxides, carbon monoxide and volatile organic compounds in the presence of sunlight [1, 2, 3, 4, 5]. Since the meteorological parameters (temperature, wind speed, wind direction, relative humidity) play an important role in the dissemination and transport of pollutants, daily and seasonal variations of ozone and other pollutants are the result of variations in local meteorological conditions [6, 7].

Over the past few years a noticeable increase of tropospheric ozone has been observed [8]. Trends of increased ozone concentrations were observed in EU countries, USA and in almost all parts of the world [4, 9] These facts have led to the establishment of a system for monitoring the concentration of ozone in the air, in almost all European countries. Increased concentrations of tropospheric ozone are associated with increased mortality and lung diseases, especially among vulnerable groups [10, 11]. Due to increased concern and interest of the scientific public, the European Commission adopted a directive for the allowed maximum daily 8-hour average for the protection of human health [12]. Republic of Serbia is also part of the European network for continuous monitoring of ozone concentration. Ozone concentrations are measured at 14 locations around the country (including six measuring stations in Belgrade in 2010). Population exposure to high concentrations of ground-level ozone in Belgrade is a problem of great importance for the local government, given that more than 2 million people live in Belgrade and its surroundings.

In Western and Central Europe and North America systematic monitoring of variations of tropospheric ozone exists over a longer period [6, 13, 14], but much less is known about the behavior of ground-level ozone in the South and Southeast Europe [15]. Although ozone is a major threat to human health, very few studies regarding the impact of O3 concentration on the air quality in Belgrade, was carried out [16, 17].

The main objectives of this study were:

- assessment of the air quality in Belgrade urban area,
- to identify city areas with similar air pollution behavior;
- to locate emission sources.

2. Materials and methods

Belgrade, the capital of Serbia, (latitude 44 ° 27 44N, longitude 20 27 44E), has about 2 million inhabitants and it is located at 116.75 m above sea level, at the confluence of the Sava and Danube (Figure 1). Climate, typical for this area is moderate continental with four seasons, while the average annual temperature is 11.7 °C.

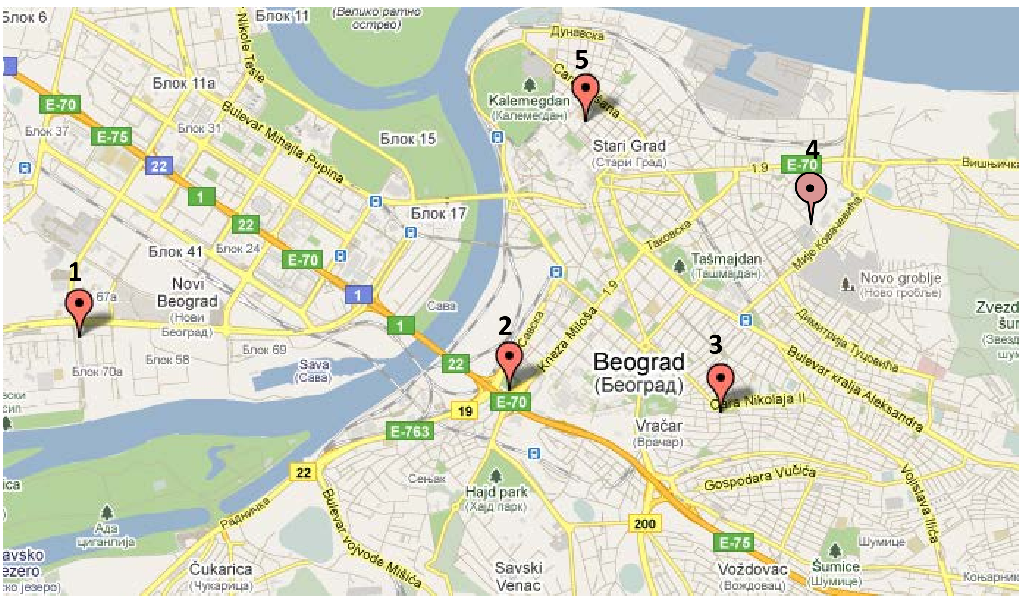


Figure 1. Locations of the measuring stations (1-Novi Beograd, 2-Mostar, 3-Vracar, 4-Pancevo Bridge, 5-Stari grad)

In Belgrade are operating 6 measuring stations for measuring of air quality. Their control and calibration is supervised by the official Agency for Environmental Protection, which operates under the Ministry of Urbanism and Environmental Protection. Air quality data are available on the Agency's website in real time (www.sepa.gov.rs).

For the purpose of this research, data collected at five automatic measuring stations in Belgrade, in October 2010, (Table 1), were used

Table 1 Characteristics of measuring stations

Name	Type of station	Altitude (m)
Mostar (MO)	traffic	87
Vračar (VR)	urban	132
Stari grad (SG)	urban	97
Novi Beograd (NB)	urban	85
Pancevo Bridge (PM)	traffic	110

In the urban areas the main sources of pollution are of anthropogenic origin. Usually in such areas, industry and traffic present the main source of pollution [18]. Since typical industrial zones cannot be found within Belgrade city borders, pollution comes from other sources, primarily, the gases emitted from cars, which mostly use internal combustion engines. The number of vehicles using Euro 4 engine is still low in this part of Europe. On the other hand, the traffic frequency grows larger every year. According to the official report of the Serbian Ministry of Interior, the total number of registered motor vehicles in the Belgrade, in 2009, is 568 200. Also, a major source of pollution is a large number of heating plants that use natural gas or crude oil and 59 smaller heating plants that work exclusively on crude oil, while households in the suburbs often use coal or crude oil for heating.

3. Methodology

3.1. Multivariate analysis

Multivariate analysis, principal component analysis (PCA) and cluster analysis (CA), were used to identify the possible emission sources of pollutants, as well as correlations among them. PCA is widely used to reduce variables and to extract a small number of latent factors in order to analyze the relationships among observed variables. To make the results more easily interpretable, the PCA with VARIMAX normalized rotation was also applied, which can maximize the factor loadings through variables for each factor. Factor loadings >0.71 are typically regarded as excellent and <0.32 very poor [19]. In this study, all principal factors extracted from the variables were retained with eigenvalues >1.0, as suggested by the Kaiser criterion [20]. When PCA with VARIMAX normalized rotation was performed, each PC score contained information about all the variables combined into a single number, while the loadings indicated the relative contribution each variable makes to that score. A cluster analysis (CA), was performed as a complementary analysis to PCA, with the purpose of classifying variables of different sources. The CA was applied to the data set using Ward's method, with Euclidean distances as the criterion for forming clusters of elements, as well as to determine if two clusters are sufficiently similar to be linked. In general, this form of CA is regarded as very efficient, although it tends to create small clusters. As the variables have large differences in scaling, standardization was performed before computing.

3.2. Multicriteria ranking

For ranking of zones according to the level of ambient air pollution caused by O_3, NOx, NO_2, NO, CO and SO_2 in the urban part of Belgrade (Fig. 2), we decided to apply multicriteria decision-making (MCDM) method [21]. In this work the PROMETHEE method was used for ranking of locations at which sampling of air was performed in accordance with determined contents of masses, while geometrical analysis for interactive assistance (GAIA) plane as an option provides graphic interpretation of PROMETHEE method. In speific it provides a clear picture of the decision-making problem in the way that it monitors PROMETHEE ranking. The GAIA visual modeling method is providing the decision-maker with information about the conflicting character of the criteria and the impact of the weights of the criteria on the final results. The GAIA plane is defined by vectors resulting from covariance matrix obtained using principal components analysis (PCA). By using the PCA, it is possible to define a plane on which as few information as possible gets lost by projection [22]. PROMETHEE represents an outranking method, for final set of alternatives [23]. In the use of this method it is necessary to define a corresponding function of preference and assign weight significance (weight coefficient) to each criterion. The preference function defines how a certain option is ranked in relation to another one and translates the deviation between two compared alternatives into a single parameter related to the preference level. The PROMETHEE method is based on the determination of positive flow ($\Phi+$) and negative flow ($\Phi-$) for each alternative in relation to outranking relations and in accordance with obtained weight coefficient for each criterion attribute. Positive preference flow expresses how much a certain alternative dominates other alternatives, namely if the value is higher ($\Phi+ \rightarrow 1$) the alternative is more significant. Negative preference flow expresses how much a certain alternative is preferred by other alternatives. The alternative is more significant if the value of outgoing flow is lower ($\Phi- \rightarrow 0$). Complete ranking (PROMETHEE II) is based on the calculation of net flow (Φ), which represents the difference between the positive and the negative preference flow. The alternative with the highest value of net flow is ranked best etc. [22, 24, 25].

3. Results and discussion

3.1. Descriptive statistics

For analysis of the pollutants' concentration in the ambient air, in Belgrade urban area (Serbia), the data obtained from five automated measuring station, were used. The data were collected during October 2010, in the time periods in which all pollutants were measured simultaneously.

During these 31 days, measurements were conducted from 0.00 to 24.00 hours, with calculation of hourly average values. This way, representative data base for credible statistical analysis was generated and total number of 744 data set was available. Summary statistics for SO_2, NOx, NO_2, NO, CO and O_3 concentrations by site are shown in Table 2.

Average ozone concentrations for the study period were in the range between 14.85 and 34.92 µg m^{-3}. Concentrations were somewhat lower than those reported by previous studies conducted in Belgrade urban area [16]. Concentrations of O_3 at all measuring points were below threshold and target values defined by European Union directive [12]. Also, during the analyzed period, the maximum daily 8h average mass concentrations of CO did not exceed limits established by the EU for protection of human health (10 mg m^{-3}) [26] at any monitoring site. Average CO concentrations were in the range between 0.58 and 1.68 mg m^{-3}.

Table 2. Descriptive statistics for SO_2, NOx, NO, NO_2, O_3 (μgm^{-3}) and CO (mgm^{-3}) daily averaged concentrations in different sites, over the urban Belgrade area

Site		SO2	NOx	NO	NO2	CO	O3
Mostar	Mean	25.52	131.95	87.26	58.51	1.16	14.85
	Standard deviation	21.28	121.36	104.42	25.54	0.96	15.76
	Min	0.5	12	2.5	12.8	0.2	1.5
	Median	20.2	91	47.5	55.1	0.9	9.3
	Max	126	688	595	152	5.5	176
Pancevo Bridge	Mean	52.51	94	87.45	48.35	1.68	25.05
	Standard deviation	6.73	66.09	72.81	20.31	0.49	17.19
	Min	40.5	5.7	1.5	8.7	0.7	5
	Median	53	78	70	47.5	1.7	21.55
	Max	66.6	305	325	121	2.9	77.2
NB	Mean	15.7	51	24.84	34.97	0.59	31.59
	Standard deviation	17.35	63.51	49.85	27.06	0.45	21.34
	Min	0.3	4	0.2	5.5	0.1	1.5
	Median	10.35	33.7	8.55	28.9	0.5	30.2
	Max	154	428	339	120	3.3	90
Stari grad	Mean	13.34	38.43	15.85	33	0.58	34.92
	Standard deviation	6.14	36.23	25.87	19.27	0.33	17.7
	Min	0.6	3.5	0.3	4.7	0.2	3.3
	Median	13.6	31.2	9.45	31.35	0.5	34.4
	Max	46.8	304	217	112	2.8	84.2
Vračar	Mean	20.98	48.05	32.26	32.64	0.74	31.6
	Standard deviation	15.36	53.59	61.09	17.3	0.63	18.84
	Min	1.8	5.6	1	6.7	0.3	2
	Median	17.5	32.5	11.55	29	0.6	30.35
	Max	92	429	460	118	4.5	86.1

Average NO_2, NO and NOx concentrations for the study period were in the range between 33-58.51, 15.85-87.26 and 38.43-131.95 µg m^{-3}, respectively. According to the legislation established for the protection of human health, the hourly mass concentration of NO_2 should not exceed 200 µg m−3, more than 18 times a year [27]. No exceedance was recorded.

Average hourly concentrations of O_3 for all five measuring stations given in local standard time (LST), are presented in Fig. 2

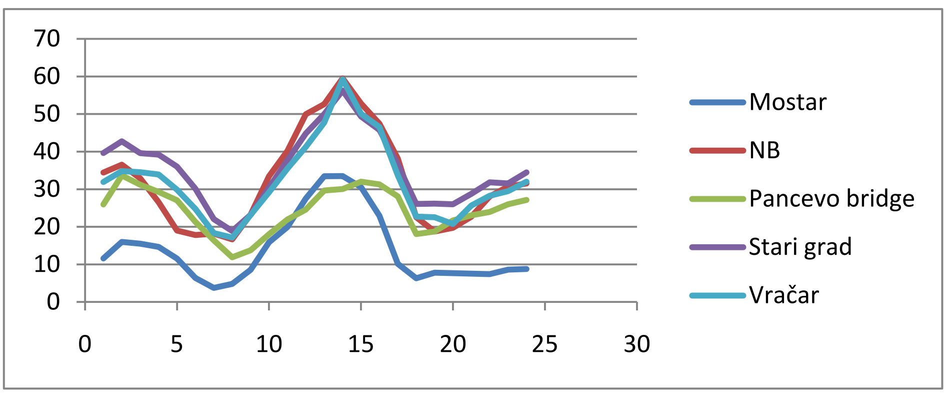


Figure 2. Average hourly values of ozone concentrations for all five measuring stations

Ozone concentration had a slight increment in a period from midnight to 2:00 and afterwards it started to decrease till 7:00. Then the O_3 concentration was slightly increased between 10:00 and 14:00 and then started to decrease. The minimal value occurred at 7:00 at the measuring station Mostar (3,7 μgm^{-3}). Afterwards, O_3 concentration slowly started to increase followed by minor variations.

The increase of O_3 starting from 8:00 (Fig. 1) associated to photochemical production was notably less intensive than in summer period due to the lower solar radiation, lower average temperature and higher average air humidity. Trend of ozone concentrations measured during autumnal period differed from the characteristic summer cycle when ozone's photochemical production was most intensive, with the highest value in the afternoon hours [28]. From 6:00 significant increase of NOx, NO, NO_2 can be observed at the measuring site PM (Fig 3) due to the intensive traffic activities.

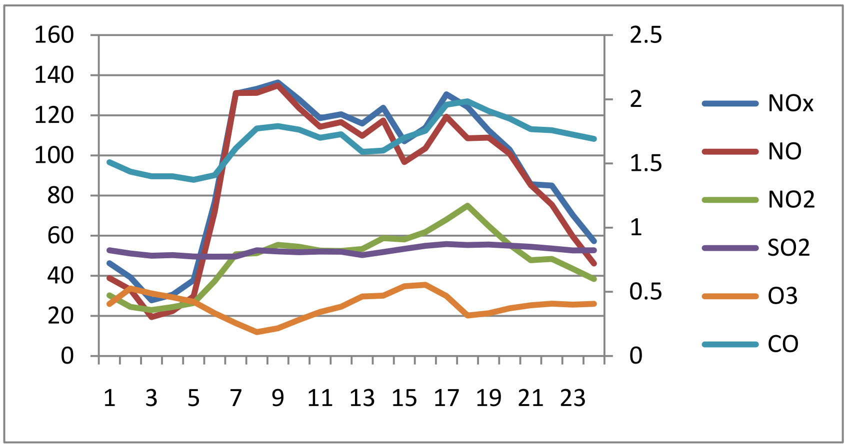


Fig 3. Average hourly values of NOx, NO, NO_2, SO_2, CO and O_3 concentrations at measuring site Pancevo Bridge.

3.2 PCA

PCA was applied as a non parametric method of classification to divide the monitoring sites into classes (PC) which have the same air pollution behavior and differing from those in other classes. Table 3 shows the main results of PCA application for analyzed pollutants at all sites. Considering eigenvalues grater than 1 (Kaiser criterion) only one PC could be selected for NOx, NO, NO_2, O_3 and CO, explaining 58.75%, 53.51%, 69.72%, 78.19% and 72.47% of the variance of the original data, respectively. Regarding SO_2 mass concentrations, two PCs were extracted, explaining 65.57% of total variance.

Table 3. Main results of the PCA application for the analyzed pollutants at all sites

Site	NOx	NO	NO_2	CO	O_3	SO_2	
	PC1	PC1	PC1	PC1	PC1	PC1	PC2
Mostar	**.932**	**.941**	**.961**	**.928**	**.954**	**.877**	-.044
Pan_Bridge	**.907**	**.849**	**.907**	**.911**	**.934**	**.871**	.065
NB	**.837**	**.765**	**.905**	**.884**	**.854**	.511	-.434
Stari grad	**.682**	**.650**	**.732**	**.818**	**.849**	-.149	**.793**
Vračar	**.286**	**.248**	**.621**	**.694**	**.822**	.558	.576
Eigenvalue	2.937	2.675	3.486	3.623	3.909	2.124	1.155
Variance (%)	58.746	53.509	69.724	72.466	78.185	42.473	23.099
Cumulative variance (%)	58.746	53.509	69.724	72.466	78.185	42.473	65.572

Values in bold indicate the variables that mostly influence the corresponding principal component

Results obtained by PCA analysis showed that there is one dominant source of NOx, NO, NO_2, CO and O_3 concentrations for all measuring points, and the similar results by pollutants for measuring locations Mostar and Pancevo bridge show that the traffic is most likely source of the pollution.

3.3. Multicriteria ranking (PROMETHEE/GAIA)

The reason for application of PROMETHEE/GAIA method lies in certain advantages of this method compared to used PCA method, which is reflected in the way the problem could be structured and explored. We have already concluded that the PCA analysis connects sites with similar pollution behavior only by one criterion (one pollutant), and so the results that we have obtained do not provide much information on the most polluted sites in city of Belgrade. This part of the paper deals with the application of multicriteria method for decision making MCDM (PROMETHEE II) with PCA (GAIA) for grouping those locations with similar pollution problems and identifying those with higher air pollution, based on multiple criteria.

For the purpose of the model creation presented in this work, the required parameters for PROMETHEE/ GAIA method were assigned to each criterion. These values include the impact of the criteria, namely presence of pollutants at certain measuring locations with tendency for their minimization, so the model implies ranking of the best alternatives- locations with the least presence of harmful gases in the air in accordance with assigned set of preference functions and weights to each criterion (Table 4).

Table 4. Weight coefficients

Criteria		Weights
O_3		0.4
NOx		0.2
NO		0.1
NO_2		0.1
CO		0.1
SO_2		0.1

PROMETHEE performed a complete ranking from the best to the worst location, in regards o the presence of pollutants in the air on those locations. By utilizing Decision Lab 2000 software package, with the PROMETHEE method, based on the data in Tables 2 and 4, values are acquired for positive (Φ+) and negative flows (Φ−) and thereby the net flow (Φ) (Fig. 7).

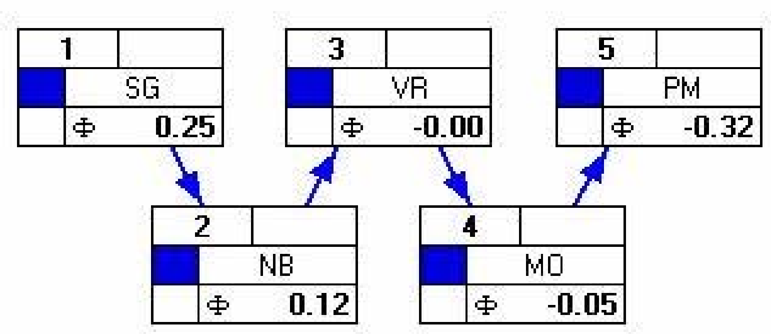


Figure 7. PROMETHEE II ranking of the locations (locations were ranked from left to right and from the best to the worst location)

The ranking results indicate that the best location is the measuring point Stari grad, while the measuring points Mostar and Pancevo Bridge are the most polluted locations (Fig 7).

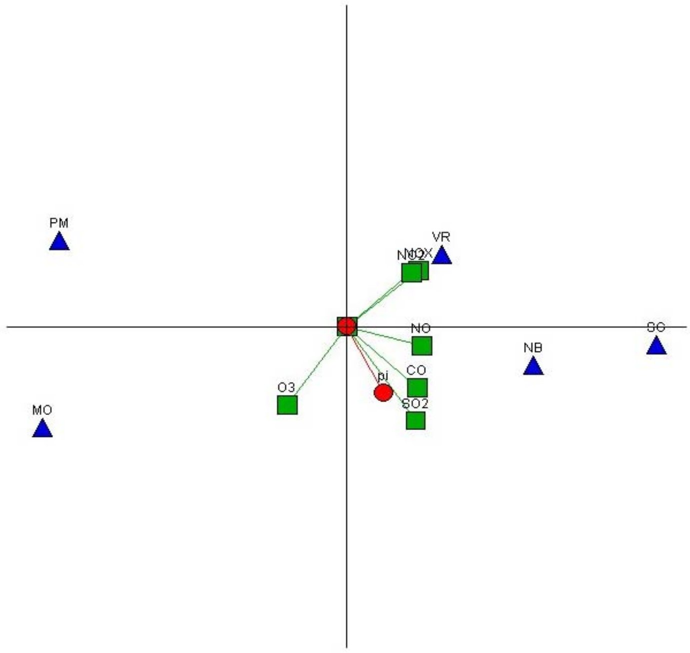


Figure 8. GAIA plane

In order to obtain clear visualization of PROMETHEE II ranking, GAIA plane was created. GAIA plane (Fig. 8) provides a clear picture of the best measuring locations according to the presence of certain pollutants. Especially, it is important to indicate their distance from the coordinate beginning, also, when decision stick *pi* is long, the most preferred locations in this case are oriented in its direction. Pollutants or criterions in GAIA plane are represented by green quadratic shapes; while blue triangles represent ranked locations. Since, in this study, the "minimized" modeling option was used, pollutants which are associated with particular locations were displayed opposite to those locations. This way, GAIA plane, for this research, indicates that locations MO and PM, are measuring locations with the largest percent of harmful gases in the air. Location PM evidently is not good according to any criterion, as well as the both locations (PM and MO) are directed in the opposite direction in regard to the decision stick pi which defines a compromising solution in accordance to the given weights of the criteria. Unlike them, measuring location VR has lowest concentrations of NOx and NO_2 in the air, NB has the lowest concentrations of NO, CO and SO_2 and, finally, location SG is the best ranked location, since it is near to decision stick *pi* and the most of the criterions are directed toward this location.

3.4. Weekend effect

In some areas ozone tends to be higher on weekends than on weekdays, despite the fact that lower emissions of ozone precursors are expected on weekends. Some researchers state that this is due to the different traffic and industrial activities between weekend and weekday [29, 30]This phenomenon is known as the 'weekend effect'[31]. The weekend effects on O3 concentrations are different in various cities. If O3 formation is under NOx-sensitive regime, the reduction of NOx emissions will lead to decrease in O3 concentrations. However, if O3 formation is under VOC-sensitive regime, the reduction of NOx emissions will lead to the increase in O3 concentrations [4]. The average daily concentrations of SO2, CO, NO2, NO, NOx and O3 during the weekdays and weekend in October ,in Belgrade urban area are shown in Fig 4.

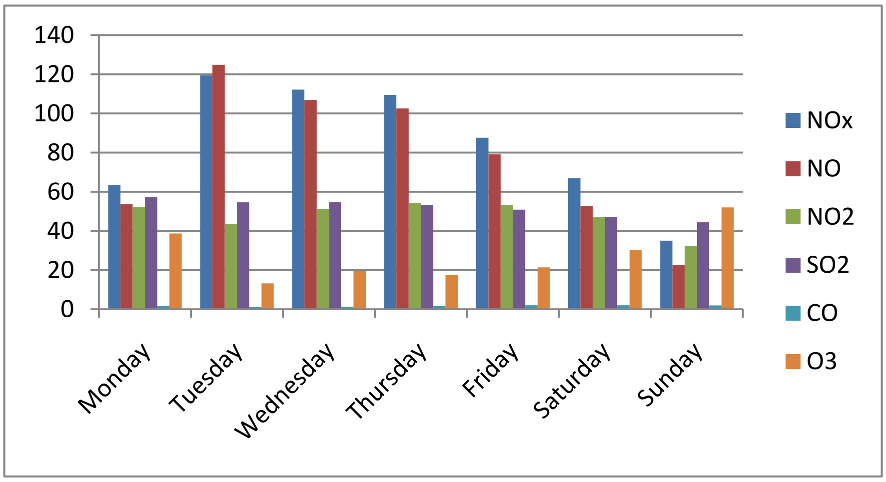


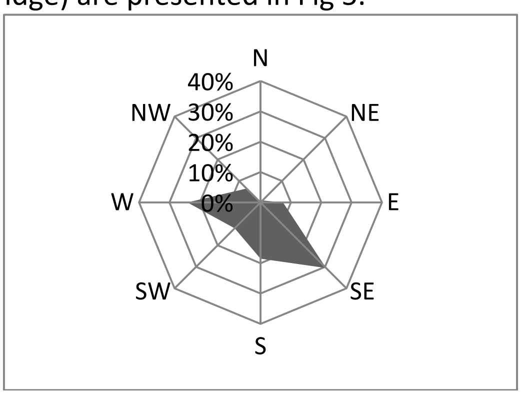
Figure 4. Mean daily concentrations of SO2, NOx, NO, NO2, CO and O3 during the weekdays and weekend at the Pancevo Bridge measuring site

The results show, without doubt, that daily average concentrations of NO, NO2 and NOx were diminished during the weekend for 82%, 25% and 71%, respectively. Due to this fact, according to Geng et al. [4], we can conclude that the O_3 formation is under VOC-sensitive regime in the city of Belgrade. Unfortunately, VOCs haven't been measured in that period.

3.5. Wind roses

The relation of pollutant concentration levels with the prevalence of winds from different sectors was studied with an aim to investigate the transport of pollutants from various zones of the city. It was already mentioned that the climate of Belgrade is moderately continental, with fairly cold winters and warm summers.

The available set of data was divided into 8 main wind directions. The frequencies of wind directions during the measurement period for two most polluted measuring stations (Mostar and Pancevo Bridge) are presented in Fig 5.



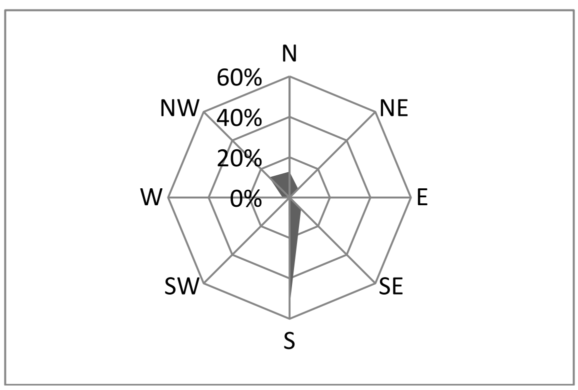


Figure 5. Frequencies of wind directions for measuring sites a).Pancevo bridge, b). Mostar.

The most frequent wind at the measuring station Mostar was blowing from SE direction, while at measuring stations Pancevo Bridge from S direction. In Figure 6 average concentrations of NOx, NO_2, NO, CO, SO_2 and O_3 during prevailing wind directions are presented.

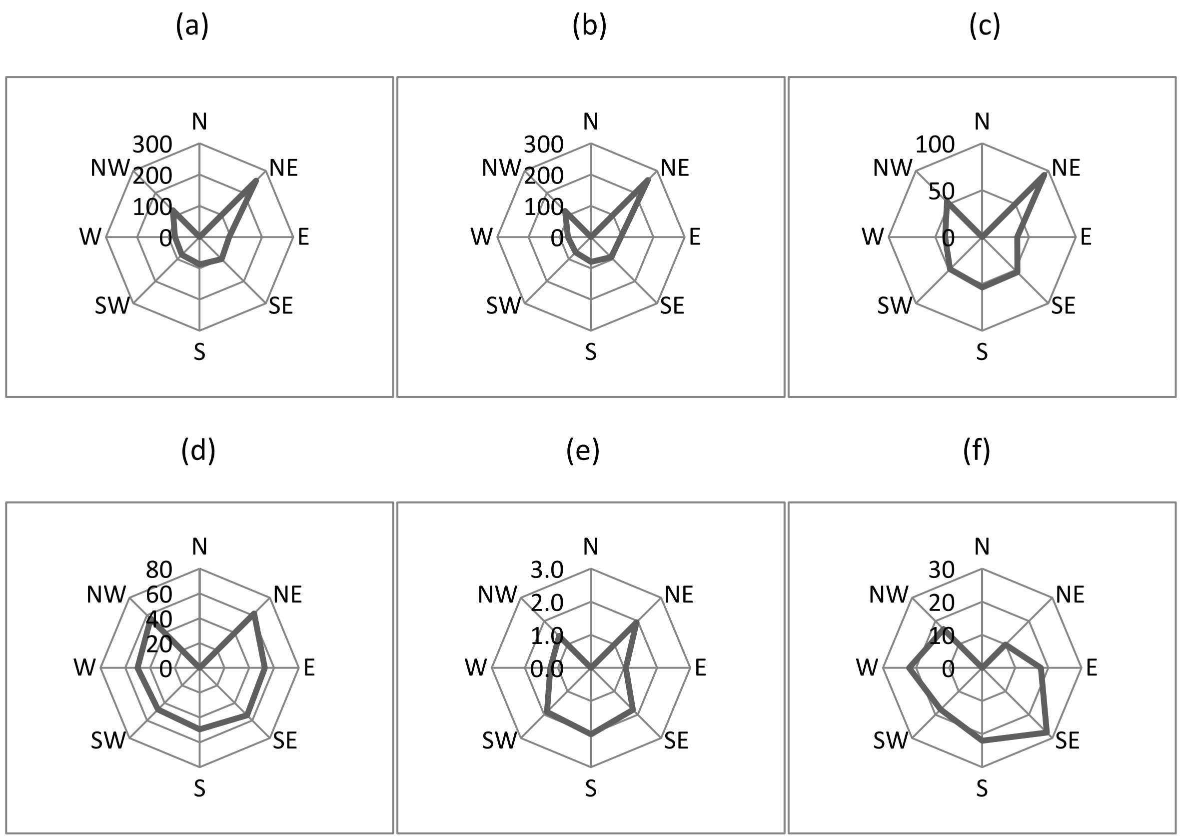


Figure 6. Average concentrations of (a) NOx; (b) NO; (c) NO_2; (d) SO_2 (µg m−3),(e) CO (mg m−3) and (f) O_3 (µg m−3) during prevailing wind directions

Maximum concentrations of NOx, NO and NO_2 (measuring station Pancevo Bridge) were associated with a local wind blowing from NE direction, which suggests possible influence of the bridge under heavy traffic load, located in N and NE direction. The prevailing wind direction for O3 maximum is SE, which might be an indication of ozone transport phenomena from rural area [16].

4. Conclusion

The results of simultaneous measurement of O_3, SO_2, NOx, NO_2, NO, and CO concentrations in an urban area of Belgrade in autumnal period of 2010 are presented in the paper. Obtained results for all pollutants were bellow limit thresholds and target values imposed by EC and daughter directives.

Higher ozone concentrations were recorded during the weekends, compared to weekdays, while the concentrations of other pollutants were significantly decreased in comparison with the weekdays.

Results obtained by PCA analysis showed that there is one dominant source of NOx, NO, NO_2, CO and O_3 concentrations for all measuring points, and the similar results by pollutants for measuring locations Mostar and Pancevo Bridge show that the traffic is most likely source of the pollution. On the other side, PROMETHEE/GAIA analysis has shown that the most polluted sites in Belgrade are Pancevo bridge and Mostar, due to heavy traffic activities.

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TECHNO-ECONOMICAL ASPECTS OF SANITATION AND RECULTIVATION OF THE OLD LANDFILL IN JAGODINA

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Abstract

Landfills and waste dumps threaten environment and pose a major environmental problem of our country. They are at every step, because the garbage is disposed daily and mostly without any control, especially on very "sensitive" areas such as waterways, forests, protected areas, roads. This is a reflection of our habits and lack of environmental culture.

A number of steps and activities are being taken up to improve the situation. Some of them are: mitigation of the existing and construction of new landfills, elimination of waste dumps, construction of new recycling centers, and education of the population. Ecological picture is changing, but very slowly.

Landfill in Jagodina has been in use for over fifty years. Located in the immediate vicinity of the city, technically unequipped, without an adequate storage technology and being filled for a long time, it poses a danger to the environment and human health. One of the solutions is to perform recultivation and rehabilitation of existing land and to construct a new landfill, one that would have regional character and include a recycling center.

Keywords: rehabilitation, reclamation, landfill in Jagodina, ecology, economic benefits.

1. Introduction

One of the characteristics of our modern development is rapid disintegration of the rural population, and therefore its increased concentration in larger urban areas and industrial centers. Among the problems that characterize such an environment, certainly is daily disposal of municipal and industrial waste. The fact that waste can be great threat for ground and surface water, soil and atmosphere, has influenced the human society to seek safer ways to manage waste. Generally, the most common technology for waste disposal in most countries is landfills waste disposal. Landfill waste disposals use a large surface area, mostly near big cities. When there are no defined sites, waste finish on land that previously has been used in agriculture. Most of the existing city landfills are at the end of life circle. In addition, many of them have overcome their temporal and spatial frameworks. Solid waste that has been disposed at landfills pollutes the soil, groundwater and surface water, thus polluting the environment itself. A special problem is gases emission creates by anaerobic process, and how Rickovski and his associates have pointed out, even three decades after the landfill closure, intense emission of methane is present [1]. For this reason stems need to perform remediation and reclamation of these areas.

Rehabilitation of landfill represents preparing of degraded space for the purpose of performing further rehabilitation. Reclamation methods and procedures vary depending on the character of degraded areas, local, geographical, hydrological, climatic and economic conditions.

Reclamation is a complex measure of environmental protection which is taken to prevent surface erosion, uncontrolled distribution of waste, disorders in the decomposition of waste and emission of gases and uneven ground settlement.

The old landfill containing municipal solid waste in Jagodina has been closed. On the degraded area that has emerged via landfill operation, it is necessary to start the process of rehabilitation and reclamation. In this paper, the authors deal with the techno-economic aspects of possible solutions to this problem through reclamation of degraded areas.

2. Possible reclamation solution of old city landfill

All procedures of reclamation of the old city dump in Jagodina are reduced to two types, namely: technical and biological. The technical procedures for reclamation of degraded areas include land preparation and recovery, for use in commercial use, or improvement in order to preserve the environment. Soil recovery is conducted by leveling, by forming stable slopes and levels, covering of uncultivable land with cultivable layer containing humus, road building, by constructing hydro-technical and melioration facilities and the like. The biological process reclamation of degraded areas include measures to establish crop rotation and crop selection for the cultivation of the soil after the completion of a technical procedure, as well as complex of biotechnical and phito-melioration measures for restoration of the flora and fauna on the land, i.e. formation of ecosystems.

In terms of spatial planning and land use, reclamated surface is categorized as a protective vegetation. Reclamation of landfill should be directed toward achieving optimal biological production in order to enhance its protection role, which is a prerequisite for the subsequent restoration of the land into an economically interesting category, if it is proven that it would be financially viable.

2.1. Technical reclamation

Minimum height of land which is spread in the process of technical reclamation should range from 30 cm to 50 cm. In the case of old garbage landfill in Jagodina thickness for the final cover is 50 cm, with the aim of providing conditions for the development of vegetation. Spreading of the land for its permanent position is carried out simultaneously over the entire area. During these operations the final cover must not be damaged. All land operations should be executed under moderately dry state, without compression.

2.2. Biological reclamation

As an adequate solution for biological reclamation of old landfill in Jagodina, a mixed meadow of grass-leguminized composition is formed. Meadow vegetation under proper care conditions provides continuous coverage of land surfaces, as well as the uniform permeation of the layer throughout its depth of roots and veins. This provides protection from erosion, the soil structure improves, becomes enriched with carbon dioxide and so through the sequences of regular annual cycle of decay and regeneration of vegetation, becomes enriched with humus component that is then connected in organic-mineral complex. The vegetation diversity of the meadow should be complex in order to better utilize underground and surface area and achieve greater overall stability of the onsite vegetation ecosystem in adverse conditions. The vegetation ecosystem includes representatives of butterfly family (Leguminosae) which take nitrogen from the atmosphere and hand it over to the land when they die. Selection of the species is aligned with the site conditions with emphasis on species with more extensive production as well as the more resistant species. Meadows must be formed and nurtured with the use of all necessary cultivation practices, given that the meaning of this phase is to start and accelerate the pedological process in order for the land to achieve the optimal properties and productive level, as soon as possible. Formed habitat eventually is settled by other organisms: small rodents, worms, insects, microorganisms and the like, which complements and enhances the environmental community pedogenetic processes. Meadows is formed by a seed sowing in autumn and spring, which must be done immediately after spreading fertile substrate. Before planting, soil should be well fertilized with matured manure. The next measure is mowing the meadow that is performed regularly throughout the growing season. Mowing promotes the development of planted buds and tillers fill the new shoots. Increased development of tillers provides the maximum protection from erosion, and performs natural drainage of the field [2] [3] [4] [5].

From the aspect of reduction of methane extraction, a mixture of grass and alfalfa is needed on the meadow, which performs its biological oxidation. Research shows that this vegetation combination only after six weeks of development renders a substantial reduction of methane emissions. Different roots morphology of these two plant species enables convenient transport of oxygen in the deeper layers of the field, and also regulates the water content, so these results come from there [2].

Supply of seedlings for the establishment of the buffer zone is done in a registered nursery. Time of seed planting is during the period of rest of vegetation, and beyond freezing period. Black poplar is the best type for forming the buffer zone around the area that is reclamated. The importance of this plant species lays in a very good reduction in emissions of harmful gases [2]. Also, willow trees are recommended as both economically and environmentally sustainable solution. They also carry out treatment of leachate waters very effectively [6]. Therefore, a combination of these two plant species, presents an acceptable solution for the forming of the buffer zone.

2.3. Technical phases of reclamation

During the reclamation of old landfill in Jagodina there are the two phases. The first phase involves the very reclamation in the narrow sense. As part of this phase it is first necessary to mark axle of the restauration before work begins, while recording the longitudinal and cross sections. Afterwards mechanical excavation of the soil of the second and third categories from borrow pits with spreading and compacting on the surface of the landfill. The last stage of the first phase of reclamation is now a selected mixture of grass, the formation of the buffer zone consisting of woody plants and installation of the system for degassing.

The second phase of reclamation is the arrangement of the surrounding area, construction of service road and the construction of protective channels. For reclamated area of the old landfill, it is necessary to provide a protective fence and gate at the end of the service road. Such measures are taken to ensure access to authorized persons and to personnel responsible for maintaining the lawns and performing other maintenance tasks.

3. Economic aspects of rehabilitation and recultivation

Restoration and reclamation of the landfill in Jagodina requires some financial investment. According to preliminary calculation that amount to 133,631 euro, for the following purposes:

- Reclamation dumps…………………….............40,520;
- Spatial planning for waste……………..............47,177;
- Construction of service road……………..……..8,997;
- Fences and gates……………………..................10,357;
- Construction of protective channels…..……….8,580;
- Works on degassing…………….……………….18,000.

Expenses are not small but the benefit is invaluable. First, the landfill would cease to be an environmental problem of the city, the great polluter of the environment and the constant threat to human health. This would have disappeared environmental costs, caused by these activities.

Second, remediation and reclamation would obtain rather large land area suitable for cultivation of appropriate agricultural crops. Crop rotation should be determined in accordance with the situation on the ground and to market needs [7] [8] [9] [10].

4. Conclusion

The old landfills, which are dysfunctional, irrational and environmentally harmful, should be recovered and possibly execute their reclamation. This will eliminate the dangers that threaten ecosystem, and create the conditions to bring the area under the landfills to useful needs.

This is an essential and urgent process. It requires time and financial resources. However, the effects that would be achieved are multiple, both environmental and economic.

The landfill in Jagodina is imminent recovery and reclamation. The dilemma is only, whether previously observed the presence of some possibly useful substances, to what extent, and whether there is economic justification for some form of recycling. It is estimated that the activities of technical and biological reclamation should amount to 133,631 euros. In turn that would be given land area, slightly larger than 5ha suitable for growing crops, probably in the early years of combined type of meadow grass-leguminozed structure. In addition to the landfill would no longer threaten the environment.

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ADSORPTION OF ZINC IONS ONTO BEECH SAWDUST

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Abstract

The paper presents the results of adsorption of zinc ions from synthetic solution onto sawdust as an adsorbent. Physical and chemical characterization of sawdust was performed. Change of the initial pH value and the adsorption capacity with time was also determined. The maximum adsorption capacity evaluated from these results was 2 mg/g. The adsorption kinetics was relatively fast, reaching the equilibrium for less than 20 min. From the adsorption isotherms it was found that the adsorption equilibrium follows Langmuir adsorption model. The results show that beech sawdust can be used as a cheap, natural adsorbent for the adsorption of zinc ions from industrial effluents.

Keywords: sawdust, zinc ions, adsorption

1. Introduction

Local legislation rules and concern for the environmental protection request the removal of heavy metal ions (zinc in this case) from industrial waste waters, in order to keep their concentrations on the value required by law, prior to their releasing into the environment. Diffrent processes of treating waste waters give different removal efficiencies[1]. Besides the existing of conventional technologies for the purification of waste waters from metal ions, considerable attention has been paid recently to the use of various sorption processes (low-cost adsorption) comprising the use of various by- or waste- products from wood industry, food industry, etc., often no economically valuable [2].

The aim of this work was to investigate the adsorption ability of beech sawdust produced by manufacturing beech trees from forests of the Balkan Peninsula, by using the adsorption of zinc ions from diluted solutions. That comprises to determine the equilibrium adsorption conditions, as well as the kinetics and mechanism of adsorption, but also to determine the total cation exchange capacity, and the dominant exchangeable cation.

2. Experimental

2.1. Material and methods

A series of the adsorption experiments were performed by using $ZnSO_4$ stock solution (0.2 g Zn^{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.

The concentrations of considered heavy metal ion during experiments were determined using a PerkinElmer -403 atomic adsorption spectrophotometer, while the pH change was measured by a WinoLab-720 pH-meter.

Beech sawdust supplied from a local timber mill was used as an adsorbent in this study. The sawdust was firstly sieved through a set of laboratory sieves and the sieve fraction <1 mm was used in the adsorption experiments. Dry sawdust was weighed then this weight was rinsed with 200 ml of distilled water, dried again at 90^o and used for further characterization or in the adsorption experiments.

In order to determine the chemical composition of sawdust, the sawdust was burned and the ash was analyzed. The percentage amount of ash was 2.06 %. The results are presented in Table 1.

Table 1. The chemical composition of sawdust

Oxides	Na_2O	K_2O	MgO	CaO	Fe_2O_3	SiO_2
Content, %	1.51	4.56	3.32	22.39	3.00	34.08
Oxides	SO_3	Al_2O_3	P_2O_5	TiO_2	MnO	Ostalo
Content, %	24.76	4.73	1.17	0.18	0.13	0.17

Total oxygen demand (TOD), as well as the concentration of alkali and alkaline earth metals leached by water during rinsing the sawdust, was also determined prior the adsorption experiments. TOD was determined volumetrically by means of $KMnO_4$ solution. Based on its consumption, the amount of oxygen needed for the oxidation of organics in the rinsed water is then calculated. The consumption of oxygen was 0.8 mg/L. Besides the TOD, the total cation exchange capacities of alkali and alkaline earth metals that are exchanged in the reaction with NH4Cl were also determined [3]. The results are given in Tab. 2

Table 2 The concentration of alkali and alkaline earth metals in solution after mixing the sawdust with 1M NH_4Cl

Ion	Na^+	K^+	Ca^{2+}	Mg^{2+}
Concentration, mmol g^{-1} sawdust	0.152	0.092	1.10	0.107

The determined total cation exchange capacity (CEC) of the sawdust was 1,45 mmol Me^{z+}/g. (Me^{z+} here denotes alkali and alkaline earth metal ions). From Table 2 it can be seen that the dominant exchangeable ion is Ca^{2+} having the highest cation exchange capacity (CEC), while the capacities of Na^+, K^+ and $Mg^{2+}$are almost equal but for one order of magnitude smaller than the capacity of Ca^{2+} is.

2.2. The adsorption of Zn^{2+} ions on beech sawdust – Experimental procedure

Adsorption experiments were carried out in a batch reactor with a stirrer in order to keep the sawdust in suspension. Stirring of the suspension was performed with a magnetic stirrer, at a constant speed of 300 rpm. Sawdust, previously rinsed with water, has been used as an adsorbent in all experiments. As the aqueous phase a synthetic solution of zinc with a constant and known initial concentration of Zn^{2+} ions was used. The initial value of pH was 5.3 in all experiments. Sawdust (weight 1 g), was brought in contact with 50 ml of the zinc 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 Zn^{2+} ions and alkali and alkaline earth metal ions. From the mass balance the amount of adsorbed zinc was determined. The adsorption capacity and its change with the process time was then calculated by using the equation (1):

$$q(t) = \frac{C_i - C(t)}{m} V \quad (1)$$

During the adsorption process the change in pH of solution with time was also monitored. All experiments were performed at ambient temperature.

In order to obtain evidence concerning the adsorption of zinc ions on sawdust, a series of the equilibrium experiments were performed by mixing equal quantities of beech sawdust (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 min; then filtered and the filtrates analyzed for the remaining part of the metal.

3. Results and discussion

The content of alkaline and alkaline earth metals in sawdust, and also the results of analyzing of samples after rinsing of sawdust by water and after loading it with zinc ions by adsorption are presented in Table 3. Evidently, there is a certain self- leaching of alkali and alkaline earth metals with water. More remarkable amounts of these ions (particularly calcium the concentration of which arose up to 2.85 mg g^{-1}) were observed in the solution after loading the sawdust with zinc ions. The supposition is that calcium, present in the wooden structure, was predominantly replaced by zinc ions from the aqueous phase. The other three alkali metals play a secondary role in this ion exchange mechanism.

Table 3 - Concentration of alkali and alkaline earth metals in sawdust, after rinsing sawdust with distilled water and after adsorption of zinc ions

Ions	Concentration in sawdust, mg g^{-1}	Concentration in sawdust after rinsing with water, mg g^{-1}	Concentration after zinc adsorption, mg g^{-1}
Na^+	0.23	0.1	0.01
K^+	0.79	0.1	0.06
Ca^{2+}	4.04	3.8	2.85
Mg^{2+}	0.41	0.34	0.22

3.1. Change of the initial pH value with time

It was assumed, accordingly to Tab. 3, that the adsorption of zinc ions onto sawdust takes place as an ion exchange mechanism, where calcium ions, which are incorporated into the sawdust structure are being replaced by zinc ions from a solution. The process is more complex because, as is shown in Fig. 1, the initial pH value of zinc ions solution was changed with time during the adsorption indicating that hydrogen ions take place simultaneously with zinc ions in the adsorption. As one can see, the pH of zinc solution suddenly decreases early on the process and after few minutes it starts increasing again. Such behavior of the pH means that the adsorption of zinc ions occurs with a simultaneous releasing and afterwards consumption of protons.

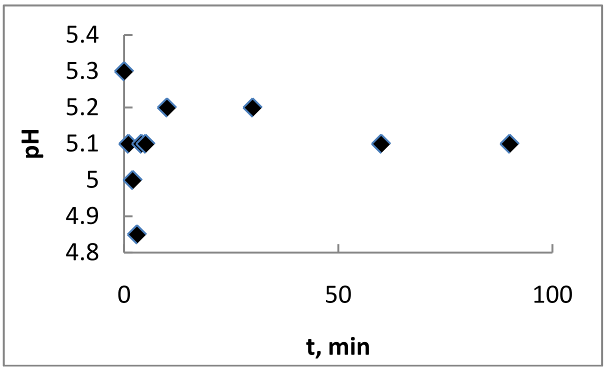


Figure 1 - Change of the initial pH value of solution with time during the adsorption

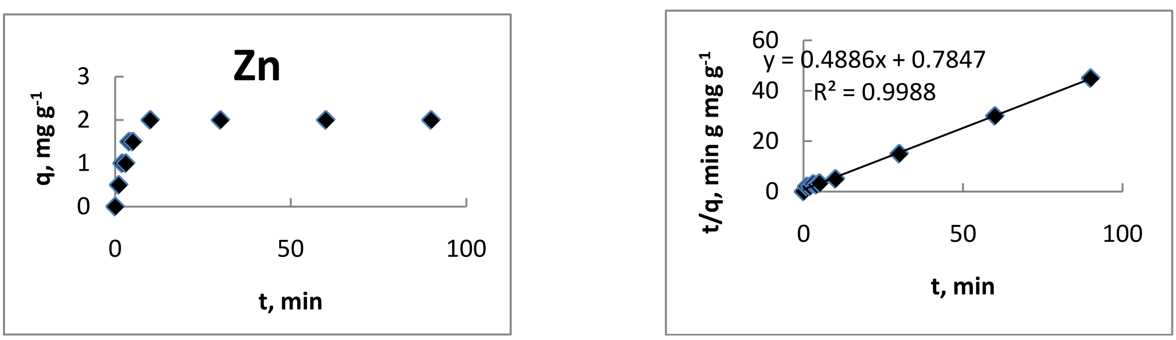
3.2. Kinetics of adsorption

The change of adsorption capacity with time is shown in Fig. 2(a). In the first 5-10 minutes of the process, adsorption takes place quite rapidly; the capacity increases with time, reaching a maximum value (2 mg g^{-1} in the considered case). Linearizing the curve from Fig. 2 (a) 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, as shown in Fig. 2(b) The regression coefficient is close to unity confirming a good fit of the experimental results with the considered second order kinetics model of adsorption.

$$q(t) = \frac{q_e^{\,2} k_a t}{(1 + q_e k_a t)} \tag{2}$$

Linearization of Eq. (2) leads to the following relationship:

$$\frac{t}{q(t)} = \frac{1}{k_a q_e^{\,2}} + \frac{t}{q_e} \tag{3}$$



a) b)

Figure 2 - Change of adsorption capacity with process time (a) and linearized form of the curve (b) accordingly to Eq. (3)

3.3. Adsorption isotherms

The equilibrium between an adsorbate immobilized on the active sites of an adsorbent and the adsorbate remaining in the aqueous phase is usually presented by adsorption isotherms. In order to describe the adsorption characteristics of „low-cost“ sorbents used in water and wastewater treatment, experimental equilibrium data are most frequently modeled by either Freundlich or Langmuir relationship [4].

The adsorption isotherm results are shown in figure 3 (a). Linear Langmuir plot is presented in Fig 3(b). According to the regression coefficient (R^2 = 0.982), the experimental results provide a very good fitting with Langmuir equation.

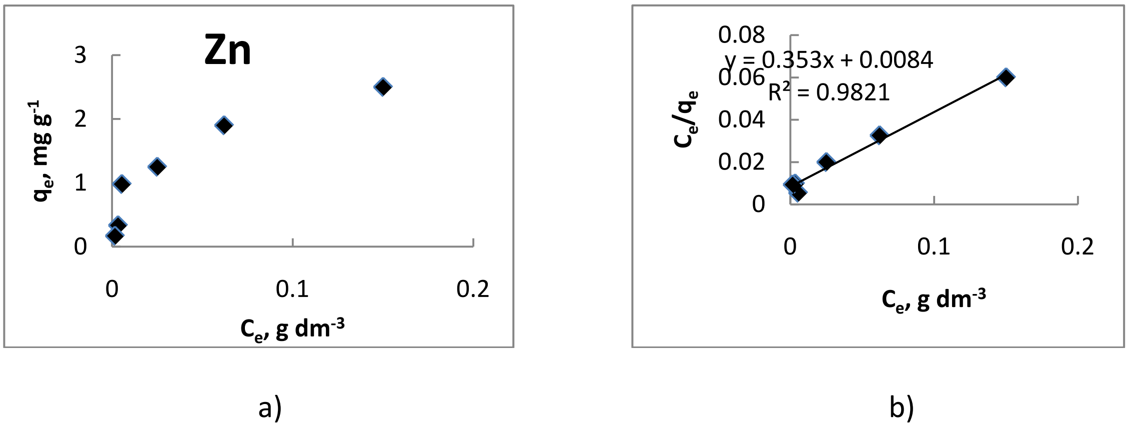


Figure 3 Adsorption isotherm (a) and linear Langmuir plot (b)

4. Conclusion

The results presented in this paper shows, that sawdust can be successfully used for the adsorption of zinc ions from aqueous solutions. Maximum capacity, corresponding to equilibrium saturation of adsorbent is achieved after 60 minutes and it was 2 mg g^{-1}. Ion exchange mechanism is supposed. It was shown that the dominant exchangeable ion is Ca^{2+}. The initial pH value changes with time in a similar manner as the adsorption capacity meaning that hydrogen atoms from adsorbent also take part in the process mechanism. Kinetics of adsorption follows the pseudo-second order reaction model. The kinetics is reasonably fast and after ten minutes the system is close to its equilibrium. The adsorption isotherm fits with Langmuir equation.

Acknowledgements

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HOW WILL SERBIA DEVELOP A "GREEN" ECONOMY?

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Abstract

We are discovering many things, technologically and technically, conceptually and creatively advanced, but we always ask: Where are we going to dispose of all the materials we use? Although Serbia is not among rich countries, it still has remarkable natural resources that we can use in the coming centuries. These are the shocking facts, which are not identical for all of the nature resources, but an optimistic forecast, given that some "basins have not yet found". Some resources are renewable, and some are difficult or impossible to restore. In the light of these new facts, it seems tentatively that Serbia only by the end of the last decade is trying to open and organize the collection centers for recycling of raw metal materials, and what to say about consciousness that non-degradable substances are not released anywhere but next to streams!

In addition to education of the youngest on the behaviour and the handling of waste, it is also necessary to teach adults not to behave as children, and that what they have been throwing, developed countries are using as a raw material from which it is possible to make money. Only a society that states that it has is enough – it is poor society, because their offspring will be rich in waste, which they will only encounter.

Necessary strategy for protecting the environment has another side which can be utilized, and this is pure ecological economics. Such economic and environmental philosophy, is against the pollution of the environment, with zero emissions of harmful substances into the atmosphere, radiation, derogation of woods and fields, with long-term focus on "waste" which means well-known resource that can be easily reused.

Keywords: nature, resources, waste, "green" economy, ecology

1. Introduction

Global problems the world is increasing every day. And often, we are not even aware that they do not occur alone, but the result of some unconscious or severely stakeholders who wish to rotate don’t matter on money for the future and sustainability of natural resources. In this effort, either by negligence or individual business strategies, which do not include social responsibility and environmental awareness, the greatest damage seems to suffer the state, population and natural environment.

Since is more impossible that exclusion of state and society in the production process, and that it only complicate the problem, if it wants to be part of the family of European nations. From that reason, Serbia has to fulfill the obligations of environmental protection, to promote the production values easily degradable material to undertake all possible efforts to educate a new generation of environmentally friendly consumers, and to encourage the development of entrepreneurship in economic sphere.

2. Natural Resources

Often the mention of the crisis, in all civilized countries of the world carries the same caution that is looked upon with notions such as economics or finance. However, the most common cause of such scarcity, occurring with social problems, the shortcomings of raw materials, energy and basic foods. The crisis, however, did not occur when some raw materials are abundant, but when there is a deficit of some market-preferred foods. Will more often be the case with energy sources such as oil, gas, coal, metals as a group of heavier material for exploitation? In the future we can expect and deal with the shortage of water, maybe more based on ultra-violet air from the atmosphere, and polluted air, biosphere, or degradation of flora and fauna, which is located in the food chain.

Effect of natural resources for many countries is crucial, while for some it is a catalyst for economic development, others eliminator social development. A certain degree of economic, technological and technical development, the structure of the economy, or international role, the resources of nature are limited to the extent determined by the need for them, with the possibility of strategic orientation on reutilization a raw materials and re-use of individual. Natural resources in our country are not jeopardized by a high degree of pollution, given that domestic industry is not in the progressive stage of development, but may concern the fact that the revitalization of the old factory halls and apparatus, not helping the environment.

In the not too distant past, predicted that it will be because of natural resources to run many disputes about boundaries, and even that will lead to wars, the fight against global threats to peace (terrorism), for which all a bit anxious about the justification or without But the globalization of world trade has produced so much penetration in smaller markets, that they speak of the invasion in an attempt to totally destroy the deposit materials.

While some are grieving over their natural reservoirs of raw materials (typical of the conspirators), others achieve technological competitiveness based on human factors knowledge and innovation. Although a small space, with no significant deposits of mineral resources, arable land and one might say, sovereignty, Japan manages to clear the traditional conception of existence, philosophy of work, environmental awareness and recycling, in particular, the production at the right time, achieve independence by many other country's only intent was to have.

The transformation of natural raw materials in production, and thus the consumer goods, is the material basis of the functioning and development of any economy. [5] Same raw materials have not valuable, and combined operations, capital, technology and entrepreneurship can economically be exploited.

This character of the relationship between economy and ecology of the natural environment is expressed in four basic properties, which has a natural environment for man[6]:

1. appears as a provider of renewable and nonrenewable resources that are used as inputs in the production process (category production factor "land"),
2. possess such public resources in their natural state should meet a series of human existential and derived requirements - air to breathe, water to drink, to enjoy the natural landscape and the like.
3. represents "a natural collector of" all types of wastes produced by man and its production and biological activity, and

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4. provides the land as a place and space for conducting all human, and therefore economic activity.



3. Environmental awareness and environmental

Barely 70s of the last century, in economic theory and practice is beginning to question the ecology and environment protection. Because of concerns a most wittingly groups of civil society and later their governments, because of the destruction of nature and limit opportunities for future economic and social development, there are movements for environmental protection. The protection is meant high costs, the industrialists did not intend to include in their work plans. Understand that the government can punish them, but that their market will not forgive the higher costs through rates.

Economic development policies of all countries are accountable to the base, because we do not have another planet; it is a single accommodated the quality of life and livelihood. Ecological situation shows that the ozone layer has decreased, that there was global warming, the oceans are polluted and there is less water for drinking, lack of selenium in the country (which acts as a prevention against cancer), the air is poisoned, but also food and other problems for the loss of arable land, increasing land under the desert, drought.

We need to develop environmental consciousness in all life ages, by:

- Acceptable behavior, to stimulate the family and the environment in which to develop social and environmental standards of conduct,
- Education policy, to develop the system knowing the environmental practices,
- Promote understanding, which will evaluate the environmental situation by priority.

Responsibility of companies is seen by their development of environmental conscience, in which there are hierarchical stages:

- The legal framework (commitments, only legal and financial sanction extends)
- Market principles (market share, profit)
- Environmental impacts (long-term interests of labor),
- The essential philosophy (conscious perspective, survival).

However, this year's disaster geo-physical scale, which operated the tectonic plates and damage to and from nuclear power plants in Japan, and many appear apocalyptical hurricane in Central America and Haiti, calling for caution.

Behind the desire of many countries to become and maintain its nuclear facilities, such as Japan and Turkey are contradictory. Since Japan is located on tectonically unstable area, and that is politically stable, the decision on the expansion of nuclear power was not good, because earthquakes are more common, and with increasing levels of earthquake. It should be borne in mind on surrendering of water, because Japan is an island nation, which this year struck repeatedly struck by a powerful earthquake that caused the tsunami, which damaged support wall on nuclear in Fukushima. The second example is Turkey, a country that is located between Europe and Asia, as an area with frequent earthquakes, but without the possibility of tsunami damages its nuclear power plants. However, in Turkey is the other important political moment, which means possible tensions around the organization, the use of nuclear materials and the threat to its neighbors (of Northern Cyprus, Kurds, etc.).

In Serbia, the awareness of environmental dangers are evident, especially after the many accidents in Paraćin repository of weapons (2006), tragedy in Užice munitions plant (2009), frequent explosions in Pančevo petrochemical factory, refinery, pollution from the previous period in the Bor RTB complex, which in the recent past produced many "silent pests" to the health of inhabitants; discharge of projectiles with depleted uranium by NATO bombing in 1999.; and pollution of rivers, rivers, lakes, nature parks.

It is necessary to make decisions about strategy:

- reduction of expenditures for armaments,
- sustainable energy than plants,
- limiting the resource-intensive industries, which have no direct impact on sustainable human survival.

Global companies are trying to respond to these challenges by developing a special area management, and environmentally friendly or "green management". On the "greening" of thought in the companies, according to Bansal and the Rot (2000), influenced by:

- Striving to obey the law
- Gaining advantage over competitors,
- Respond to environmental pressures,
- Ethical interest
- Critical events and
- Top management.

If it is known that the number of the world's population increases each year as a result we can expect poverty, malnutrition, lack water, and thus the desire to market's factor on the basis of lack of income.

Industry will grow in proportion to energy facilities, which will be spent, and create new environmental problems.

4. Unused resources and energy opportunities of Serbia

Climate change, economic and energy crisis, water shortage and food prices pose a need for radical socio-economic changes in the direction of encouraging "green economy". This concept of economics, involves extensive use of renewable energy, job growth and investment in so-called green industries. [7]

With greater environmental sensitivity, and thus the tranquility of conduct "green area" of the administration, change is produced in a manner to be environmentally friendly, leads to changes in processes, while reducing consumption of polluting fuels, and non-use of waste, or policy and management system.

Given that Serbia is at the bottom of the ladder among the countries that the rationality of using energy in Europe, and that the need for costly energy increasing (liquid fuels and gas), should be directed to the strategy of increasing usage of renewable energy sources:

• Energy of solar radiation,

[7] www.rec.rs

- wind energy,
- Biomass,
- hydro-energy and natural and artificial watercourses,
- water energy (tidal waves),
- Geothermal energy.

4.1. Solar Resources

Energy from the sunlight is more than sufficient to meet the increasing demand in the world. Within a year, solar energy that reaches the earth 10,000 times greater than the energy necessary to meet the needs of the entire population of our planet. About 37% of world energy demand in the production of electricity (about 16,000 TW/h in 2001.). If this energy generated by PV systems with modest annual output of 100 kWh per square meter would be required area of 150 x 150 km2 of solar capture. A large part of the absorption area could be placed on the roofs and walls of buildings, so it would not require additional land area.

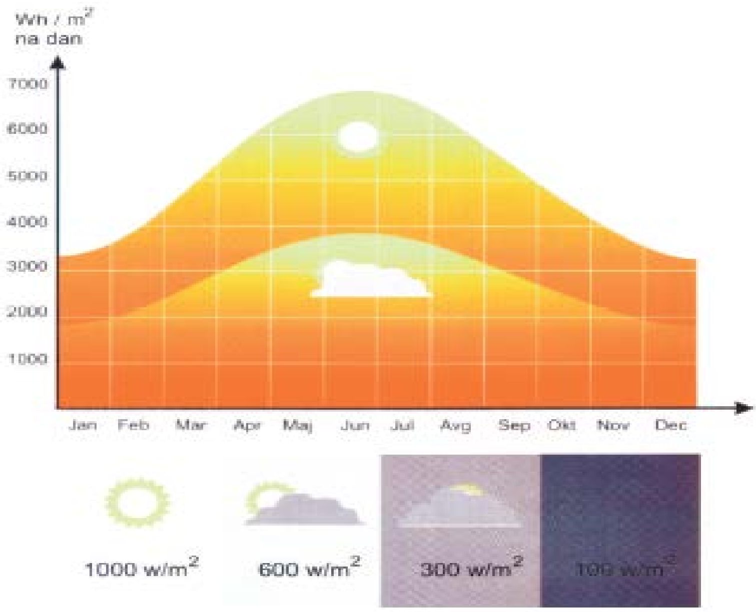

Figure 1: Direct and diffuse solar radiation on the surface of Belgrade

4.2. Possibilities of wind energy

The use of wind energy and wind energy development has recently been a very dynamic growth, especially in Germany, USA and Spain. Thanks to improved technologies cost electricity from these plants are very reasonable when the average wind speed greater than 6 m / s, with a value orientation of building wind turbines between 700 and 1,000 per installed kW.

According to the research institute of the Republic hydrometeorology, our country is one of the areas with significant energy potential, the specific location of mountain systems and continental-Mediterranean relations are highly significant winds from the eastern component, such as wind, south, east wind, in which is assignment a parts of Vojvodina and the mountain areas of Southern and Eastern Serbia, mostly 100-1500 m above sea level.

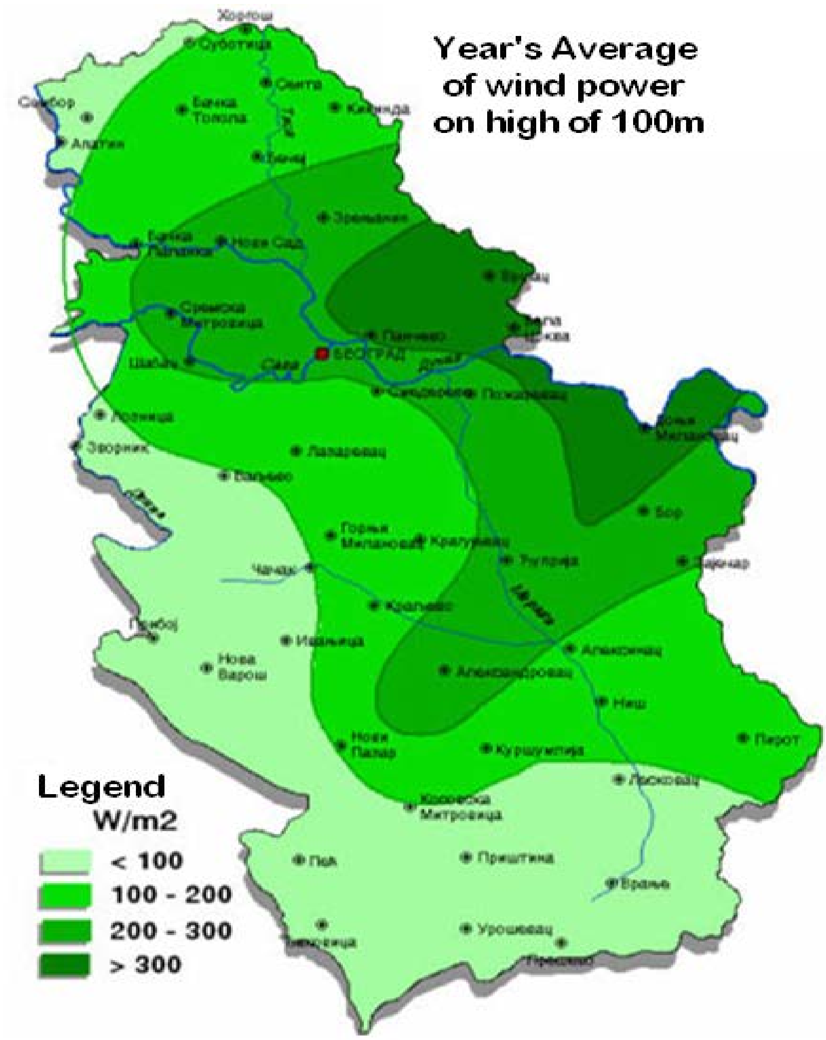

Figure 2: Average annual wind power at an altitude of 100 meters

No matter what kind of strategic model of development of electric power to choose will always be available to the needs, and possibly liability for the use of environmentally clean sources. If our overall objective of integration into the European Union, it is clear that the energy sector reform must be implemented in a way to monitor all processes of energy development in the European Union, and just the experience of most European countries show the necessity of including wind energetic in the national development strategy of the Serbian Energy. In this regard, the first step could be establishing wind energy potential and the determination of suitable sites for building the future of modern wind turbines for power generation in Serbia.

4.3. Hydro potential of Serbia

Research at the end of the last century has shown that Serbia can build about 850 small power plants whose installed capacity is estimated at 500 MW, annual production of about 1,600 GW/h, whose construction would save about 400,000 cubic meters of gas and 2.3 million of lignite per year which corresponds to value of 52 million dollars. The total production of electricity from hydropower plants this would increase by about 14%. If we bear in mind that for each kWh produced electricity consumed 1.4 kg of coal which combustion is releasing 1-1.5 kg of carbon dioxide, depending on coal quality and that we will soon have to apply the requirements defined in the Kyoto agreement on reducing greenhouse gases in the atmosphere, it is possible to see the real effects of investment in construction of small power plants. In the long run, high starting price investment compensates through environmental protection, renewable energy sources, reduction of electricity import and engagement of local expertise, industry and in construction of these facilities.

Hydropower is the economically most efficient, because they are included in the price exploitation cost of the production process and price maintenance, at no cost for the fuel which is the starting and basic raw materials in other processes.

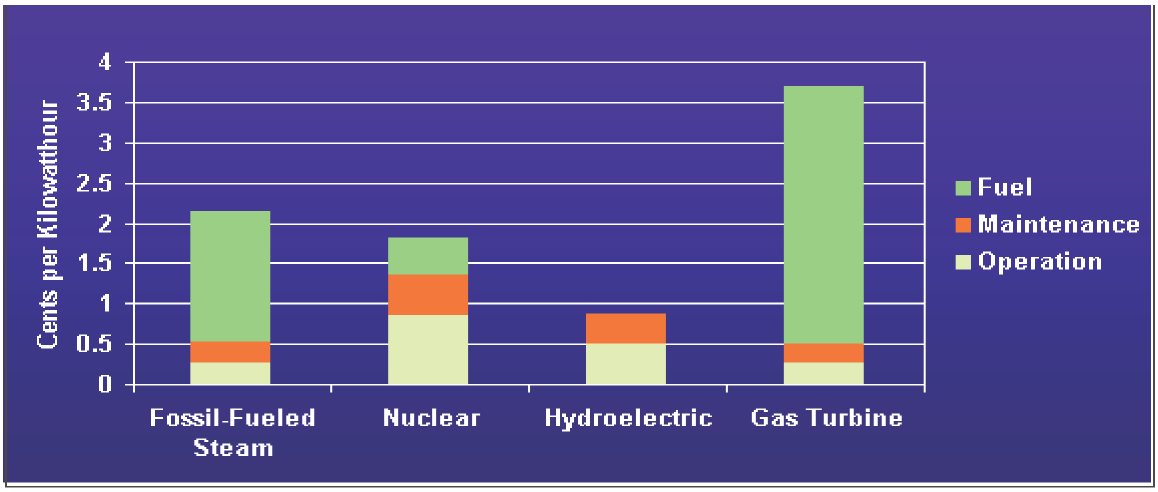

Figure 3: The cost of getting electricity to different processes

4.4. Capability of biomass

Under the biomass energy means energy that is released by oxidation of various organic materials, plant and animal biomass in terms of energy used to extract heat, either by direct combustion of solid wood forms of matter - trees and branches, wood, various plants, or combustion of gaseous and liquid fuels can receive appropriate technological processes of various forms of biomass. The share of biomass in total world energy consumption is about 15% (developed countries ~ 3% ~ 38% undeveloped).

When talking about these energy sources is usually made to:

1. **bio-mass** - wood, bark, wood waste, leaves, non-timber plant - in various forms, mostly fine-grained (chips, granules) or compact (pellets) for easier manipulation and mechanized;
2. **bio-fuel** - various oils or alcohol substitutes conventional liquid fuels, especially suitable for use in existing engines with inside combustion engines - bio-diesel, ethanol;
3. **bio-gas** - byproducts of decomposition of organic matters, usually at the waste disposal, a huge waste on farms and there it could be collect.

4.5. Waste potential

Biomass is the thing that is usually considered a waste. Biomass are the things lying around - the branches, garden waste, crop residues, crop straw, wood chips, bark and sawdust from sawmills, roots.

In addition to being largely eroded landscape of our country idyll, but also harmful for the ecosystem, the waste is considered one of the biggest problems and pollution of our environment, which have short and long term effects on the quality and length of our lives as well as the quality air, food and water that we take.

Useful solution in reducing an huge amount of waste is technological progress and civil development of environmental awareness, changing habits and adopting new ones. You need to have standards that will promote biodegradable materials, recycling or compression materials, and declared to be labeled with complete, partial and possibly the percentage of recycling. In particular should take care of the materials slowly or hardly dissolve, and manage scarce resources such as wood, metal.

Figure 4: The cycle of PET

Things that seem to no one need, can be used to produce electricity, heat or fuel. In the science, there are thought to be of the total annual increase of plant mass 1 / 3 can burn, 1 / 3 can be used in industry and 1 / 3 should be left outdoors for the development of vegetation and animal nutrition.

Thus, the life cycles of paper looks raw wood by consumers to the recycling and re-back the customer.[8]

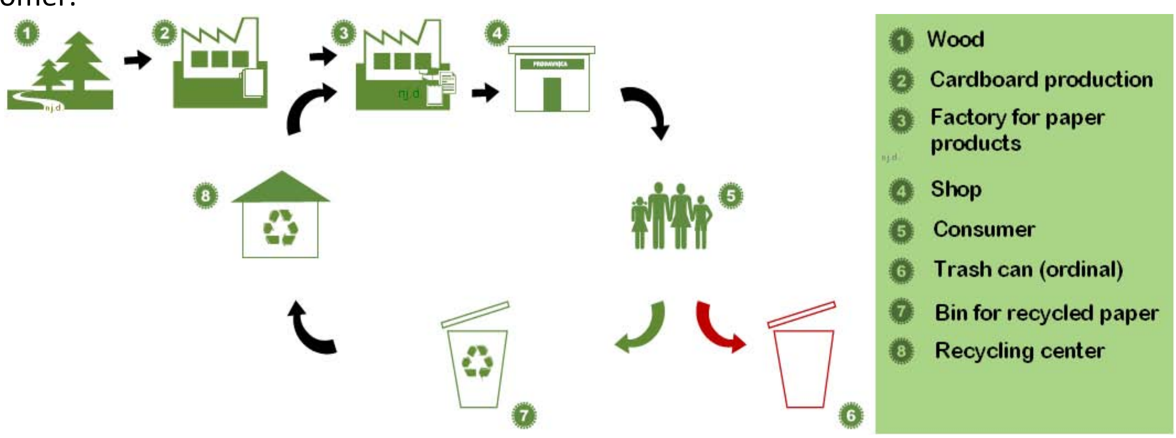

Figure 5: The life cycle of paper

Serbia has a relatively large energy potential of biomass due to the fact that forests cover about 24,000 km2, while agricultural land covers 45,000 km2. The energy potential of biomass is estimated at 115,000 TJ per year, of which 65,000 TJ rest of agricultural biomass, and 50,000 TJ potential of forest mass after forest exploitation. If we bear in mind that the production of coal from Kolubara basin of about 35 million tons can be obtained from 247.000TJ energy potential,

[8] www.sekopak.rs

then we can figure out what kind of energy potential for the biomass sector. Significant opportunities exist in and to produce biogas from various organic wastes, especially manure.

Some farm of 100 to 120 cattle given the amount of fertilizers that can be produced per day 400kWh 210kWh of heat and electricity. A necessary investment in building such a plant is around 60,000 euros with maturities between three to four years.

5. Instruments of development "green" economy

Achieving the goal to maintain or achieve a better quality of environment, it is necessary to carry some costs for the damage (on the side of pollutants and / or state), because, as a criterion for implementation of environmental policy performance occurs, i.e., than with the minimum resources that are available to achieve objectives in the field of environmental protection? Adopted the general rule is "PPP - Polluter Pays Principle", or the principle of polluter pays. As the most important goal of environmental management under the concept of "integral pollution control is the implementation of protection action in advance (prevention), then economic instruments must be subordinated to that goal, and sanitation have caused environmental problems.[9]

ECONOMIC - ENVIRONMENTAL INSTRUMENTS IN DEVELOPED MARKET ECONOMIES	
Taxes on emissions	proved to be most effective for stationary sources of pollution, and where there arise significant differences in their marginal cost of lowering between certain pollutants;
Taxes on products	usually applied to those items that are produced and used in large quantities and in different ways to use (in extreme cases, very dangerous and harmful products can instead put the tax on a product ban, in production or using);
Deposit System	used in those products that can be successfully recycled, reused or who seek to destroy properly disposal after use;
Trade Rights	contamination can be forth limited on specific region or entities (initially determining rights to pollution can be made direct allocation (assignment) or exogenous variable in a particular environmental program, or different types of auctions, how much of this initial distribution determines the eligibility of the program, as it is directly related to the costs of implementation.

Figure 6: Economic and environmental instruments in developed economies

[9] Aleksić Jordan, et al, *The Economics of ecology-ecology economy*, models and instruments, Obrenovac, 2008

ECONOMIC - ENVIRONMENTAL INSTRUMENTS IN SERBIA	
The fee for the use of natural resources	Special laws (exploitation of mineral resources, land use, water, forests, collecting and trading of wild flora and fauna, fishing, etc.)
Compensation for pollution	Government (determines the type of contamination, criteria for calculating payer compensation, amount and method of calculation and payment of compensation)
Special funds of the budget	Government to the ministries
Means of international financial assistance	Government through integrated programs

Figure 7: Economic and environmental instruments in Serbia

5.1. Induction of cleaner production

Activity that is related to all economic sectors, encompassing goals and priority actions, the introduction of cleaner production in accordance with international instruments[10]: IPPC, BAT, BEP, BATNEEC EIA, and LCA. This activity is closely related to the efficient use of factors of production, reducing energy intensity and the intensity of use of materials, development and implementation of management systems to industrial, and especially hazardous waste. [11]

Republic of Serbia can no longer provide a competitive advantage in international markets or cheap labor, or an abundance of natural resources. Either the structure or the quality of natural resources in Serbia is not sufficient for the growing needs of dynamic development.

Other problems include undefined strategic policy objective of cleaner production, non-harmonized legislation and non-enforcement of existing regulations in the field of environmental management, lack of regulations that detail the status of cleaner production (taxes, customs and other privileges), insufficient control of raw material use efficiency , production and products, the lack of a register of polluters, the lack of national BREF's (BAT Reference document - a reference document on best available technologies), lack of developed mechanisms for resolving problems inherited pollution during the process of privatization, an inefficient financial system and stimulate the economy for the introduction of cleaner production and environmental management system (EMS), lack of investment for infrastructure construction, lack of appropriate statistical monitoring of pollutants; technological inferiority of the industry, lack of appropriate modern attest

[10] *IPPC*- Integrated Pollution Prevention and Control
BAT -Best Available Techniques
BEP - Best Environmental Practice
BATNEEC -Best Available Technology Not Entailing Excessive Costs

LCA – Life Cycle Assessment

[11] National Strategy for Sustainable Development, Republic of Serbia, 2008

laboratory for testing features of the facility, lack of information and low awareness of pollution in terms of environmental protection.

Main programs and activities in this area are:

1) changes of the existing and adopting new regulations in order to foster the use of cleaner production and harmonization with EU legislation;
2) Introduction and / or promotion of efficient, sustainable and clean production and efficient use of energy;
3) construction of infrastructure in the field of cleaner production - realization of investment projects in the field of research (research and development research, and construction of industrial plants) - the development of industrial and technological parks, clusters, innovation centers and incubators;
4) establishing a system of waste management, with special emphasis on the possibility of waste minimization and utilization of waste as secondary raw materials and energy sources;
5) rapid completion of the restructuring and privatization;
6) the reconstruction or improvement of existing technological processes required to comply with the relevant BAT's;
7) improving environmental management in enterprises (EMS);
8) training in the field of environmental protection, implementation of cleaner technologies, energy efficiency.

Priority is the adoption of secondary legislation under the Law on Environmental Protection relating to: environmental quality standards and emission standards, system of environmental management, eco-label, import and export of substances that deplete the ozone layer, import, export and transit of waste; handling of hazardous materials, monitoring, information system and integrated database of main pollutants, the introduction of economic instruments (fees for use of natural resources and compensation for environmental pollution).

It is necessary to strengthen the Cleaner Production Centre to implement cleaner production projects and help the industry. It is necessary to accredit laboratories according to standard JUS ISO/ IEC 17025.

Economic instruments that are necessary for increasing the use of cleaner production are:

- *Compensation* for pollution and emission of pollutants;
- S*ubsidies* for research and development, for development projects in order to use renewable sources of energy and materials, financial assistance for the transfer of knowledge and technologies that already exist in the environment, tax breaks for manufacturers of equipment, subsidies for equipment and laboratory accreditation and the creation of conditions for the application and implementation of control measures, long-term loans on favorable terms for organizing and improving production, the introduction of EMS, the existing tariff concessions on import of necessary equipment and raw materials, tax incentives to potential foreign investors;
- *Stimulation* of economic operators to use cleaner production;
- *Tax incentives*, subsidized prices of products made in enterprises with cleaner production and documented who will be eligible to obtain the ecological character, subsidizing prices of energy obtained from renewable energy sources, vehicle registration subsidy, tolls and parking for those vehicles that use fuels obtained from renewable sources energy subsidies to manufacturers that have introduced EMS.

6. Agreements and strategies of Serbia in the "eco-industry

Consequently the company would promote the economic objective to ensure the production of consumer goods and services, with no adverse effects and not responsible for the consequences which may endanger the lives of future generations.

The main policy objectives of cleaner production and waste minimization are: reduction of waste generation, the introduction of technology, materials with low waste and recycling in interconnected industrial production, the introduction of programs to increase production to simultaneously reduce energy consumption, giving priority to preventive approach by reducing the amount of final waste any prevention of waste generation (using clean technologies, life extension of products and planned treatment of rejects) or re-use (recycling) and the introduction of the polluter pays principle, which would mean that the primary responsibility for waste generation bears the same one who produces. [12]

An objective through the introduction of cleaner technology to improve the competitiveness of the economy, encourages the development of “knowledge economy”, and raises the total welfare of the nation.

Political, economic and ecological reasons, as well as the growing need for ever more intensive use of existing energy resources that would follow accelerated industrial development, demand that Serbia is developing new energy sources and energy efficiency. In the next decade Serbia could move closer to more developed countries, if they take appropriate measures in the field of energy efficiency. The implementation of measures of efficiency of energy consumed, it could be saving $ 70 million annually, which can be invested, and in other development projects, or for the introduction of models of funding from savings.

Serbia is one of the signatories to the Treaty establishing the Energy Community Secretariat for East Europe, which is committed to cost-effectively improve end-use energy efficiency through institutional, financial and legal framework and create conditions for the development and promotion of markets for energy services and improvements that will be felt by consumers.

In the past five years, the Assembly of Serbia adopted an average of five bills per year, with some three hundred laws, thus fulfilling the obligations of domestic programs for integration into the European Union. Following the adoption of this schedule, you may be losing a real picture of things, requiring not only promises, but also the realization and implementation of regulatory policies, such as the promotion of environmental incubators, technology transfer to implement renewable energy, recycle the used packaging equipment, and follow hiring new workers.

In addition to the economy of Serbia on additional responsibilities around the harmonization of laws with "energy-climate package of the EU, harmonization will involve legislation, institutional change, strengthening human resources and investment in sectors that us the largest emitters of GHG (greenhouse gases), such as thermo-power plants, industrial energy, cement factories, refineries, steel mills and steel mills, paper, glass, Fertilizer, and others.

By establishing the first international "system of the EU emissions trading (ETS) in the world, in order to effectively deal with climate change, the application 2005., Showed the possibility of cooperation in 30 countries of the European Union, and Norway, Iceland and Liechtenstein. This agreement is important because emissions of carbon dioxide, a company reduce the goal to 2020.god. "20-20-20" means increased use of renewable sources, efficiency and reduces emissions by 20 percent. These systems have many companies reduced costs, improved the management of investments, and are open to new jobs.

[12] LIBER PERPETUUM, OSCE book on the potential of RES in Serbia and Montenegro

Trade requires a system for measuring, reporting and verification, i.e. verification of greenhouse gas (MVR-Monitoring, Verifying, Reporting), which gives information what each participant broadcasts, which collect data and determine the reference body. ETS is currently the second phase, which began in 2008.year and lasts until the following year, when the next commit 2013th and lasts until 2020, when it will be introduced in the stock purchase emissions for its own purposes. Exceeding certain emissions allowances, provides for fines, and savings through energy efficiency measures can sell them. [13]

Based on the project which was signed in 2005th vol. between UNIDO and the State Union of Serbia and Montenegro in the realization of "clean production" in a number of business organizations attended the six companies from Serbia, who have a desire to “give a rise” to other companies in the best way to learn about activities planned in the future the National Center for Cleaner Production in Serbia, whose center is to be, formed of Technology and Metallurgy in Belgrade.

Republican Ministry of Environment has initiated many actions to “clean up Serbia”, which is oriented towards environmental protection, raising environmental awareness, removal of illegal dumps and capacity building of eco-industries. The fund for environmental protection are intended assets classified as support the development of eco-industry, whether private persons or entrepreneurs, who had the obligation to repay after one year of waiting, in the following five interest rate of 4% per annum. The second line was to support local governments in carrying out environmental projects, which are administered grants to address local or regional environmental problems. From the investment plan is intended to grant to municipalities the most critical utility equipment to use, while the Employment Service employ certain persons.

Serbian Chamber of Commerce at the end of 2010 established the Council for the recycling industry, at the initiative of members of the recycling sector, whose mission is to promote "green" industry, to raise environmental awareness and management of employees in companies, to develop the market of recycling and environment, and that there ongoing dialogue with management and the wider regional business ties recycling centers.

It can be suggested and development of environmental industries, made up of mini-entrepreneurs, with their ideas, which would use biodegradable materials, with no negative impact on the environment. Other potential ideas in the field of agricultural production, pharmacy, chemical industry, construction, electrical components, a perspective from renewable energy sources in Serbia.

According to the current minister in charge of ecology, wins a green economy is possible with a reliable legal framework, so that all authorities will start to do their job by punishing those who pollute the environment, but it is forgotten that Serbia is one of the polluted countries in Europe. European institutions have made a series of guidelines that compose the state regulations, which she did, has signed international agreements, but not the check of assets and liabilities relating to the audit of compliance with them.

[13] www.pks.rs , “Корак”,(Step) Journal PKS, 2011

7. Concluding remarks

Analysis of the overall industrial development in the last decade of the last millennium shows that sustainable development requires the implementation of institutional reforms and the wider economy by increasing productivity and gross national income.

Most of the measures undertaken to protect the environment is ex post character. It comes down to healing the environment through various projects to reduce pollution using the purification installations and the introduction of fines for broadcaster's harmful substances. It seems that the only possible to conserve the existing accident, in a way to track the perpetrators, to introduce technologies that are prescribed confirmed that there are strategies of international environmental council at the UN, which will act preventively, so as not to mean more jeopardized.

One of the main goals of the "Millennium Declaration" UN environment both nationally and globally, as the basic conditions for future development and reduce poverty in the world. UNIDO as a specialized UN organization is focused on two main elements: exchange of technology and construction of new facilities which will lead to overall development of society and taking a more favorable market position. The aim is to increase productivity and market competitiveness and the development and application of technologies that are in accordance with the requirements of environmental protection and sustainable development.

In addition to all of Serbia's aspirations to join the modern countries of the world, at least for its environmental consciousness and behavior, seems to be a long time afore environmentally advisedly population of our country. Not only regulation, which was taken from the strategies of the Association, for several generations more advanced standard of the Scandinavian countries, to further slow down the fact that here it is difficult to implement.

It is essential that the strategy of sustainable development recognize the contribution to environmental protection, which will consist of economic and environmental justification for the exploitation of raw materials from nature, but also the potential use of harmful substances in the biosphere and in general a normal life.

If most of the strategies adopted and the rules and acts dignified a light of application, which regulate the incentives, obligations and fiscal elements, the environment would be the best practice and staff training, could not wait the real economic effects in the forthcoming period. The time is upon us. Nevertheless, the (p) turns cleaner conscience!

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POSSIBILITY OF COPPER EXTRACTION FROM THE FLOTATION TAILINGS OF THE BOR COPPER MINE

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Abstract

Flotation tailings of the Bor copper mine contains on average 0.2% copper, and represents a potential raw material for production of copper. Leaching of low-grade ores and tailings is very applicable for obtaining additional quantities of metals, as well as regarding the concept of environmental protection. This paper presents the results of the physical-chemical characterization of the starting sample. Furthermore, a number of factors were investigated, which affect the leaching of copper from flotation tailings (sulphation temperature, leaching temperature, leaching time, concentration of sulfuric acid, agitation speed and solid/liquid ratio).

Keywords: flotation tailings, sulphation, leaching

ADSORPTION OF ZINC IONS ONTO WHEAT STRAW

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Abstract

The paper presents the results of adsorption of zinc ions from synthetic solution onto wheat straw. Physical and chemical characterization of wheat straw was performed. Adsorption of zinc ions onto wheat straw was found to be a quick process. The equilibrium was reached for less than 20 minutes Change in the initial pH value as well as the adsorption kinetics of zinc ions were both investigated and considered. Kinetic studies indicated that zinc adsorption followed the pseudo-second order model. The maximum adsorption capacity was 3.25 mg/g. The adsorption equilibrium fallows Langmuir adsorption model. The results show that wheat straw can be used as cheap, natural adsorbents for the adsorption of zinc ions from industrial effluents.

Keywords: wheat straw, zinc ions, adsorption

1. Introduction

Different processes of treating waste waters give different removal efficiencies. Besides the existing of conventional technologies for the purification of waste waters from metal ions, considerable attention has been paid recently to bio-sorption processes [1]. Biosorption of heavy metal ions from aqueous solution is a new, still in development, a process that has proven effective for the removal of heavy metal ions from aqueous solution [2]. Different natural by-or waste materials as called. "low-cost" adsorbents have been examined. It can be said that biosorption could become a potential alternative to conventional adsorption technologies for purification of industrial water with low content of ions of heavy non-ferrous metals [3].

The main advantages of biosorption as potential method for removing heavy metal ions from aqueous solutions are its effectiveness in the elimination of metal ions from water, accessibility and price of natural adsorbents, which are waste and very often have no economic value.

The adsorption capacity of wheat straw for the following ions of heavy metals: Cu, Cd, Cr, Zn, Ni, Pb was investigated [4-5]. Straw is characterized by high contents of cellulose and hemicelluloses (71.24%) and lignin (23,22%), which makes it a potentially effective biosorbent for waste water purification of heavy metal ions [6].

The aim of this work was to investigate the adsorption ability of wheat straw as a potential adsorbent for the adsorption of zinc ions from aqueous solutions. That comprises to determine the equilibrium adsorption conditions, as well as the kinetics and mechanism of adsorption, but also to determine the total cation exchange capacity (CEC), and the dominant exchangeable cation.

2. Experimental

2.1 Materials and methods

A series of the adsorption experiments were performed by using $ZnSO_4$ stock solution (0.2 g Zn^{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. The concentrations of considered heavy metal ion during experiments were determined using a PerkinElmer - 403 atomic adsorption spectrophotometer, while the pH change was measured by a WinoLab - 720 pH-meter.

Wheat straw collected from a local field was used as an adsorbent in this study. The wheat straw was firstly sieved through a set of laboratory sieves and the sieve fraction (-1 + 0.4) mm was used in the adsorption experiments. Dry wheat straw was weighed, then this weight was rinsed with 200 ml of distilled water, dried again at 90^oC and used for further characterization or in the adsorption experiments. No chemical pretreatment of wheat straw has been performed.

In order to determined chemical composition of wheat straw, wheat straw was burned, annealed, and the ash was analyzed. The percentage amount of ash after burning wheat straw was 6.2 %. The chemical composition of wheat straw are presented in Table 1.

Table 1 - Chemical composition of wheat straw

Oxides	SiO_2	CaO	K_2O	P_2O_5	Al_2O_3	MgO
Content (%)	36.36	6.83	28.62	3	0.29	3.25
Oxides	Fe_2O_3	SO_3	Na_2O	TiO_2	MnO	Ukupno
Content (%)	0.57	16.12	4.14	0.017	0.11	99.31

Total oxygen demand (TOD), as well as the concentration of alkali and alkaline earth metals leached by water during rinsing the wheat straw, was also determined prior the adsorption experiments. TOD was determined volumetrically by means of $KMnO_4$ solution. Based on its consumption, the amount of oxygen needed for the oxidation of organics in the rinsed water is then calculated. The consumption of oxygen was 18 mg/L.

Besides the TOD, the total cation exchange capacities of alkali and alkaline earth metals that are exchanged in the reaction with NH_4Cl were also determined [7]. The results are given in Table 2.

Table 2 - The content of alkali and alkaline earth metals in solution after mixing the wheat straw with 1M NH_4Cl

Ion	Na^+	K^+	Ca^{2+}	Mg^{2+}
Concentration (mmol/g wheat straw)	0.27	0.41	0.90	0.28

The determined total cation exchange capacity (CEC) of the wheat straw was 1.86 mmol Me^{z+}/g. (Me^{z+} here denotes alkali and alkaline earth metal ions). From Table 2 it can be seen that the dominant exchangeable ion is Ca^{2+} having the highest cation exchange capacity (CEC), while the capacities of Na^{+}, K^{+} and Mg^{2+} are presented in a much lesser extent. This means that the calcium ions present in the straw structure, changes most likely with zinc ions by ion exchange mechanism during the adsorption process.

2.2 The adsorption of Zn^{2+} ions on wheat straw – Experimental procedure

Adsorption experiments were carried out in a batch reactor with a stirrer in order to keep the adsorbent in suspension. Stirring of the suspension was performed with a magnetic stirrer, at a constant speed of 300 rpm. Wheat straw, previously rinsed with water, has been used as adsorbent in all experiments. As the aqueous phase a synthetic solution of zinc with a constant and known initial concentration of Zn^{2+} ions was used. Wheat straw (weight 1 g), was brought in contact with 50 ml of the zinc 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 Zn^{2+} ions. From the mass balance the amount of adsorbed zinc was determined. The adsorption capacity and its change with the process time was 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 zinc ions on 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.

3. Results and discussion

The results of analyzing of samples after rinsing of wheat straw by water and after loading it with zinc ions by adsorption are presented in Table 3. It can be seen that there is a self-leaching of a given ions with water (mostly potassium). After the adsorption, in solution are largely calcium ions present, which probably together with hydrogen ions by an ion exchange mechanism changed with zinc ions.

Table 3 - Concentration of alkali and alkaline earth metals in the solution after rinsing wheat straw with distilled water and after adsorption of zinc ions

Concentration (mmol/g wheat straw)	Na^{+}	Ca^{2+}	K^{+}	Mg^{2+}
Rinsed water	0.0064	0.027	0.154	0.012
Zinc solution after adsorption	0.014	0.045	0.012	0.022

3.1. Change of initial pH of solution with time

Monitoring the changes in pH values during the adsorption experiments with the process time, it was obtained dependence shown in fig. 1.

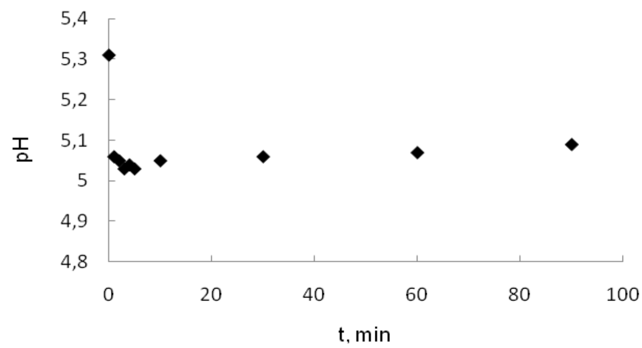
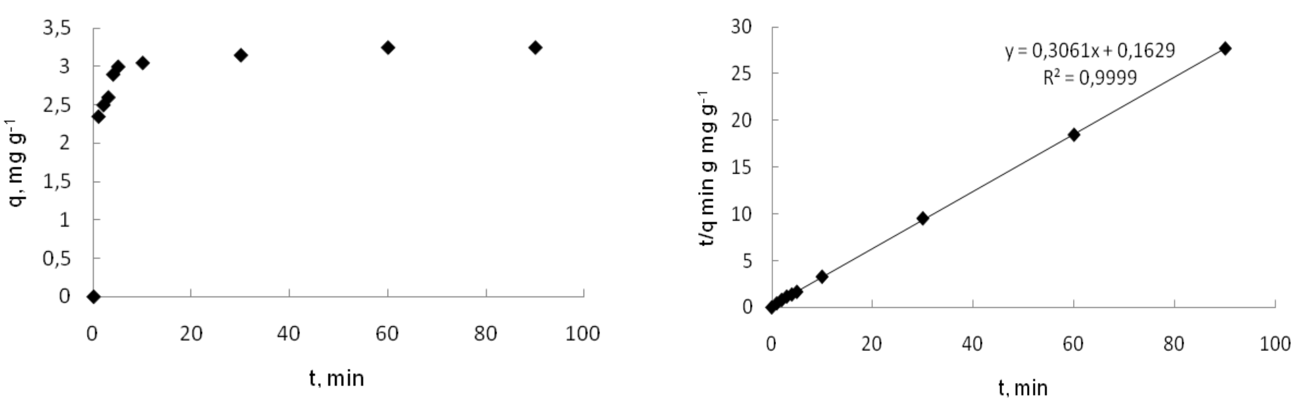


Figure 1 - Change of initial pH value of solution with process time

From figure 1 can be seen that pH value suddenly drops in the first minutes of the adsorption process, reaching a constant and unchanging over time value. Decreasing in pH during the adsorption process are due to the deprotonation of functional groups (hydroxyl, carboxyl, etc.) present in molecular structure of wheat straw and release hydrogen ions, which by an ion exchange mechanism exchange with zinc ions.

3.2. Kinetics of adsorption

The change of adsorption capacity with time is shown in fig. 2a. In the first 5-10 minutes of a process, adsorption takes place quite rapidly, the capacity increases with time, reaching a maximum value (3.25 mg/g). Linearizing the curve from fig. 2a by plotting t/q(t) against the process time gives a straight line with a very good fitting with the pseudo-second order reaction model (fig. 2b). From fig. 2b it can be seen that the regression coefficient is close to unity (R^2 = 0.99), confirming a good fit of the experimental results with the considered second order kinetics model of adsorption.



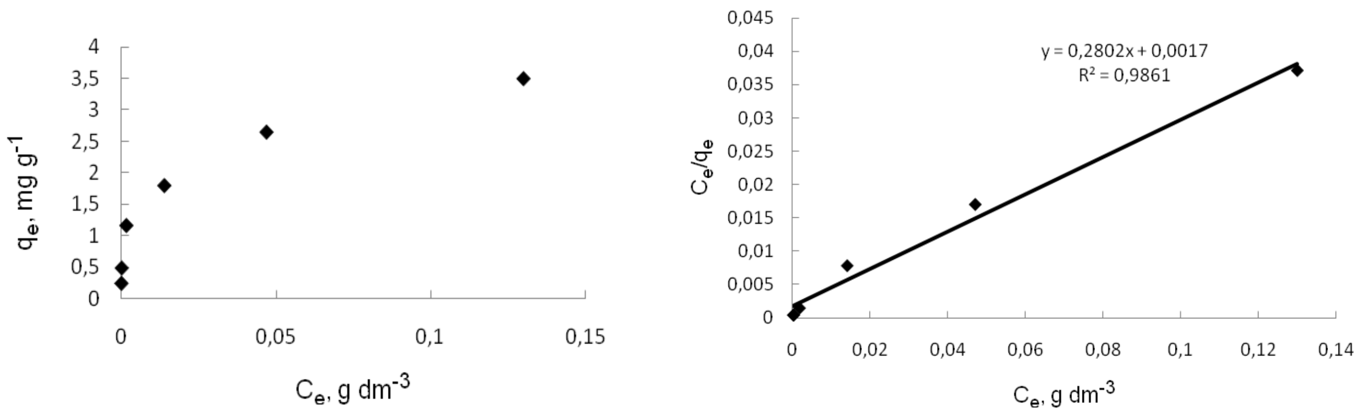
a) *b)*

Figure 2 - a) change of adsorption capacity with process time; b) pseudo second order kinetic model

3.3 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 used in water and wastewater treatment, experimental equilibrium data are most frequently modeled by the relationships developed by Freundlich and Langmuir [8].

The adsorption isotherm results are shown in fig. 3a. Linear Langmuir plot is presented in the fig. 3b. According to the regression coefficient (R^2 = 0.986), the experimental results provide a very good fitting to the Langmuir model.



a) *b)*

Figure 3 - a) adsorption isotherm; b) linear Langmuir plot

4. Conclusion

The results presented in this paper shows, that wheat straw can be successfully used for the adsorption of zinc ions from aqueous solutions. Maximum capacity, corresponding to equilibrium saturation of adsorbent, is achieved after 60 minutes and is 3.25 mg / g. Kinetics of adsorption follows the pseudo-second order reaction model. The ion exchange mechanism is supposed, where zinc ions exchange both with calcium and hydrogen ions present in molecular structure of wheat straw. The adsorption isotherm fits with Langmuir equation. The results show that wheat straw can be used as a cheap, natural adsorbents for the adsorption of zinc ions from aqueous solutions.

Acknowledgements

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SOOT AS ENVIRONMENTAL POLLUTANT

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Abstract

This paper presents and analyzes the data which influences on the formation and movement of soot particles, with the aim of comparing daily concentrations and determination of seasonal variation in mentioned pollutant concentrations. The data in this paper are related to the industrial area of eastern Serbia, which is, by geographical location, population, level of use of outdated industrial technologies and presence of coal as a fuel in heating systems of residential buildings, a zone with a high degree of pollution. For easier determination of variations in pollutant concentrations, the measurement results are divided to winter and summer. Based on the results analysis it can be observed that the presence and position of winds greatly influences on the manner and degree of contamination from soot particles. Soot from the air is increased in winter months and it influences on environment pollution in whole.
Keywords: Soot, pollution, wind impact, environment, eastern Serbia, air, soot.

1. Introduction

Particulate matter consisting of a mixture of solid and liquid particles of organic and inorganic substance that are suspended in the air, and one as a complex mixture of very negative impact on the human body, because inhalation of entries and deposited in the respiratory system. At the same time air pollution directly affects soil and water. Size, chemical composition, and the life of particles in the air, depend on the process by which the particles are formed. The basic components of particulate of air are sulfates, nitrates, ammonia, sodium chloride, carbon, mineral dust and water. Particulate matter in the air appears in different shapes and sizes starting from the diameter size from several hundred to several microns [1]. The concentration of particulate matter in ambient air is now generally quantified by measuring the concentration of PM10 (particles with diameters smaller than 10µm) or PM2.5 (diameter less than 2.5µm).

Carbon black is a form of air pollution in the form of particles of carbon with tar, which occurs in the process of incomplete combustion of fuel materials that are carbon based. Chemical composition of soot particles are the substance of organic and inorganic origin. Substances of organic origin, such as benzopyrene, benzantracen, pyrene, fluoranthene, krisen, have a carcinogenic effect. In addition to the substances of organic origin soot particles containing inorganic acids also, of which sulfuric acid is the most frequent [2].

Diameter of soot particles is the order of about 0.1µm. Because of its size soot have a low rate of sedimentation. Under certain conditions, small particles combine to form particles of about 5µm. In urban areas, annual concentrations of soot particles are high. The main source of carbon black urban areas is broken boiler that does not perform complete combustion of fuel. A smaller source of soot particles are vehicles that are used as fuel oil. Soot particles create a problem to communal by increasing the external contamination of exposed surfaces (facades, monuments, streets, etc.).

Concentrations that would be safe can be safely recommended. Air protection in Serbia is regulated by a relatively new law and regulations: the Law on Air Protection [3] and the Decree on conditions and requirements for monitoring air quality [4], where among other things, defines the conditions of measurement of concentration levels, as well as limits concentration of pollutants harmonized with EU requirements.

Regular measurements of airborne particles are of great importance for understanding the degree of air pollution in urban areas. The content of heavy metals in airborne particles was increased to measuring points that are in the direction of the wind and that are closer to the industrial zone.

Monitoring of air pollution based on particles of soot, its emergence and impact on the living world and its environs is a relevant today topic and as such is studied from different aspects by different authors [5-10].

Serious consequences of air pollution that have occurred in the twentieth century made it necessary, regular monitoring of the presence of pollutants in the air, water and soil. A special emphasis is given to the introduction of effective methods and establishment of border control system for water and soil composition on this basis we can make an objective assessment of the quality of environment.

This paper provides information about the presence of soot particle in the air, which directly affects the water and soil pollution in urban zones. The experience of one analyzed region can serve as an example for other regions.

2. Experimental

In order to have regular monitoring of the presence of pollutants in the air, it is necessary to perform a detailed analysis of the air and make a good choice of measuring points on which will be followed of suspended concentration of particles. Measuring the concentration of suspended particulate matter is carried out periodically at several locations using a portable station in the period of one year. The choice of temporary measuring points is planned on the basis of activities of industrial production facilities and its surrounding areas and weather forecasts (the prevailing wind direction), which depends on the season and condition of vegetation.

Soot sampling is done at the appropriate filter paper which is placed on automatic device, with eight cannels sampler, which is done in 24 hours atmospheres air sampling to determine SO_2, NO_x, HF and soot by the standard British method. From solution is determined automatic device SO_2, and filter paper are collected dusts of soot and heavy metals.

Carbon black is determined by photoelectric Reflect-meter intensity spots on filter paper. As air passes through the filter paper soot particles are retained on it to form a stain. Particles that are retained are more or less about 10µm in diameter. The density of spots partly depends on the mass of soot particles, and partly from the origin of soot. The concentration of soot is determined by measuring the density of spots obtained by the photoelectric Reflect-meter where the measured intensity, based on standard tables, given the amount of soot in $\mu g/m^3_N$. Values of the results are recorded in the monthly newspaper of record.

3. Results and discusion

Special importance to the spatial distribution of air pollution has a frequency of wind. Measurements were taken at the exact point. Results are obtained from the data in the period of one year. The average monthly maximum wind speed was 0.7 m/s in March and the minimum average value was 0.3 m/s in September. In Figure 1 can be seen that increasing the wind speed decreased the average particle concentration.

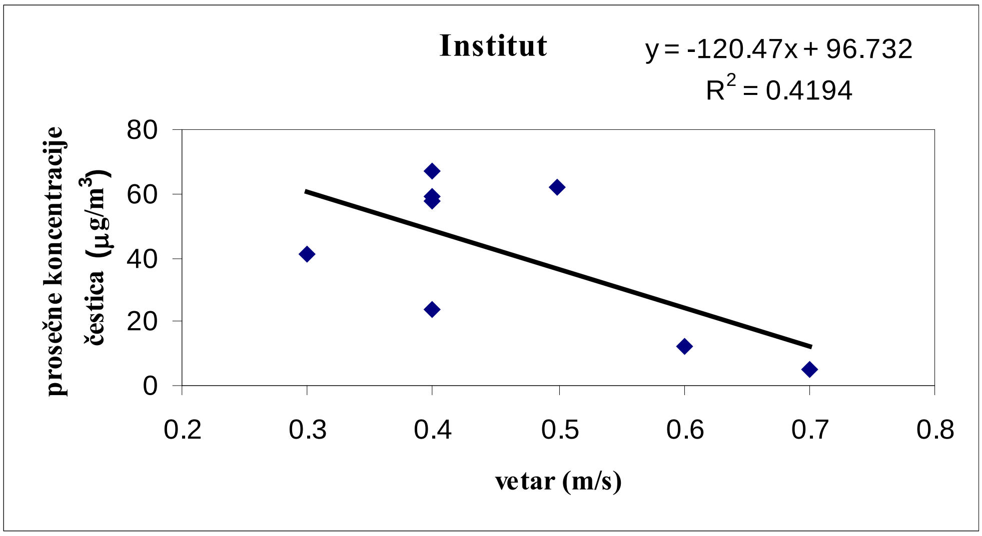

Figure 1 - Effect of monthly mean wind speed at an average monthly concentration of airborne particles.

Primary importance in the spread of pollutants is the direction of transport of air pollutants which, when there is no wind, spread solely by diffusion. In this case, the transport of substances in the air is slowed down as allows increase their concentration per unit time. In Figure 2 shows the effect of monthly mean wind of silence to the average monthly concentration of airborne particles in the same year at the measuring point. In Figure 2 can be seen that when the wind does not mean concentrations of particles are slightly increasing.

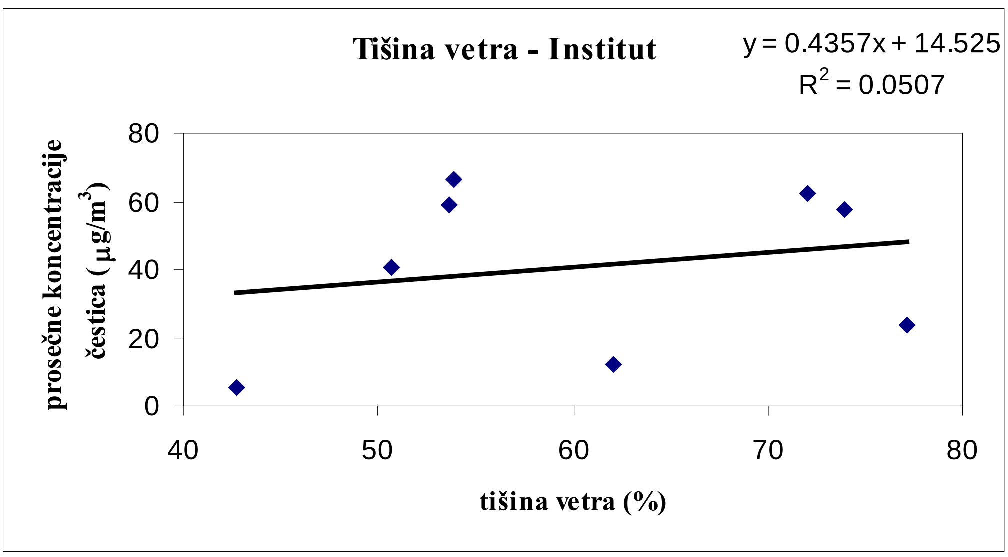

Figure 2 - Effect of monthly mean wind of silence to the average monthly concentration of airborne particles in the period of one year.

The contact of water vapor or droplets (precipitation) in pollutants such as sulfur dioxide, nitrogen dioxide and others there is a chemical reaction to create products and changes acidic and pH values. The amount and intensity of rainfall is influenced by pollutant particles in the air. In Figure 3 presents the effect of monthly mean precipitation on a monthly average concentration of airborne particles on the measuring in point. From the figure 3 we can see that with increasing concentration of precipitation particles is not significantly changed.

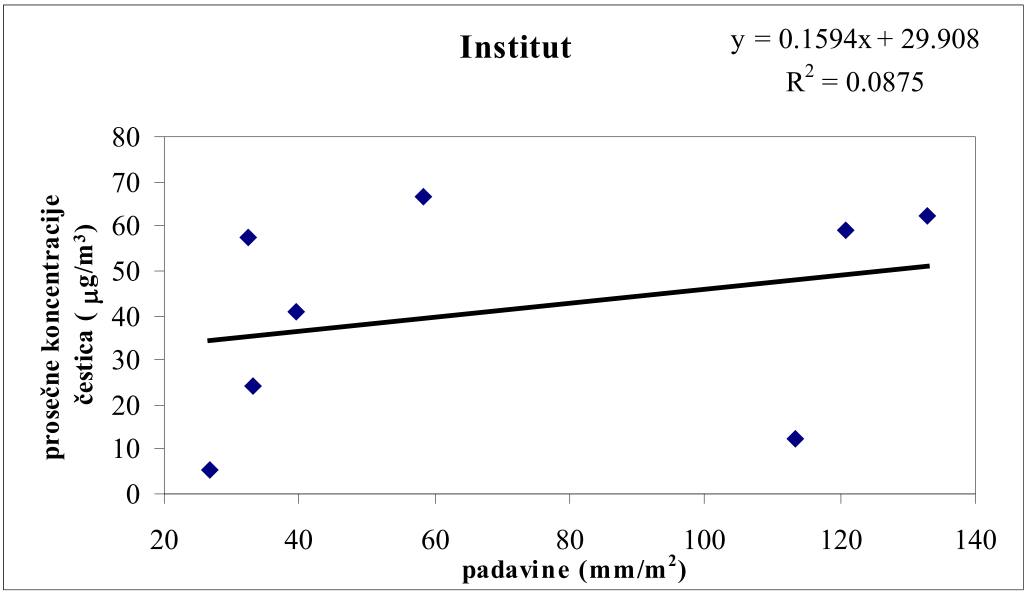

Figure 3 - Effect of monthly mean precipitation on average concentration of suspended particles in the period of one year.

Current state of air quality in Bor and its surroundings a need for urgent actions impact on recovery and rehabilitation of the entire environment, and in particular to reduce further pollution.

4. Conclusions

For understanding and proper monitoring of water quality and soil, it's a good knowledge of air pollution, too. In addition to quantitative results of analysis of the composition of air, you need to know the influence of external factors such as impact of winds and weather influence on physicochemical transformation of pollutants in the air. Transport and industry are the main sources of air pollution in Bor region in Serbia. During the combustion of different types of fuel in the engines or factories, but the release of energy is released into the atmosphere and a large amount of substances, such as CO, CO_2, SO_2, oxides of nitrogen, ash and soot. The result of increased concentrations of soot particles is a cancer of skin and manifestation affect which carbon dioxide. The effect of sulfur dioxide from the air in the respiratory organs of man is amplified in the presence of soot particles whose presence is usually higher in winter and we should have attention.

Acknowledgment

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GOLD EXTRACTION FROM THE POLYMETALLIC SULPHIDE ORE

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Abstract

This paper presents an analysis of processes and technological flow-sheet for processing the polymetallic sulphide ores containing the precious metals. The chemical separation processes of separation the lead, copper, zinc, gold and silver were discussed. A detailed overview of the existing experiences was given on more and more increasing application of pressure oxidation in treatment of refractory gold ores. Also, the ecological aspects of treatment the polymetallic ores are presented.

1. Introduction

Since 1954, when it was first developed and worldwide patented the hydrometallurgical process for production of nickel, cobalt and copper from sulphide ores was developed for the first time and used in the world, the researchers are intensively going in this area [1]. In recent years in the U.S. using the hydrometallurgical processes gets about 20% of the total copper production [2]. Using partial or complete hydrometallurgical processes can extract almost all of 82 elements with metallic properties.

The successful application of heap leaching to the extraction of gold from low-grade deposits has been one of the main factors in higher output since the 1970s, especially in the United States. It is a low cost process that extracts a soluble precious metal or copper compound by dissolving the metal content from the crushed ore.

A sprinkler system is then laid along the top of the ore pile through which a solution of dilute cyanide is sprayed. The cyanide percolates down through the heap for several weeks, leaching out the gold. This solution, now enriched with gold, drains off the bottom of the pad into what is known as the "pregnant pond", from which it is pumped to the recovery plant.

It should be noted that cyanide is extremely toxic and must be handled with special care.

Heap leaching of gold was pioneered in the United States in 1973 at Placer Development's Cortez open pit in Nevada and proved on a larger scale at Pegasus Gold's Zortman Landusky mine in Montana. Although it is low cost, recovery rates average only sixty to seventy per cent, significantly less than with conventional milling. But it has enabled low-grade ores, which otherwise might not be economically viable, to be processed. In the United States, where heap leaching is used most extensively, half of all production is won by this method.

Despite the fact that hydrometallurgical processes are based on well-known methods of analytical chemistry, the technological flow-sheets of hydrometallurgical procedures are inherently more complex than the other conventional methods, such as gravity concentration or concentration by flotation. The complete process involving the treatment of hydrometallurgical processing of raw materials allows processing not only the oxide ore but also the ore and concentrate with very complex structure, such as sulphides [3].

This paper discusses the processes and technological flow-sheet for treatment the polymetallic sulhide ore. The focus of this presentation is referred to the possibilities gold and silver separation from the refractory ores and concentrates. Starting material for definition of this hydrometallurgical process is a polymetallic sulphide ore, containing gold (10g/t) and silver (150g/t). Polymetallic sulphide ore contains sulphides of copper, zinc, lead, iron and other metals. It is believed that there are real prospects for processing the gold-bearing sulphide ore using purely chemical procedures, with the possibility of 95% extraction of precious and nonferrous metals. The basis for this possibility lies in the fact that there is no need for any previous flotation concentration of metal and that the fine comminuted ore can be economically processed.

The flow-sheet of considered process, predicts the oxidation of ore in the presence of oxygen under pressure. The excess acid from the solution, obtained by the pyrite oxidation is neutralized by limestone, the pulp is filtered and copper and zinc are obtained from sulphate solution. Insoluble residue is treated to produce lead, silver and gold.

2. Basics of the process

Polymetallic sulfide ore with high content of gold and nonferrous metals is a suitable raw material for treatment by hydrometallurgical process. Treatment of this ore by pyrometallurgical process would not be optimal, because in addition to copper, high degree of extraction could not be achieved for other metals. In addition, the problems, related to environmental protection, should be expected because of release the significant quantities of arsenic zinc and lead.

Technological flow-sheet, shown in Figure 1, implies a complete oxidation of ore in an autoclave using the oxygen as oxidant. By this, all copper and zinc are transferred into soluble sulphates, until lead, silver and gold lag in the insoluble residue. Sulphuric acid is concentrated by pyrite oxidation, which is neutralized with lime milk, and it is precipitated using ferric hydroxide.

Insoluble residue is filtered, and copper and zinc sulphate remain in the solution. Copper is separated from solution by selective liquid-liquid extraction, and then extracted in the form of cathodes in cells with insoluble anodes. Cathode zinc is obtained by electrolytic treatment. Lead is dissolved from the undissolved residue by diethylene triamine, and separated in a soluble form and using carbon dioxide precipitated as the lead carbonate. Pure lead carbonate is reduced to the metallic lead in a melting furnace.

Particles of gold and silver, obtained by the process of sulphide dissolving, are transferred into cyanide solution. After adsorption and desorption processes from active carbon, gold is transferred into solution of higher concentration from which the gold-bearing sludge is obtained using the electrolytic process, and it is suitable for obtaining the high purity precious metals (99.99%).

Today, in the world, a large number of facilities is in the use where some parts of the process, presented by flow-sheet in Figure 1, are present. Based on the available literature data, the data on production costs could be found. In addition, the aspects of prior treatment of this ore will be discussed in detail using the oxidation under pressure as well as the basic processes in the auto cyanide solutions from which the anode slime is obtained.

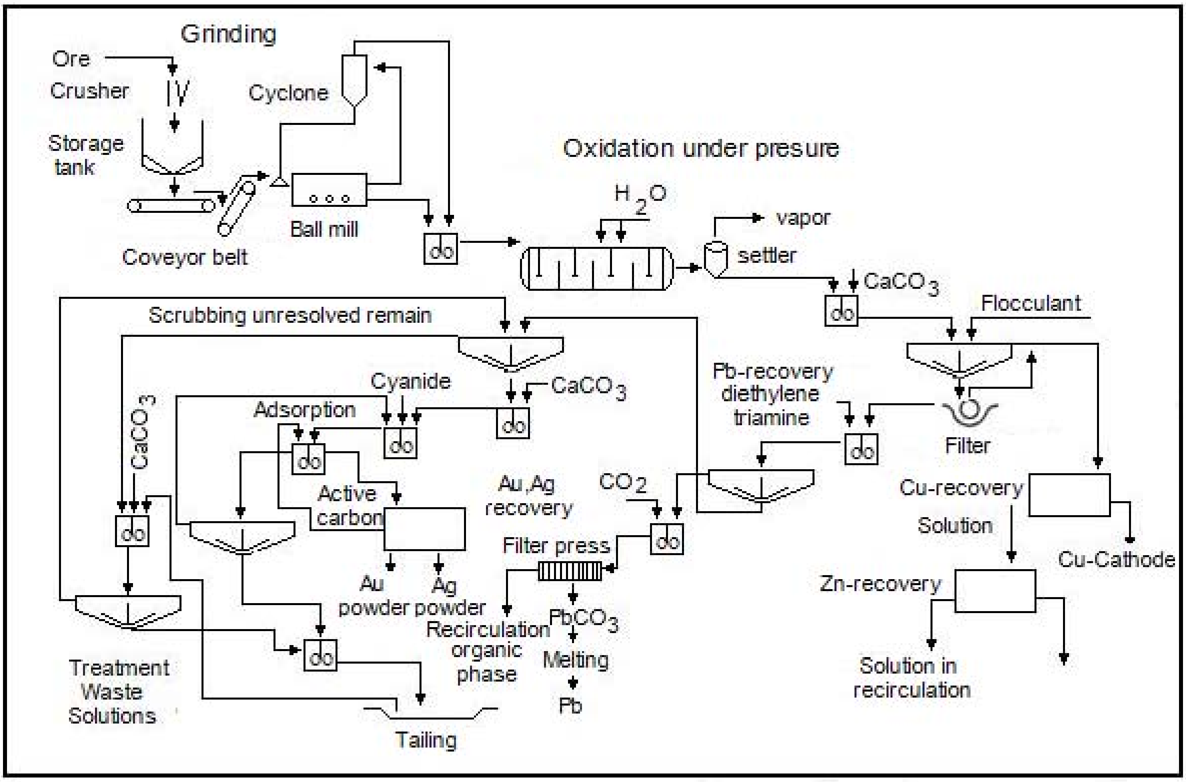

Figure 1. Technological process of treatment polymetallic ore

2.1. Oxidation under pressure

Before the oxidation process, the procedure of grinding ore is carried out to the particles of suitable sizes. Wadsforth showed that there is a correlation between oxygen consumption and particle size. In fact, oxygen consumption and therefore energy is proportional to the surface, but if the particles are too small, then there was a sudden increase in demand for energy. In the case of treatment the polymetallic sulphide ore with increased content of precious metals, as much as possible degree of comminution is desirable, but to some extent in the particle size of 75 μm. The parameters of laboratory tests with particles of much smaller sizes (3, 5 and 7μm) would be find in literature, which, however, are not applicable in the real conditions because of the economic irrationality [4].

Due to a lack of clear specific objective criteria to qualify the certain gold ores as the refractory ores, the existing literature presents some confusions about the definition of this term [5]. However, most of the term refractory gold-bearing ores and concentrates include raw materials from which a significant amount of the total present gold cannot effectively extract by the common method of cyanidation, even after high degree of comminution [4].

Pyrite (FeS_2) and arsenic pyrite (FeAsS) possess typical characteristics of refractive gold ore while the other sulphides (Fe_7S_8, AsS, As_2S_3, Sb_2S_3, ZnS, Cu_2S and $CuFeS_2$) are refractory to a higher or lower degree. An important task that arises in connection with the previous problems is precisely defining the specific causes of specific refractory behavior as only the treatment that fits the specific part of sulphides would be applied in practice. Based on some studies [5, 6, 7], it can be stated that the refractory properties of precious metals are influenced by:

- presence of carbon components (active carbon and material that absorbs gold from solution)
- degradation of associated minerals (sulphides are dissolved in the form of cyanide and thus reducing the amount of oxygen)
- formation of coating on gold due to the possible reaction between the present metal sulphide particles and solvent
- formation of insoluble gold alloys or compounds (e.g. arsenic: $AuSb_2$ and Au_2Bi).

In addition, the certain sulphides such as Sb_2S_3 can be absorbed on gold particles when they are in a solution as electrically charged colloidal particles [5].

It is obvious that before the process of cyanidation, the suitable treatment of refractory gold-bearing ore or concentrate have to be carried out, mostly using the oxidative roasting process. However, this procedure regarding to the realized standards for the environment protection is as less as possible attractive. Oxidizing roasting still must be applied during treatment of refractory ores containing carbonaceous components. It is known that in the process of oxidative roasting of refractory gold ores occur products such as SO_2 and As_2O_3 [8]. Efforts to avoid problems related to the environment have led to the development of various hydrometallurgical oxidation processes under pressure. There are opinions that the oxidation pressure in sulphuric acid is still the most effective pre-treatment of refractory ores and concentrates of gold [9]. The oxidation process of oxygen under pressure in the autoclave is used successfully for treatment of similar raw materials in several countries. The main goal of this process is to realize the gold particles of submicron sizes that are embedded in mineral by the use of oxidation the sulphide minerals. In relation to the oxidation roasting, the pressure oxidation process has a certain advantage in terms of increasing the degree of gold and silver extraction in direct treatment of ore with lower sulphur content. Besides that, this process achieves also greater sensitivity to the presence of certain metals such as arsenic, zinc, copper, lead, what contributes to easier solving the environmental problems.

As the chemical reactions in the oxidation processes are accompanied by the exothermic heat effects, the removal of generated heat is required. Regarding to the mineralogical composition of polymetallic ore, the following reactions are of interest that take place during the oxidation process under pressure:

$$4FeS_2 + 15O_2 + 8H_2O \rightarrow 2Fe_2O_3 + 8H_2SO_4 \quad (1)$$

$$2FeAsS + 7O_2 + 6H_2O \rightarrow 2FeAsO_4 \cdot H_2O + 2H_2SO_4 \quad (2)$$

$$Cu_2S + 1/2O_2 + H_2SO_4 \rightarrow 2CuSO_4 + H_2O \quad (3)$$

$$PbS + 1/2O_2 + H_2SO_4 \rightarrow PbSO_4 + H_2O + S \quad (4)$$

$$ZnS + 1/2O_2 + H_2SO_4 \rightarrow ZnSO_4 + H_2O + S \quad (5)$$

Sulphur, which occurs as a product of reactions (4) and (5) is unstable because of the working conditions prevailing in the autoclave (temperature above 120°C) is converted into sulphuric acid by reaction [16]:

$$S + 1/2O_2 + H_2O \rightarrow H_2SO_4 \quad (6)$$

Quantity of required oxygen for oxidation reactions can be determined based on the reaction of stoichiometry (1-5). However, the utilization of oxygen in these reactions is affected by the following factors:

- purity degree of oxygen (presence of nitrogen and argon);
- operating Pressure;
- operating temperature, and
- content of carbonate in the ore or concentrate.

After realized oxidation by the oxygen under pressure, the pulp solution contains all acid as well as 99% zinc and copper contained in the ore. Phase separation is performed by the filter-press, the filtrate is purified and the electrolytic copper and zinc are produced. The washed insoluble residue is removed to the production of lead.

Table 1. Plants in the world that use pressure oxidation for the treatment of refractory gold ores

Mine	State	Media	Raw material	Capacity (t/day)	Autoclave number	Start Work
McLaughlin	USA	Acid	Ore	2.700	3	1985
Sao Bento	Brazil	Acid	Concentrate	240	2	1986
Mercur	USA	Alcaline	Ore	680	1	1988
Getchell	USA	Acid	Ore	2.730	3	1989
Goldstrike	USA	Acid	Ore	1.360 5.450 11.580	1 3 6	1990 1991 1993
Porgera	N.Guinea	Acid	Concentrate	1.350 2.700	3 6	1991 1994
Campbell	Canada	Acid	Concentrate	70	1	1991
Olympias	Greece	Acid	Concentrate	315	1	-
Lihir	N.Guinea	Acid	Ore	13.250	6	-

The advantage of the oxidation pressure led to the introduction of a few [10-12] commercial plants in operation, starting from 1985. Table 1 gives an overview of nine plants for treatment the refractory gold ore by the pressure oxidation. The raw materials from the first five mines, as given in Table 1, contain from 1.5% to 7% sulphur in sulphides, while the content of this element in the last four concentrates ranges from 9% to 42%. The processing capacities are in the range from 680 to 13.250 t/day (1 to 6 autoclaves in the plant).

2.2. Production of gold and silver

After lead separation with the appropriate solution of diethylene triamine, the washed, oxidized insoluble residue is converted to a form of pulp and the alkalinity is adjusted to pH = 11, in order to the leaching by the cyanide solutions as gold and silver would be dissolved.

Aurocyanide solution is placed into contact with the active carbon, then its desorption is carried out with the hot concentrated cyanide solution and electrolytic treatment on cathodes of steel fibers is done. Steel cathode is dissolved in sulphuric acid, the insoluble residue is filtered, dried and melted in the electric furnaces to produce "dore"-metal. The processes can be shown by the following reactions:

- leaching of gold and silver

$$2Au + 4NaCN + O_2 + 2H_2O \rightarrow 2NaAu(CN)_2 + 2NaOH + H_2O_2 \quad (7a)$$

$$2Ag + 4NaCN + O_2 + 2H_2O \rightarrow 2NaAg(CN)_2 + 2NaOH + H_2O_2 \quad (7b)$$

- adsorption on activated carbon,

$$C|\cdot OH + Au(CN)^-_2 \rightarrow C|\cdot Au(CN)_2 + OH^- + \quad (8)$$

- desorption of gold

$$C|\cdot Au(CN)_2 + OH^- \rightarrow C|\cdot OH + Au(CN)^-_2 + OH^- + \quad (9)$$

Concentrations of CN^- and CNS^- ions in cyanide solution can reach the value of 200 to 500mg/dm^3. If a date is taken into account that the allowed concentration in the water flows for cyanides and rodanides in the range of 0.05 to 0.1 mg/dm^3 , the importance of treatment the solutions prior to eventual discharge into water flows can be seen. In addition, the harmful arsenic, lead and mercury compounds can appear in cyanide solution.

Leaching of gold and silver from their ores under the influence of alkali cyanides was introduced for commercial purposes in 1889 and it is widely used nowadays [13,14] . The reasons for presence of this process are the economic and technical nature, the possibility to achieve high recovery of precious metals, process simplicity and economic viability of the process also in the ores with very low gold and silver

3. Conclusion

The processes of treating the non-ferrous sulphides, started in the sixties of the last century, ceased after 1980, and manifest a rapid progress thanks to the application of pressure leaching technology. Initially, it was only used for treatment of nickel and zinc concentrates; the leaching under pressure is increasingly used for processing of sulphide with higher content of gold and silver.

- electrolytic separation of gold,

$$Au(CN)_2^- + e^- \rightarrow Au + 2CN^- \quad (10)$$

Since in the oxidation pressure process the main sulphides are dissolved and removed from the insoluble glass, the possibility is small for reaction development that would spend cyanides, for example:

$$Cu_2S + 6CN^- \rightarrow 2Cu(CN)_3^{2-} + S^{2-} \quad (11)$$

$$ZnS + 4CN^- \rightarrow Zn(CN)_3^{2-} + S^{2-} \quad (12)$$

It is also favorable for the process of cyanidation that the polymetallic sulphide ore does not contain the carbon components because the complexes with cyanides could be enriched at their presence.

Many unsuccessful attempts were carried out for replacement the cyanide solutions with other reagents (thiourea and amonium-polysulphide) [1], less harmful to the environment. In addition to the possibility of creating the poisonous cyan hydrogen gas, due to the hydrolysis of CN^- ions, or under the influence of CO_2 from atmosphere, it should have in mind the fact that the solution may be found in the aurocyanide solution and other types of harmful ions: the complex cyanide ions of iron, zinc, copper and nickel and rodanide ion (CNS^-).For example, if the chalcocite (Cu_2S) is present in the solution, the rodanide ion can occur as the reaction product:

$$2Cu_2S+11NaCN+5/2O_2+H_2O \rightarrow 2NaCu(CN)_2+2Na_2Cu(CN)_3+NaCNS+Na_2SO_4+2NaOH \quad (13)$$

Acknowledgement

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OPPORTUNITY FOR CLEANER COPPER PRODUCTION

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Abstract

The main goal of the sustained development is to provide the future generations with as much possibilities as we have had so far. One of the key issues of its sustainability is the awareness of the fact that the natural and material resources on our planet are limited. The cleaner production presents the goal which perfectly fit into the efforts leading to the sustained development.
The strategy for Sustainable development in the mining industry is being reduced to permanent, long-term reduction of consuming primary metals reserves, with the constant increase of the recycling metal production. The intent is to equalize the production with consumption.
Metal waste present a very important secondary resource, and if it is being collected and returned into the process of a new treatment, we will reduce the usage of primary resources, prolong the life of their reserves and reduce the pollution of the environment. The metal reprocessing from waste, as well as the general reprocessing of some other materials (RECYCLING), present the future, which can be accomplished only by an integral approach to the problem and which in its essence tends towards the sustained development.

Keywords: Sustainable development, cleaner production, primary resources

1. Introduction

Natural resources usually mean all the matters that come out from the Earth-soil, plants, animals, water, oil, metals and so on. All we eat, use or buy present either the natural resource or something that have come out of it. Natural resources are all around us, and due to the increased needs, we consume them very quickly. A lot of natural resources are being exhausted faster than they can be replaced by new ones.

Regardless the type, structure and particular quantities, they are the base for the future economic and business development of every country, and Serbia too. It is quite logical that there is part of natural resources which must stay away from any economic and business flows, which in fact, must be saved for today's and future generations, and it is particularly true for those resources which are hard to renew and those nonrenewable resources.

2. Sustainable development

The generally accepted definition of sustained development is the one which created the Brundthland's commission:

"The sustained development is the development which satisfies the needs of today's generation without jeopardizing the rights of future generations to satisfy their needs".

The main goal of the sustained development is to provide the future generations with as much possibilities as we have had so far. One of the key issues of its sustainability is the awareness of the fact that the natural and material resources on our planet are limited. The cleaner production presents the goal which perfectly fit into the efforts leading to the sustained development.

The strategy of sustained development in the field of exploiting mineral raw materials, leads towards a permanent and long-term reduction of using the primary mineral reserves accompanied at the same time by a permanent increase of metal (mineral) production out of the recycling process, leading up to the “final” goal, that is, to equalize it with its usage.

3. Cleaner production

The beginning of the twentieth century has become the turning point with the appearance of the globalization of ecological problems and more intensive degradation of human environment as well. The former approaches to these problems were avoided, and they could be grouped into three categories:

- **Make it dirty and run away** – this approach was typical for the places with a small number of inhabitants and it consisted of population migrations caused by the degradation of the surrounding (most commonly due to the cultivable soil degradation).
- **Dilute and disperse** – this was one of the ways how to control waste in the pre-industrial period based on the natural capacity of self-cleaning.
- **Concentrate and keep** – for some time, it was considered a good method of waste management in situ, that is, for controlling dumping of toxic and nuclear waste. However, due to the destroying of containers and/or the mere control, it was impossible to guarantee a long-term dumping without a leaking process.

It was only in the last 10-15 years that experts got an idea that the reduction of harmful element emission should be done at the source of their presence. This strategy of preventing pollution and minimizing waste was really necessary in order to reduce the enormous expenses for cleaning up, especially from the moment when the legal system introduced the regulation: “the polluter pays”.

This new approach, called “cleaner production”, is promising as it unites both ecology and business sides of the problem.

The cleaner production is, in fact, a preventive approach. The main aim of the cleaner production is to focus on the prevention or reduction the quantity of waste, as well as the non-efficient usage of energy and resources. In order to achieve all these issues, it is necessary to adopt new technologies and techniques, together with new values and ways for satisfying needs of mankind. Besides, this new approach should be applied to the production process, consumption and supplying goods and services in order to get the same or higher production rate with much less energy and resources consumption.

4. Opportunity for cleaner copper production

Mineral resources belong to the group of non-renewable resources. These are exhaustive resources and that is why it is necessary to use them rationally, that is, to save them. The proper way to do it nowadays can be achieved by recycling, substitution and import.

For example, in Bor, the average copper content in the ore amounts to around 0,25%. For the production of one tone of cathodic copper, some 999 tones of dangerous waste have been produced.

The usage of mineral resources causes a dangerous environmental pollution and it is usually accompanied by the following issues: high soil degradation, high air pollution, high pollution of surface and underground water, high quantities of solid and liquid waste, high quantities of waste waters

Copper can also be obtained from secondary raw materials, for example, from electronic waste. The average copper content in printed circuit boards amounts to around 9,7%. The content of precious metals is also higher in these printed boards (Ag~0,06%, Au~0,023%, Pd~0,01%) in relation to their content in mineral raw materials, consequently all of these facts point to the economical importance of recycling.

As an IC board contains a high copper concentration, it can be directly sent to the plant for smelting without any previous treatment. However, by smelting process it is not possible to obtain plastics and ceramics, which are present with some 30% in the printed circuit boards and which, during the melting process, cause the formation of dioxine and fuaran which pollute air and have a negative influence on the environment. If these materials are extracted in some other pretreatment (by a mechanical procedure), they can be applied in the civil-engineering industry. For the pretreatment of printed circuit board (IC) there are the whole series of different technological processes, but the things that are of special interest for mineral processing engineers are that the majority of them are based on the procedures and technologies of mineral processing. By means of these processes, it is possible to achieve the metal recovery of 80%. A great variety of materials, which are used in electric production, have a direct influence on the complexity of technologies of the mechanic recycling of these products.

The most common separation methods in the recycling process of electronic devices-printed circuit boards-are:

- Magnetic concentration
- Electric concentration
- Gravity concentration

With these methods can be achieved higher recovery of the present metals, and in accordance with the fact that there is no water or chemical additions in combination with these procedures, there is no problem of waste waters and it is the proper thing that makes this process economically more convenient, and what is more, for the environment more acceptable than the metallurgical processes.

5. Final consideration

Metal waste present a very important secondary resource, and if it is being collected and returned into the process of a new treatment, we will reduce the usage of primary resources, prolong the life of their reserves and reduce the pollution of the environment. The metal reprocessing from waste, as well as the general reprocessing of some other materials (RECYCLING), present the future, which can be accomplished only by an integral approach to the problem and which in its essence tends towards the sustained development.

Metal waste is a very rich raw material compared to the mere ore; what is more, the transport and handling are much cheaper. The investment expenses for building up the facilities for waste processing and metal production amounts only 16 to 20% out of the costs necessary for building up facilities for processing the primary material-ore.

Besides, the processing, technologies based on processing the secondary minerals (metals), are much simpler and even more convenient for the environment.

Acknowledgements:

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GENERAL WASTE MINIMIZATION OPTIONS FOR METAL CLEANING

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Abstract

Metal cleaning is an essential function in manufacturing, repairing, and maintaining parts and equipment in industries such as furniture, machinery, electric and electronic equipment, instruments and metal fabricating. The purpose of metal cleaning is to remove impurities from the metal surfaces in preparation of finishing processes such as electroplating and/or coating; a clean product diminishes the potential for rejects during further processing steps. The cleaning methods and materials used depend upon the type of contaminants, which typically are soils, rust, paint, and oil. Usually, because more than one type of contaminant is present on the metal surface, a series of cleaning operations is required to fully prepare a metal surface for its final treatment. The basic waste minimization options applicable to metal cleaning operations including strategies for developing pollution prevention techniques for most metal cleaning applications are presented in this paper.

Keywords: waste minimization, metal cleaning, parts cleaning

1. Introduction

Parts cleaning is an important process for a large variety of organizations involved in the manufacture, repair, and maintenance of parts and equipment. From large metal fabrication plants to captive maintenance shops of industrial facilities, parts cleaning operations are essential to doing business.

The reason for focusing attention on minimizing waste in parts cleaning operations is because the solvents and other chemicals used in parts cleaning often result in significant air emissions, wastewater discharges, and the generation of hazardous wastes. Waste minimization offers a significant and often cost effective opportunity to reduce the emissions and discharges of toxic pollutants into the environment.

Waste minimization is the elimination or reduction, to the extent feasible, of hazardous waste that is generated and would otherwise be subsequently treated, stored or disposed of. It includes any source reduction or recycling activity undertaken by a generator that results in either the reduction of total volume or quantity of hazardous waste, or the reduction of toxicity of the hazardous waste, or both, so long as such reduction is consistent with the goal of minimization present and future threats to human health and the environment.

2. General waste minimization for parts cleaning

"Waste" describers material that was not used for its intended purpose or unwanted material produced as a consequence of another process. In any industry, waste is either considered inert or contaminated. Inert waste can be recycled or released into the environment.

No matter what type of waste you have, waste costs money. In short, there is much motivation to minimize waste in any industries.

Each cleaning process generates a specific type of waste that must be managed and disposed. The costs of proper waste treatment and disposal, more stringent environmental regulations, and increased liability are forcing industries to reevaluate wastes generation practices.

Waste minimization in metal cleaning operations can be accomplished through source reduction, material reuse, and product recycling. The following steps will assist in reducing wastes from most metal cleaning operations:

1. Avoid the need to clean.
2. Select the least hazardous medium for cleaning.
3. Maximize cleaning efficiency.
4. Segregate cleaning wastes.
5. Maximize recycling and reuse.

This strategy is consistent with the multi-media approach and general emphasis of reducing the waste at the source.

3. Preventing surface impurities

The primary step for control of surface impurities is to identify the sources of the pollutants. Surface pollutants can be incoming soils applied by metal vendors or contaminants such as coolants, stamping fluids, and rust inhibitors applied in-house.

Peel coatings or shrink wrap may substitute for protective coatings of grease or paint which require solvent removal. These coverings will prevent dust and oils from depositing on the metal surfaces during shipment, storage, and handling. Because the used wrapping materials may be sellable to a recycler, revenues may be generated and disposal fees may be eliminated.

Moisture which causes rust to form can also be eliminated or reduced by properly drying the parts between operations or by storing them indoors away from condensation or rain.

4. Selecting the Least Hazardous Cleaning Agent

Selection of a cleaning process for specific parts is determined by several factors including physical and chemical properties of contaminants, substrate surface, and cleaning media; the amount of contaminant to be removed; the required level of cleanliness; the complexity of the surface to be cleaned; the quantity of parts to be cleaned; the costs of materials/equipment/labor; and worker/environmental protection.

In the search for a less polluting cleaning process, the user should select the least toxic and most environmentally friendly medium that performs with the desired efficiency. Below are cleaning media and the order in which they should be evaluated:

1. Water or air
2. Abrasive media with water or air as carrier
3. Aqueous solutions
4. Acidic or caustic solutions
5. Solvents

A new cleaning process or any proposed process changes must be carefully evaluated for potential effects on substrate and downstream processes such as anodizing, plating, and painting. Additionally, all regulations and existing permits that the facility must comply with should also be evaluated for the effects of a process change.

5. Optimizing Cleaning Efficiency and Segregating Wastes and Reuse/Recycling

If cleaning steps cannot be eliminated and the least toxic/hazardous materials are being used, the absolute smallest amount of cleaner necessary to obtain an acceptable product should be applied. Also, proper worker training and retraining are essential to ensure the materials are applied with the greatest achievable efficiency. Employees should also be given the opportunity to identify wastes and determine ways to eliminate and reduce them.

Source segregation will minimize the amount of wastes generated and disposed and also save on purchases of raw materials. In the metal cleaning industry, separating, reusing, and recycling used solvents result in enormous economic and environmental savings. With careful attention to the following handling and safety tips, a facility can profit from successful waste segregation.

1. The solvents should not be allowed to mix with contaminants such as water, solids, and garbage.
2. Hazardous materials should be separated from non-hazardous so that the latter will not be misclassified as hazardous.
3. All used solvent containers should be properly labeled, covered, and stored in a restricted area that is kept cool and provides containment in the event of a release.
4. Employees working with any type of material whether new or spent should be trained on proper handling practices.
5. To comply with applicable regulations and prevent a spill incident, the facility must ensure that required procedures are followed and personnel safety equipment is worn when workers handle any regulated raw materials or wastes.

Facility conditions such as space for materials storage and/or recycling equipment; costs of equipment, training, and manpower; and suitability to processes determine whether spent solvents may be segregated and recycled on or offsite.

6. Conclusions

As increased regulation raises the cost of waste treatment and disposal, efforts to decrease waste volumes and toxicity become more economically justifiable. Implementing waste minimization techniques to reduce cleaning waste can produce treatment and disposal cost savings which more than offset the expenditure.

In addition, material costs, regulatory compliance, and other costs can be cut since the life of the cleaning solutions will be lengthened.

Proper equipment operation requires only that management thoroughly train the employees using the equipment and that the equipment be correctly maintained. These low-cost measures generally have a fast payback and are among the first a firm should implement.

Making employees aware of the cost of waste generation due to cleaning operations and involving them in identifying solutions may encourage the design of more efficient production processes.

With the adoption of efficient production processes and the waste-minimizing measures, companies with parts cleaning operations should be able to reduce their waste disposal costs and liabilities, and reduce their contribution to the environmental problems associated with waste disposal.

Acknowledgement

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INFLUENCE OF POWDER METALLURGY ON THE ENVIROMENT

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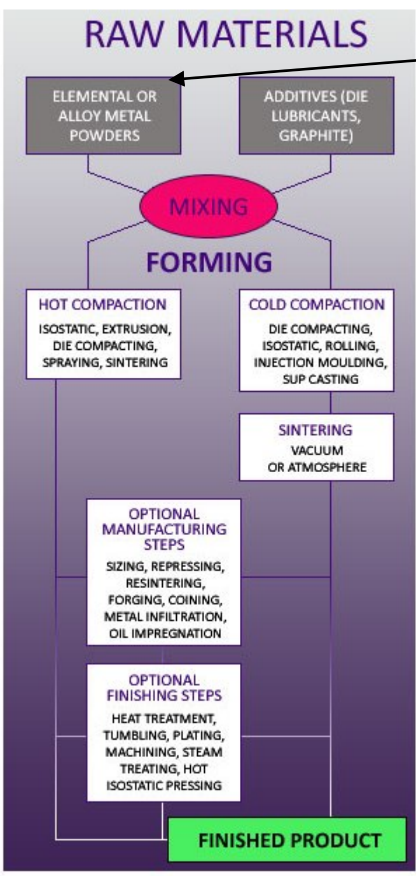
Abstract

This article is devoted to powder metallurgy (PM) and the peculiarities of that branch of materials science in ecological aspects. The technological and economical advantages of PM methods compared with traditional metallurgical processes for production of metal products are discussed. The main stages of PM technology: the processes of powder production, shaping and sintering, and the effects of these operations on both human health and the environment are also discussed. In that respect, the methods of metal powder production are viewed in more detailed. Toxicity and other harmful properties of certain metal powders are also discussed.

Keywords: Powder metallurgy, sintering, enviroment

1. Introduction

Powder metallurgy has been used since 1920s to produce a wide range of structural PM components, self-lubricating bearings and cutting tools. The basic procedure in the manufacture of PM parts is shown in Fig. 1.



Elemental metal powders

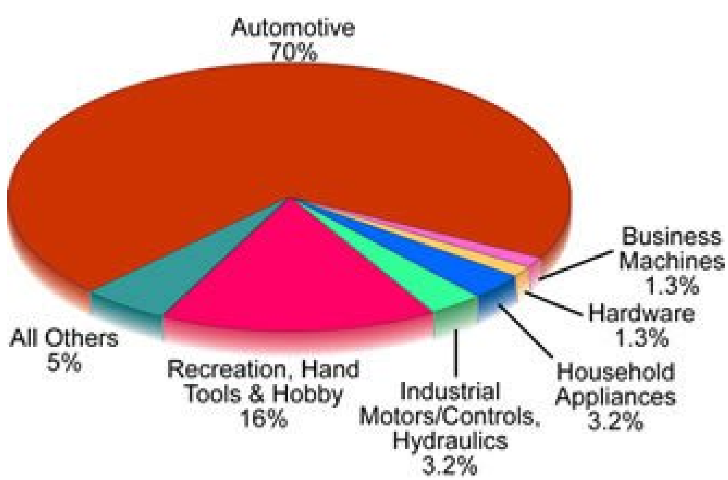


Figure 1. Schema of powder metallurgy

Figure 2. PM Structural Component Market process

PM is the forming of metallic powders into parts by means of high pressure and subsequent heat treatment called sintering. This process takes place below the melting point of the metals and therefore guarantees the manufacture of compact, almost absolutely dense work pieces avoiding melting. Sintering is the central technological step of powder metallurgy. Sintering causes the transformation of porous green compacts of powder into metallic components suitable for further processing, by means of a combination of diffusion and surface tension under high temperatures. Forming technology makes it possible to convert the sinter parts with a residual porosity of 10-15 % into components absolutely free from pores [2, 3].

PM processing encompasses an extensive range of ferrous and nonferrous alloy powders, ceramic powders, and mixes of metallic and ceramic powders (composite powders). PM competes with several more conventional metalworking methods in the fabrication of parts including casting, machining and stamping. Characteristic advantages of powder metallurgy are close tolerances, low cost, net shaping, high production rates and controlled properties. Other attractive features include compositional flexibility, low tooling costs, available shape complexity and a relatively small number of steps in most powder metallurgy production operations. PM is a highly flexible and automated process that is environmentally friendly, with low relative energy consumption and a high level of materials utilization. Thus it is possible to fabricate high quality parts to close tolerance at low cost [4].

PM components are used in a variety of markets but the automotive industry being the predominant one, consuming approximately 70 % of the ferrous PM products. Other important markets include recreation, hand tools and hobby products; household appliances; industrial motors and controls; hardware; and business machines [5].

2. Technological and economical advantages of PM

The ability of sintering to combine alloys difficult or impossible to produce using conventional ingot metallurgy (IM) has made it possible to produce almost any material as an alloy compound with combined or new properties. This feature can be especially useful when the components have greatly different melting temperatures, have limited mutual solubility in the liquid state, have very different densities, a refractory constituent in solid form is attacked by the liquid metal. In these cases it may be impossible to produce such alloys by IM [2].

The growth of the PM industry during the past few decades is largely attributable to the cost savings associated with net (or near net) shape processing compared to other metal working methods such as casting or forging. The net-shape characteristics of PM components generally result in a finished component ready for packaging and shipment after sintering. However, PM components can be given a wide assortment of secondary finishing operations such as machining to exacting tolerances, plating, or coating. But PM final machining operations are minimal [5]. In some cases the conversion of a cast or wrought component to powder metal provides a cost savings of 40 % or higher.

There are two principal reasons for using a powder metallurgy product: cost savings compared with alternative processes and unique properties attainable only by the PM route. PM typically uses more than 95 % of the starting raw material in the finished part and is specially suited to high volume components production requirements. It can be seen from Fig. 3 that PM process has the highest raw material utilization and the lowest energy requirement per kg of finished part comparing with the other manufacturing processes [1].

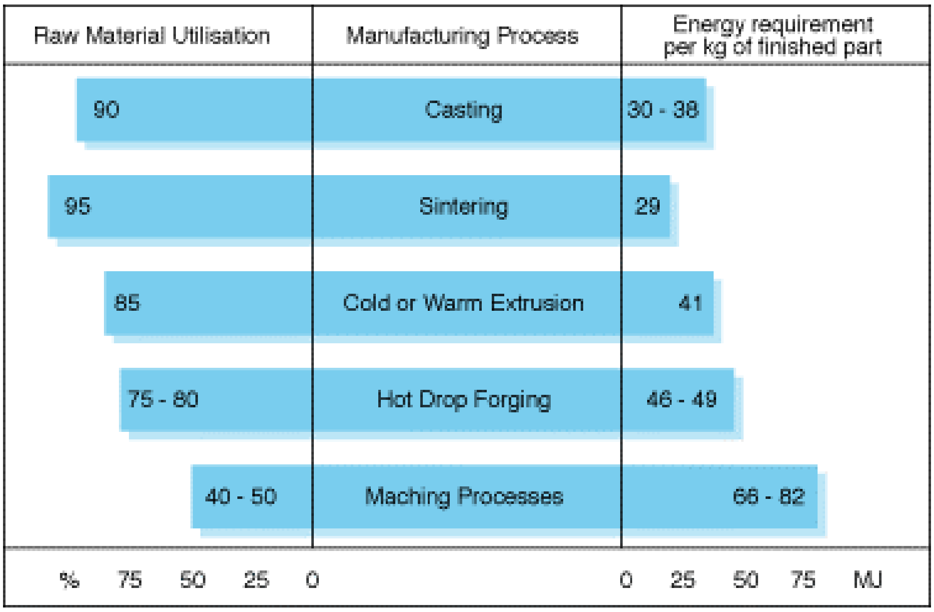


Figure 3. Raw material utilization and energy requirement of various manufacturing processes

The PM process provides a host of advantages over competing metal working technologies [5]:

- Eliminates or minimizes machining by producing parts at, or close to, final dimensions
- Eliminates of minimizes scrap losses by typically using more than 95 % of the starting raw material in the finished part
- Permits a wide variety of alloy systems
- Produces good surface finishes
- Provides materials which may be heat treated for increased strength or increased wear resistance
- Provides controlled porosity for self lubrication or filtration
- Facilitates manufacture of complex or unique shapes which would be impractical or impossible with other metal working processes
- Is suited to moderate- to high-volume component production requirements
- Offers long-term performance reliability in critical applications
- Is cost effective

3. Environmental impact of PM

It is estimated that 85 % of all PM powders are produced from recycled material. Most metals can be repetitively recycled in collectable quantities. The predominant metal powder used, iron/steel, nearly a 500 000 t/yr is produced via atomization of electrically melted steel scrap [5]. At present, there are two main methods for production of iron and steel powders. Together, the production of sponge iron powders by reduction of iron oxides and by water atomization of iron or low alloyed steel powders accounts for more than 90 % of iron and steel powders produced around the world [6].

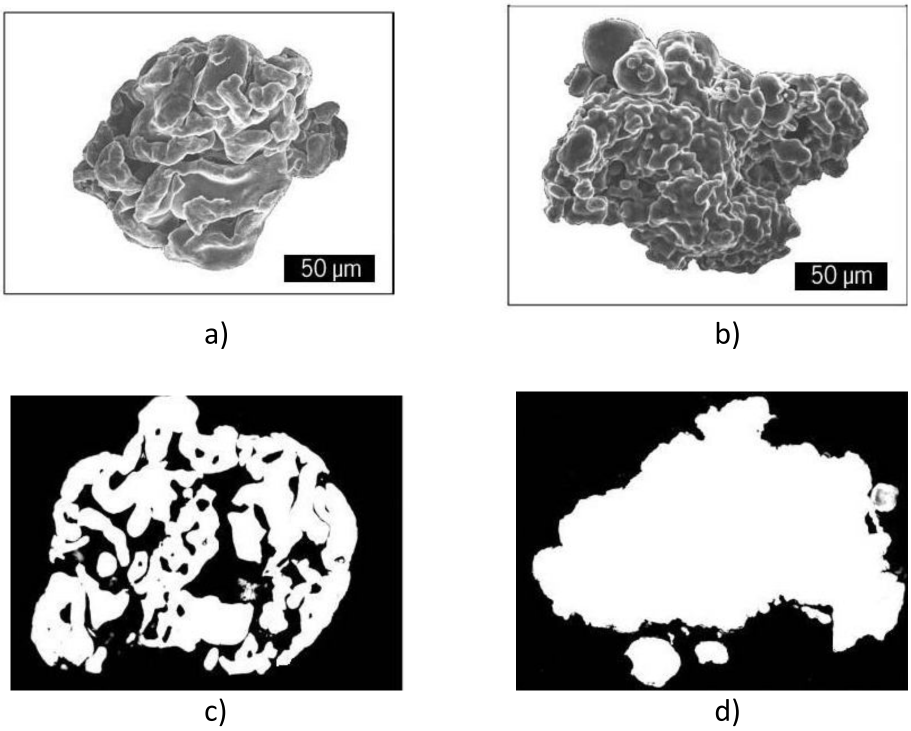


Figure 4. SEM of sponge iron powder (a) and water-atomized iron powder (b) and internal particle structure (cross-section) of sponge iron powder (c) and water-atomized iron powder (d)

Typical structural differences between these two kinds of powders by SEM photographs and cross sections of iron powder particles are shown in Fig. 4. The external shapes of both particles are irregular and fairly similar to one another. But the sponge iron particle has a spongy internal structure, while the water atomized particle is internally compact [7]. Obtaining fine grained metal powders having high sinterability, may results in products with pyrophoric properties. Any very finely divided particles (ultra fine powder) may burn in air. Iron and cobalt powders are good representatives of these materials. Strict safety measures should be taken during manipulation and storage of fine (< 10 μm) and ultra fine (< 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 [8].

Interaction of certain metal powders with water and hydrogen (e.g. Al powders) makes water pulverization very dangerous. Strict measures to prevent hydrogen accumulation and its explosion should be taken [8, 9].

Effects of long term or repeated exposure to metal powders may include respiratory disease, pneumoconiosis, bronchial asthma, lung fibrosis, obstructive airway syndrome and possibly cancer, depending on the alloy components.

Nickel powders find numerous applications in many branches of industry: production of special steels, super alloys, alloys with controlled expansion, shape memory alloys, Ni-La hydrogen accumulation alloys, dental alloys, implants, etc [10]. Being technologically attractive these particles could be harmful and dangerous for human health. Nickel is an allergic agent and may cause different dermal effects. It is estimated that as many as 10–20 % of women and 1–2 % of men are sensitive to nickel. The mechanism of nickel penetration by skin is based on the dissolving of pure metal by sweat. It is advisable not to wear cheap jewelry and to always demand a test for nickel allergy from dentist if alloys for dental constructions contain nickel [8]. Chronic inhalation overexposures to nickel may also cause cancer of the nasal passages, larynx and lung.

Copper alloys may discolor skin and hair with chronic overexposure. Long term or repeated overexposure to iron dust can cause pneumoconiosis. Repeated or long term ingestion of large quantities of iron may result in fibrosis of the pancreas, diabetes mellitus, liver cirrhosis and cardiac poisoning. Chronic overexposures to manganese dust and fume may affect the central nervous system and cause headache, restless sleep, personality changes, lack of coordination, irritability, uncontrolled and inappropriate laughing or crying, visual hallucinations, double vision. Toxicological data of metal powders are listed in Table 1 [10].

Table 1. Toxicological data of metal powders

Powder	Testing	Lowest observed toxic dose TD_{LO} or Lethal dose LD
Carbon	Acute oral, small lab animals	LD_{LO} > 5 mg/kg
Chromium	Acute oral effect, human	LD_{Lo} = 71 mg/kg
Cobalt	Acute oral, human	LD_{Lo} = 0.28 mg/kg
Copper	Acute oral, human	TD_{Lo} = 0.1 mg/kg
Iron	Acute oral, human	20-60 μg/kg
Manganese	Acute inhalation, human	TC_{Lo} = 2300 μg/m^3
Molybdenum	Acute oral, rat	TD_{Lo} = 5800 μg/kg
Nickel	Acute oral, guinea pig	LD_{Lo} = 5 mg/kg
Nickel	Acute inhalation, guinea pig	TC_{Lo} = 15 mg/m^3
Silicon	Acute oral, rat	LD = 3160 mg/kg

It can be seen that there are many materials that can be toxic but are safe to use when handle in the right way and exposures keep 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 [8, 9].

PM plants are generally well clean and healthy workplaces with an increasing level of automation, minimizing the direct handling of the product from forming through final packaging. Also, most plants only emit cooling water to public water-septic systems minimizing the likelihood of toxic releases. The PM process requires the use of graphite or other lubricants in the compaction stage, but recent improvements in binder and lubricant technologies have resulted that most companies have shifted from chemical systems such as zinc stearates to more innocuous materials in order to minimize or eliminate the potential for gaseous toxic releases from sintering operations. Gaseous emissions are also minimized by the net shape conservation of product. Since nearly all scrap produced is metallic, it is routinely recycled, thus minimizing the PM’s contribution to landfills [5].

4. Conclusions

PM supplies the industry with low cost production of precision, high performance materials and products and no other metal working process can match its competitive advantages. PM is especially suited to the production of large series of pieces with narrow tolerances. By producing parts with a homogeneous structure PM enables manufacturers to make products that are more consistent and predictable in their behavior across a wide range of applications.

Compared with other manufacturing processes PM displays few environmental hazards. Again, the low energy intensity per kg of product minimizes overall environmental impact. 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 environmentally friendly processes.

Acknowledgement

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EFFICIENCY OF PYROMETALLURGICAL COPPER EXTRACTION

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Abstract

Copper production is a major energy consumer, which accounts for almost all fossil fuels, including electricity. In this paper, special attention has been paid to the specific energy consumption for a few manufacturers and for various copper concentrate melting technologies. Also, mathematical and statistical dependence between energy consumption and copper extraction costs with copper content in processed ore and melted concentrate is shown. For the observed case, the energy consumption increase in pyrometallurgy is 2.08 times of the copper content change in concentrate (from 13 to 21% Cu). When copper content in processed ore changes from 0.30 to 0.45% Cu, power consumption drops by about 3 times. With capacity increase in annual copper production, energy consumption decreases, so, with annual copper production raise from 15 to 110 kt, energy consumption falls down by 1.74 times (with copper pyrometallurgical capacity increasing for each 1000 tons of copper, energy consumption is lowered for about 8.5%).
Also, the significant part is devoted to energy participation costs in the copper production and their structure in energy consumption and costs. Special attention was paid to secondary (waste) energy usage, which, in the addition, raises energy efficiency and economical efficiency of the process and the impact on reducing ecosystems vulnerability directly and indirectly. During the one-year observation of the pyrometallurgical copper extraction impacts, following emissions effects amounts have been achieved: carbon dioxide 2993.424 m CO_2/tcCu, sulfur dioxide and 1363.594 m SO_2/ tcCu flying dust 16 g/tcCu.
When selecting and building new copper extraction technological processes, the best effects, as a prerequisite, can be achieved by selecting the optimal process and equipment solution, on the one hand and on the other, the choice of energy system with the best performance and full usage of secondary (waste) energy.
In any case, arguably and clearly should be noted that the copper production costs are in correlation with energy consumption.

Keywords: copper, energy, pyrometallurgy, production costs, environment.

1. Preface

The copper production consumes large amounts of energy, as follows: for machinery and equipment operation, for charge burning and melting, copper matte converting, for the fire refining of blister copper, the electrolytic refining of copper, etc. The energy consumption analysis of the process often comes down to making the heat balance of this process or only some of its phases. But such an analysis does not give a realistic picture of energy consumption. To obtain a complete review of energy consumption it is necessary to take into account the energy consumption during ore mining, the flux and fuel for the ore enrichment into concentrate, as well as energy consumption for raw materials and semi-products transportation and preparation, thereby, taking into the account, the energy "losses". All forms of energy consumption have to be reduced to the primary energy or the same energy form *(or the energy equivalent)* of the process, raw materials and process materials, and also to balance equivalent energy of products and by-products (steam, heat, etc.). In this paper special attention is dedicated to energy consumption in copper production company that deals with the mining production of copper concentrates and metallurgical extraction of copper, which includes technological components: copper smelter (roasting, reverberatory furnace smelting, converting the Peirce Smith converters and fire refining of copper), electrolytic refining of copper with initial copper cathodes and sulfuric acid production by contact process in the plant with a single adsorption and single catalysis.

The general development trend of new autogenous melting process in pyrometallurgical copper production occurs as a result of increasing demand for copper in the world market, on the one hand and the rapid development of productive forces-structural materials, machinery and automation primarily, and increasingly stringent laws on environmental protection and the energy crisis in the world on the other side. New development-philosophical approach to the individual companies integrate all their creative human resources by creating a new generation of autogenous smelting process of copper concentrates. This development trend has lasted for 50 years, while copper sulphide high energy value was used for the design of technologies in which the melting process has been brought almost to being complete autogenous.

2. Energy consumption in the copper production

In the copper production the energy consumption depends on the copper content in ore, copper content in concentrate, technological process excellence and equipment efficiency. For the same technological process of copper ore and copper cathodes production, the energy consumption shown in [6], Table. 1. was 2,24 times lower than the realized structure of energy consumed in the copper production of in the observed copper smelter company *(in further text under code 'MSCB')* during the 2009 business year [2].

Table 1.- Specific energy consumption in the copper cathodes production

PROCESS	Energy consumption, measure	Source [6]	'MSCB' [2]	Source [1]
1.Technological parameters	%Cu in the ore	0,67	0,247	
	%Cu in copper concentrate	25	15,27	
	Copper production, kt/y	1.568,0	16,839*)	
2. Mining	Liquid fuel, dm^3/t Cu	235,025	679,173	
	Electrical energy, kWh/t Cu	742	2.702,264	
	Coal, kg/t Cu	1,157		
	Natural gas, m/t Cu	9,842		
	Total 2, $t_{ec.}$/t Cu	**0,600**	**1,528**	
3. Flotation	Electrical energy, kWh/t Cu	3.577	14.854,663	
	Liquid fuel, dm^3/t Cu	17,552	56,000	
	Natural gas, m/t Cu	56,290		
	Total 3, $t_{ec.}$/t Cu	**1,423**	**4,009**	
4. Roasting, smelting, converting and fire refining of copper	Liquid fuel, dm^3/t Cu	125,356		
	Natural gas, m/t Cu	870,958		
	Oxygen, t/t conc.		0,138	0,106
	Coal, kg/t Cu	105,298	1.239	0,25t/t_{conc}
	Coke, kg/t Cu	24,300		
	Beechwood, m^3/t Cu		0,059	
	Electrical energy, kWh/t Cu	148,610	2.199,463	430
	Total 4, $t_{e.c}$/t Cu	**1,336**	**1,979**	
5. Electrolytic refining	Electrical energy, kWh/t Cu	260	448,573	300
	Steam, t/t Cu		0,478	0,230
	Total, $t_{e.c.}$/t Cu	**0,113**	**0,165**	
Total (2÷5), $t_{e.c}$/t cathode Cu		**3,472**	**7,783**	**-**

*) Domestic raw materials

For the copper production in the 'MSCB' company (where the process takes following order: roasting, smelting in reverberatory furnace, converting the Peirce Smith converter, fire refining and electrolytic refining) in 2009 ore contained 0.287% Cu, concentrate was processed with 16,50% Cu, copper exploitation in flotations was on average 68,20%, technological utilization of copper (from concentrate to the anode) in the smelter 92,16%, utilization of copper from concentrate to cathode copper 92,15% and the utilization of technological copper ore to copper cathodes 62,85%. In other words, thich means, that from 100 tons of copper ore 62,85 tons of cathode copper is produced and the rest represents copper losses.

Energy consumption from ore to copper cathodes in the "MSCB", in the period of 2007 - 2009. year, adjusted to equivalent coal, respectively, was realized in the amount of 6,441; 6,300 and 7,783 t_{ec}/ t_{cCu}. In the review (Table 2) is shown that the power consumption had been far beyond the achievements of consumption in smelters in the world [8]. Energy consumption in the copper production is, in most cases, below 15 GJ / t_{Cu}, except in smelters with a reverberatory furnace, where the consumption is above 20 GJ / t_{Cu}, (Fig. 1.) [3]. In the smelter complex 'MSCB' energy consumption in 2010 was 54,659 GJ per ton of anode copper (1,865 t_{ec} / $t_{anode\ Cu}$). Achieved electricity equivalent in 'MSCB', since the electrical energy is being produced in hydro- and thermal power plants of Public Enterprise "Electric Power Industry of Serbia" (in further text EPS), has a value of 7430 kJ / kWh.

Copper concentrate processing capacity in 'MSCB' during 2008. was reduced for 3,12 times (time utilization 62,03%) compared to 1990, while the capacity of smelting process is lower for 67,03% achieved in 1990 (time utilization 89,25%). Copper anodes production in 2008. year was reduced by 4,34 times compared to 1990, cathode copper production was lowered for 4,48 times, while energy consumption increased from 0,633 (in 1990) to 1,319 $t_{ec}/t_{anodeCu}$ (in 2008).

Table 2 - Energy consumption in the copper cathodes production

OPERATION	**ENERGY CONSUMPTION** *(accord. to prof. C. H. Pitt),* [8]			**In 'MSCB'** *(accord. to dr M. Mitovski [2])*			
				2007.	2008.	2009.	
	GJ/t_{cCu}	t_{ec}/t_{cCu}	%	$t_{ec.}/t_{cCu}$	t_{ec}/t_{cCu}	t_{ec}/t_{cCu}	%
1. Mining	17,584	0,599	16,86	1,190	1,139	1,528	19,63
2. Flotation	41,719	1,424	40,00	3,259	3,308	4,009	51,51
3. Pyrometallurgy	39,165	1,337	37,56	1,708	1,569	1,979	25,43
4. Sulf. acid prod.	2,521	0,086	2,42	0,163	0,127	0,102	1,31
5. El. refining	3,294	0,112	3,16	0,121	0,157	0,165	2,12
TOTAL:	**104,283**	**3,558**	**100,00**	**6,441**	**6,300**	**7,783**	**100,00**

In the copper production, as an energy source, reduced to the equivalent energy, the largest contributor is the electricity - up to 70% of total consumption and energy costs up to 50%. Largest consumer of electricity in the copper production is the flotation, then mining, smelting and electrolytical refining of copper *(Table 3)*. Given that, a dozen current technology of melting copper concentrate mainlyare current in the world, in Table. 4 the overview of technological and energy parameters of metallurgical furnaces is shown.

Based to that, and Figure 1 it can be seen that the largest energy consumer are smelters which use reverberatory furnace, while the most energy-efficient technology is ISA Smelt, following Teniente Converter, Autogenic shaft furnace, etc.[2,3,4,5,15].

Change in the energy consumption by type in the anode copper production in 'MSCB' company during 1994 - 2010 period is shown in Figure 2. In 2010 the equivalent coal price incl. VAT achieved the amount of $ 228,22 per t_{ec} and electrolytic refining of $ 236,91 per t_{ec}.

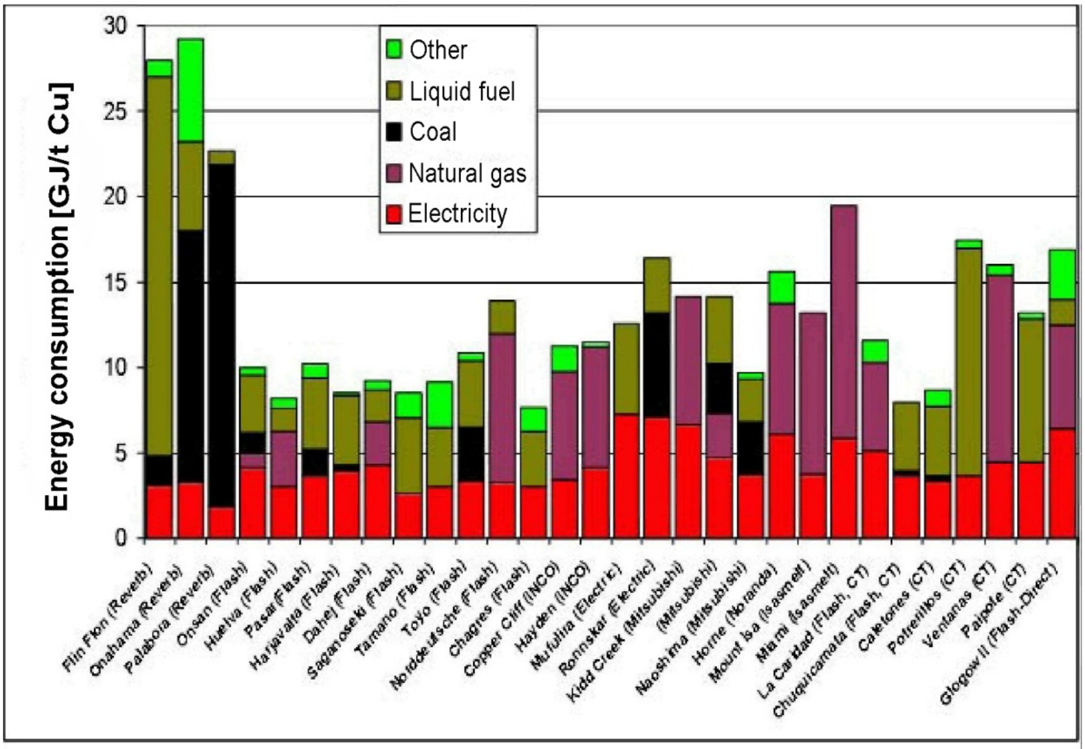

Figure 1. An overview of specific energy consumption in smelters in the world in GJ per ton of copper

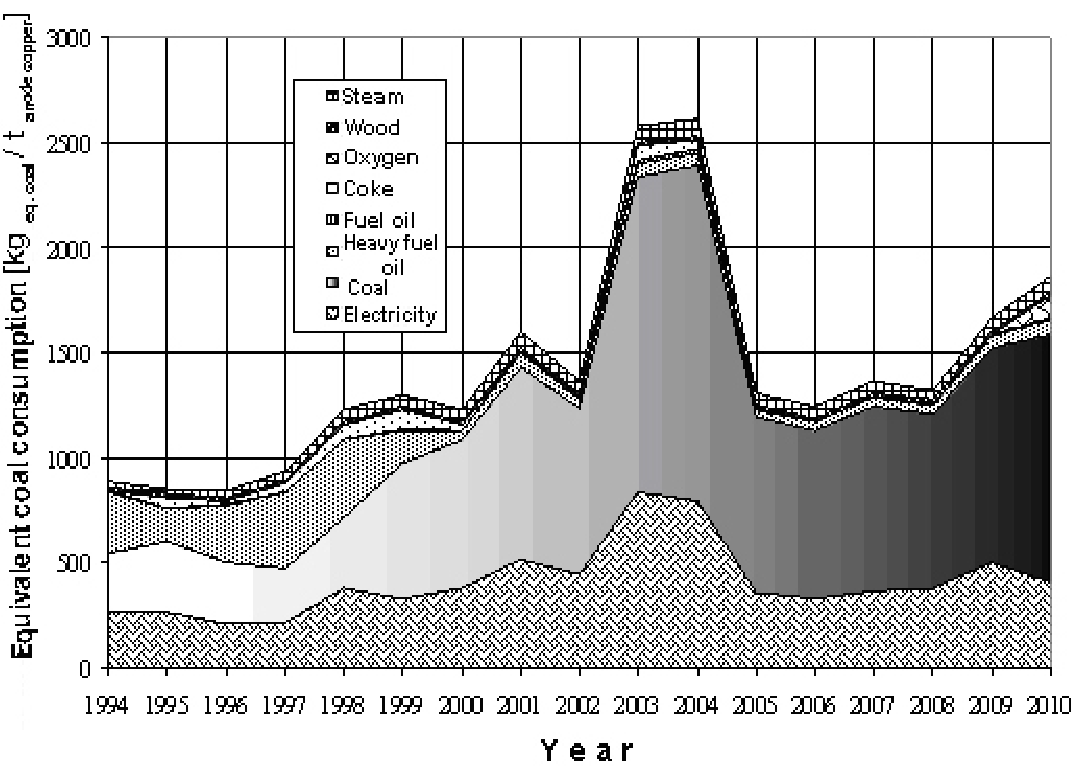

Figure. 2. Specific energy consumption in anode copper production in smelter company 'MSCB' reduced to a mass of coal equivalent per ton of copper anode during 1994 – 2010

Table 3 - Electricity consumption in the copper cathodes production

OPERATION	Energy consumption *(accord. to prof. C. H. Pitt),* [8]		In 'MSCB' *(accord. to dr M. Mitovski [2]*			
			2007	2008	2009	
	kWh/t_{cCu}	%	kWh/t_{cCu}	kWh/t_{cCu}	kWh/t_{cCu}	%
1. Mining	742	13,91	3.040,281	2.345,103	2.702,264	13,15
2. Flotation	3.577	61,05	13.357,886	13.558,164	14.854,663	72,31
3. Pyrometallurgy			1.859,611	1.831,112	2.199,463	10,71
4. Sulf. acid production	736	13,79	429,798	431,310	336,794	1,65
5. Electrolitical refining	280	5,25	502,021	500,644	448,573	2,18
TOTAL:	5.335	100,00	19.189,597	18.666,333	20.541,757	100,00

Specific energy consumption, among other influences, depends on annual copper production capacity and copper content in the processed concentrate. With the increase of copper production capacity (for every 1000 tonnes of copper) energy consumption decreases by about 8,5%, (Figure 3), and with the increase of copper content in concentrate (for each % Cu in concentrate) energy consumption decreases by about 21,4%, (Figure 4). This directly and proportionally spreads over the copper production total cost. For these reasons, the justification for ore smelting with copper content of 4 ÷ 7% is highly questionable. On this issue before the management is indeed a responsible task, contrary to previous practice.

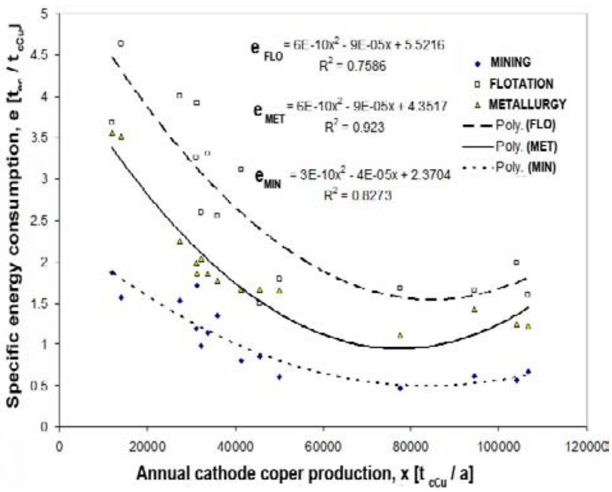

Figure. 3. Specific energy consumption in the cathode copper production from ore to copper cathodes in*:* mining (*MIN),* flotation (*FLO)* and smelting*,* electrolytic copper refining and sulfuric acid *production* (*MET)*

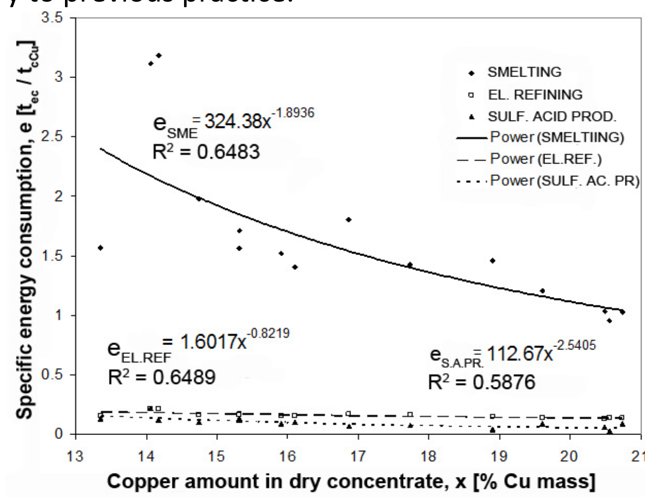

Figure*.* 4. Specific energy consumption in the cathode copper production from concentrate to copper cathode *through* production stages*:* smelting (*SME),* electrolytic refining of copper (*EL.REF.)* and the sulfuric acid production (*S.A.PR.) in terms of* copper content in dry concentrate

Reducing energy consumption and production costs per unit weight of the product, but more rational energy management, adequate quality copper concentrate and energy, it is necessary to achieve optimal capacity at maximum capacitive and time utilization of metallurgical aggregates.

Table 4 - Copper concentrates melting process parameters in the world's smelters

PARAMETER	Reverb. furnac 'MSCB'		Autog. shaft furnace	Teniente konverter	ISA Smelt furnace	FLASH Outokumpu	NORANDA	MITSUBISHI	REVERB. FURNACE	
	2007	2008							Raw charge	Roasted Cu conc.
1. Specific capacity, t/(m²·day)	3,700	3,675	60-120	80-90	80-90	9-12	10-11	do 20	2,5-5	4,5-8
2. Flying dust, %	1-2	1-2			0,8-3	7-10	5	3-5	1-2	
2.1. Flying dust, g/m^3_n					10	100÷200	15÷20	100	30	
3. Content of O_2 in the air, %	25	25,23	25-27	29-35	50-60	35-40	26-28	45	do 25	do 25
4. SO_2 in gases, %	0,18-1,68		3-7	12-25	20-27	18-20	6-7	35	1-2	
5. Energy consumption, MJ/t Cu	27.007	26,201		4.250		10.969	11.225	12.862	18.832	14.984
6. Equivalent coal consumption, % charge	20	16,9	6-12		0,33	do 5	9-10	3-5	18-22	14-16
7. Physical heat of gases, kJ/kg charge	2.437,84		2.397			1.117,85	1.958,1		3.769	2.934
8. Heat input into the furnace, kJ/kg charge	7.047,55	6.286,61	6.639			3.950	5.014,9		7.176	7.749
9. Used heat in the furnace, kJ/kg copper concentrate	1.227,20	1.033,37	3.459			2.196,2	2.786,9		2.303	2.913
10. Utilization heat coefficient in the process η_{lip}	0,1741	0,1644	0,5210			0,5560	0,5557		0,320	0,376
11. Furnace base area, m²	193		3-40		9,60	90	80		240-330	
12. Charge moisture, % mass	10	do 10		0-8	10	do 1	10-13	do 1	6-8	0
13. %Cu in copper-matte	34,3-43,6	37,7-43,9	28-30	72-75	55-60	60	70-75	65	25-35	35-45
14. %Cu in slag (without copper removal)	0,44-0,68	0,41-0,68	0,35-0,45	6	0,7-0,8	1-1,5	5	0,5	0,5-0,5	0,4-0,5
15. Max. charge coarseness, mm	5		40-50		pelets ?	0,1	10	1,0	5	
16. Temperature of gasses, °C	1170÷1350			1220÷ 1250	1150÷ 1220	1270÷ 1350	1200÷ 1240	1240÷ 1250	1250	
17. Copper utilization, %	94,54	95,46		92,7	97÷98					
18. Sulphur utilization, %	37,01	35,85			97÷98	95÷99,9				
19. Equivalent energy consumption in the pyrometallurgical copper production process and H_2SO_4, GJ/t_{Cu}	41,27	38,66		22,49	13	19,96	25,33	20,86	37,12	32,63
20. Fuel consumption in smelting, GJ/t copper concentrate	5,868	4,953	2,204	1,667	1,278	3,377	2,215	2,918		4,120

Note: *All the values are reduced, instead of per 1 ton of charge, to per 1 ton of dry concentrate*

3. Secondary energy usage effects on energy and economic efficiency and environmental conditions improvement

By using secondary (waste) heat of the technological processes, which has every producer of copper as specificity, the consumption of primary energy reduce will contribute, but economic efficiency and less environmental pollution. Secondary energy is released from the technological process, used or not, will be pollutant in each case, and the producted energy usage, as it is now, further will be polluting the environment. Usage of secondary (waste) energy will provide the energy increase and economic efficiency of the current technological process. This issue must be given more importance in the construction of "new" smelter and sulfuric acid plant, primarily the use of high temperature waste heat, such as smelting and converting processes in the copper smelter and build modern and efficient energy system.

The construction of "new" copper smelter, which is current most important issue, based on autogenous technological process, it should be expected the elimination of sulfur dioxide and flying dust emissions and with it also lead, zinc, mercury, cadmium, arsenic and other components, including reduction of carbon dioxide and nitrogen oxides emissions. This will lead to a reduced share of the copper production process on the global warming effects, such as the effect of "greenhouse" gases and the emergence of "acid" rain in the vicinity of smelters and beyond, as well as the elimination of direct damage from smelter gases on agriculture and eco-system around.

Selection of favorable technological process solution and the entire energy system within the rational energy management would reduce energy consumption by more than three times over the current situation, and the equivalent energy in the copper production will be far lower. Also, production costs will be lower by more than 50% of the current cost of copper production.

Emissions of sulfur dioxide gas in the environment [18] from the current 1.363,591 m_n^3/t_{Cu} (directly 1.356,347 m_n^3/t_{Cu} and indirectly with electricity from the EPS and heat generation plant 7,244 m_n^3/t_{Cu}) will fall to below, the estimated, 10 m_n^3/t_{Cu}.

Carbon dioxide gas emissions in the environment [18] from the current 2.993,424 m_n^3/t_{Cu} (directly 1.524,894 m_n^3/t_{Cu} and indirectly with electricity from the EPS and heat generation plant 1.468,53 m_n^3/t_{Cu}) will fall to below, estimated 130 m_n^3/t_{Cu} direct emissions, rational management of secondary energy and good choice of energy systems and equipment to guarantee that smelters can cover most of its electricity and heat, that is indirect emicija gaseous CO_2 should not exist.

4. Conclusions

Copper production, as a large energy consumer, from ore to copper cathodes optimal energy is 3.5 $t_{ec.}/t_{cCu}$ [7] (mining 61 MJ/t of ore, grinding 270 MJ/t of ore, pyrometallurgy 11 GJ/t of refined copper [13]), fuels make up 50% of copper production. Reducing energy consumption and production costs per unit of the product weight, as a permanent assignment, except for rational energy management, adequate quality copper concentrate and energy, it is necessary to achieve optimal capacity at maximum capacitive and time utilization of metallurgical aggregates. This activity have to be performed at all production stages in all working periods.

However, using secondary (waste) heat of the technological processes, which has a specificity, it will reduce the primary energy consumption, which will contribute, but economic and energy efficiency of a rational energy management affected the reduction of pollutants in the environment and impact on reducing the effects of "greenhouse" gases and the occurrence of "acid" rain. Secondary energy is released from the technological process, used or not, is the pollutant in any case, and the production of energy use, as it is now, further polluting the environment. Using secondary energy to increase energy and economic efficiency of the current technological process. This issue must be given more importance in the construction of "new" copper smelter, primarily using high temperature waste heat, such as smelting and converting processes in the copper smelter and build modern and efficient energy system.

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RECYCLING OF SPENT NICKEL BASED CATALYSTS FROM OIL HYDROGENATION PROCESS

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Abstract

The results of the spent nickel based catalysts recycling, that appear in the oil hydrogenation process are presented in this paper. Nickel based catalysts are used for selective hydrogenation of the highly active plants oils. The used catalysts become a hazardous waste after the hydrogenation process cycle, and they are stored at generation site. The used catalysts are classified in the H11 category of hazardous materials. The research was performed to define the catalysts recycling treatment, which consists of the phases: thermal treatment, degreasing, and dissolution, as well as the influences of temperature, time and solid-liquid ratio at each recycling phase. Hence, extracted nickel becomes non-hazardous, useful and valuable.

Keywords: spent nickel based catalysts, recycling, nickel sulphate

1. Introduction

The rapid development of industrial production influenced the increase of industrial waste quantity. Much of the industrial waste is recycled and returned to the production, while the small part of it is being minimized or stored according to the environmental standards and regulations. Environmental standards, which are becoming more rigorous day by day, are forcing many research teams to think about how to deal with waste [1-6]. Non-hazardous waste that is degradable over time, or not degradable at all, is not a danger to the environment.

Hazardous waste, which is a byproduct of primary production, represents a major problem for the environment beginning from its proper storage, through transportation and further treatment. The best solution to the problem of hazardous waste is its processing at the source, although it rarely happens. Especially dangerous materials are those that contain heavy metals and their compounds that are soluble or insoluble in various media.

During the selective hydrogenation of the highly active plants oils, the spent nickel based catalysts that are hazardous waste are produced. Catalyst activity decreases during the process and after a certain time become unusable. The used catalysts are hazardous waste with index number of 160802 and classified in the H11 category of hazardous materials. Currently they are stored at generation site, and exported with high costs. Investigations on similar materials [7-9], conducted in ITNMS, have led researchers to attempt to get a useful component of nickel from hazardous wastes, and hazardous waste transform into non-hazardous or less hazardous.

Based on the literature, there are two types of processes for the recycling of spent nickel catalyst, such as pyroprocess and hydroprocess. Pyroprocess includes the high-temperature oxidation of spent catalyst and nickel ore, smelting the oxide mixture, then reduction and finally the separation of nickel. Hydroprocesses are based on selective dissolution of components with appropriate leaching solution and their separation from these solutions. Recently, are used a combined pyro- and hydro- processes for processing of spent catalyst [10].

2. Experimental

Based on laboratory investigations, the technological parameters for the hazardous waste, which has a practical value, processing in non-hazardous waste and commercial product, were defined. Spent catalyst which is a powdered form, with a highly developed surface, is suitable for hydrometallurgical processing. Table 1 shows the chemical composition of hazardous waste and the referent value.

Table 1. Chemical composition of hazardous waste and the reference value*

	Content of metals, mg/kg														
	Pb	Cd	Zn	Cu	Cr	Hg	As	Ba	Sb	Co	Mo	V	Al	Be	Ni
U1	27,2	0,5	21,7	0,2	4,4	0,2	2,2	4,6	2,2	69,2	0,4	3,5	1134,2	0,05	195000
RV	1000	60	5000	60000	2500	7	50	100000	700	100000	9000	2000	-	30	3000

U1-The sample of hazardous waste
RV- Referent value
*- Results of the Municipal Institute of Public Health

Presented chemical composition of the investigated sample makes waste dangerous primarily because of the high content of nickel. Removing of nickel, the hazardous waste is converted into harmless or less dangerous.

First of all, the preparing of hazardous waste for the hydrometallurgical treatment was done. The preparation involves two steps: degreasing and thermal treatment to remove organic substances. Hydrometallurgical treatment includes two steps leaching by sulphuric acid, with initial concentration of 220g / l.

3. Results and discussion

The influences of temperature, time and solid-liquid ratio on the degree of recovery of nickel for both single and double-step leaching were determined. The results are shown in the Figures 1, 2 and 3.

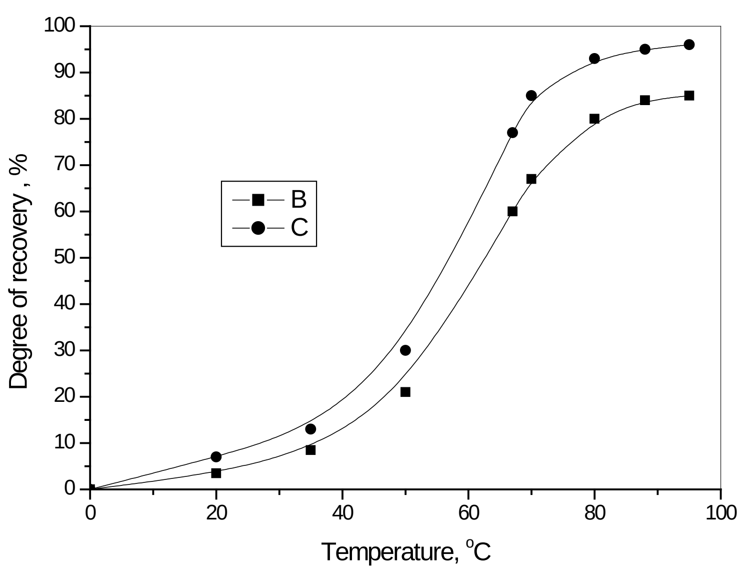

Figure 1. Influence of the temperature on the degree of recovery of nickel; B) one-step leaching, t=3h C) two-step leaching, t_1=3h, t_2=2h

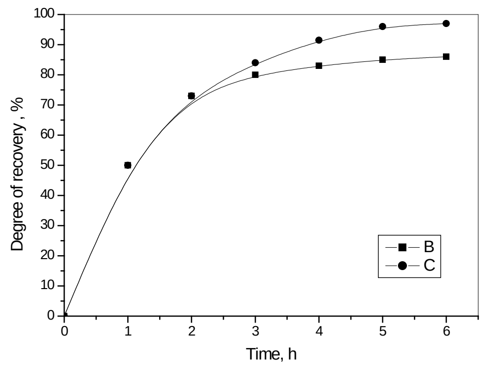

Figure 2. Influence of the time on the degree of recovery of nickel, T=90^{o}C; B) one-step leaching, C) two-step leaching

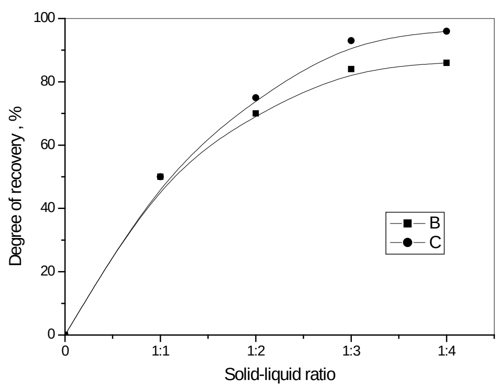

Figure 3. Influence of the solid-liquid ratio on the degree of recovery of nickel, T=90^{o}C; B) one-step leaching, C) two-step leaching

The nickel leaching process from the spent catalysts is exotermal. Experimental results, Figures. 1 and 2, show that the reaction is very slow in its initial stage, until temperature is below 60^{0}C. When the temperature reaches 60^{0}C the onset of reaction is observed and the solution begins to boils, what enables better contact between catalyst and solution. Optimal leaching parameters are: temperature 80-90^{0}C, time 2-5h and solid-liquid ratio 1:4. The reaction stops when sulfuric acid concentration reaches 30g/l. When the acid concentration decreases below this limit, the reaction can be reactivated with an addition of acid and oxidant.

In the first leaching stage of the double–step process, the nickel recovery degree of 80% is accomplished. In the second leaching stage, with the subsequent acid addition, the nickel recovery degree accomplishes 95%. The obtained solution is evaporated till $NiSO_4 \cdot 7H_2O$ is crystallised, while the sediment from the first leaching stage is sent to the second leaching stage. If the quality of the $NiSO_4 \cdot 7H_2O$ crystals is satisfying, they are dried and packed, and if not, they are sent to the recrystallization. The residual sediment contains Al_2O_3 (catalyst bearer) and SiO_2 from the filtration agent. In further treatment of the sediment, the remaining nickel is removed to a referent value of 3000 mg / kg. On that way, the hazardous waste is converted into non-hazardous.

Based on this investigation, the process flowsheet for reprocessing of the spent nickel catalyst is suggested, and presented in Figure. 4.

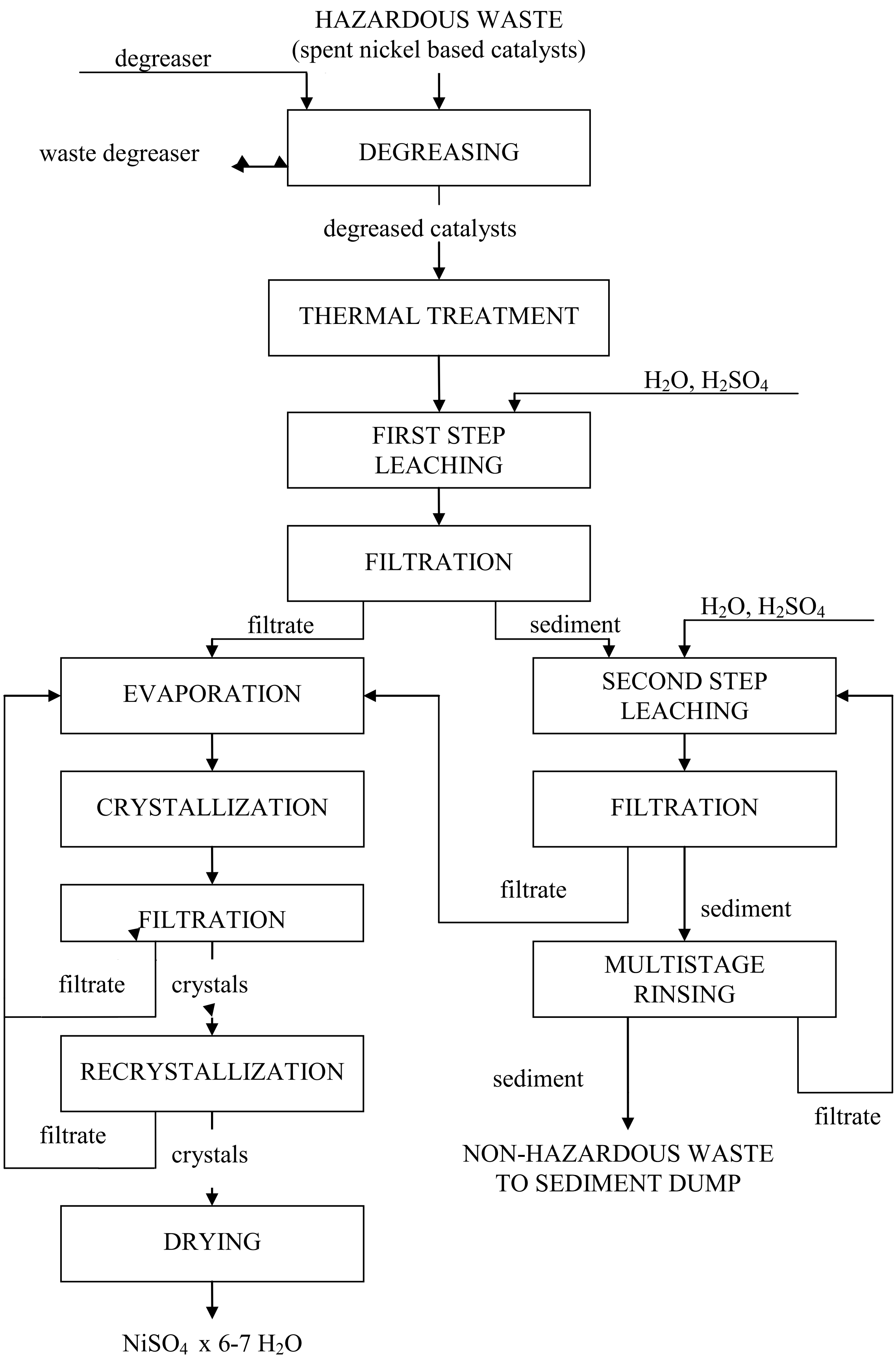

Figure 4. Flowsheet for the recycling of spent nickel based catalysts from oil hidrogenation process

4. Conclusion

Hazardous waste, generated during hydrogenation of the highly active plants oils can be successfully recycled. By suggested hydrometallurgical treatment the following effects are achieved:

- hazardous waste converted to non-hazardous, environmentally friendly according to lawful regulations
- obtained a commercial product

Based on the experimental investigation, the optimal technological parameters of spent nickel based catalysts recycling were determined, and the process flowsheet for processing is suggested.

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NEW ECOLOGICAL NI-BASED MATERIAL FOR APPLICATION IN ELECTRONICS

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Abstract

RoHS directive - restriction of the use of certain hazardous substances in electrical and electronic equipment, has been adopted since 2003, and finally took affect from 1 July 2006. According to this legislative, all EU states adopted their own enforcement and implementation policies using the directive as a guide, often referred to as the lead-free directive, although it restricts the use of the following six substances: lead (Pb), mercury (Hg), cadmium (Cd), hexavalent chromium (Cr6+), polybrominated biphenyls (PBB) and polybrominated diphenyl ether (PBDE).
This paper presents a new ecological, lead-free Ni-based material – Ni-Sb-Zn alloys and their structural, mechanical and electrical characteristics, showing advantages comparing to old lead-based electronic materials.

Keywords: Ni-based alloys, ecological materials, Ni–Sb–Zn ternary system

INTERDEPENDENCE OF DUST EMISSIONS AND GEOLOGICAL RELATIONSHIPS IN THE "OLD CAVE" IN ZENICA

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Abstract

For exploitation on the facility "Stara jama" economically most important major, above major, I, II, III floor coat. The most intensive extraction of coal dust occurs at: service (receipt and transport) of coal, construction of mining facilities, transportation excavations, at the onset of the current manifestation of deep pressure.

Dust around the fan installation is not exceeded the allowable limit, and therefore does not affect the environment. Security measures for mining scope who's making into loading, transporting, and preparation coal reflected in the form of setting up sprinklers and water dams and watering before and after blasting.

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