Synthesis : : Materials : : Corrosion : : Environment : : Energy

XIX YuCorr

Analyse : : Discover : : Coat : : Green : : Protect : : Save : : Sustain

September 12-15, 2017, Tara Mountain, Serbia

Ovaj USB sadrži elektronsku Knjigu radova
(u pdf formatu) prezenovanih u okviru
Međunarodne konferencije **XIX YuCorr**

U knjizi su **plavom bojom** obeleženi aktivni linkovi ka pojedinim njenim delovima, iz Sadržaja do naznačenih stranica.

U vrhu svake strane nalaze se prečice ka **Impresumu** i **Sadržaju** knjige, ka **Indexu** autora, kao i opcijama za štampanje (**Print**), zatvaranje dokumanta, odnosno izlaz iz knjige (**Exit**), i za povratak na ovu stranicu (**Intro**)

This USB contains Proceedings
(single pdf file) from
International Conference **XIX YuCorr**

One can navigate easily through the book contents by a single click on the appropriate links in Contents (**showed in blue**)

All contents of the Proceeding can be accessed through following shortcuts existing at the top of each page: **Impresum** (Impress of the Proceedings), **Contents**, **Index** (Author Index), **Print** (Print manager), **Exit** and **Intro** (which leads to this page).

Autori snose punu odgovornost za sadržaj, originalnost, jezik i gramatičku korektnost sopstvenih radova.
Authors bear full responsibility for the content, originality, language and grammatical correctness of their own works.

Synthesis : : Materials : : Corrosion : : Environment : : Energy

XIX YuCorr

Analyse : : Discover : : Coat : : Green : : Protect : : Save : : Sustain

MEĐUNARODNA KONFERENCIJA

INTERNATIONAL CONFERENCE

STECIŠTE NAUKE I PRAKSE U OBLASTIMA KOROZIJE, ZAŠTITE MATERIJALA I ŽIVOTNE SREDINE

MEETING POINT OF THE SCIENCE AND PRACTICE IN THE FIELDS OF CORROSION, MATERIALS AND ENVIRONMENTAL PROTECTION

PROCEEDINGS

KNJIGA RADOVA

Pod pokroviteljstvom

Under the auspicies of the

MINISTARSTVO PROSVETE, NAUKE I TEHNOLOŠKOG RAZVOJA
REPUBLIKE SRBIJE

MINISTRY OF EDUCATION, SCIENCE AND TECHNOLOGICAL
DEVELOPMENT OF THE REPUBLIC OF SERBIA

September 12-15, 2017 : : Tara Mountain, Serbia

CIP - Каталогизација у публикацији
Народна библиотека Србије, Београд

620.193/.197(082)(0.034.2)
621.793/.795(082)(0.034.2)
667.6(082)(0.034.2)
502/504(082)(0.034.2)
66.017/.018(082)(0.034.2)

МЕЂУНАРОДНА конференција ЈУКОР (19 ; 2017 ; Тара)
Stecište nauke i prakse u oblastima korozije, zaštite materijala i životne sredine [Elektronski izvor] : knjiga radova = Meeting Point of the Science and Practice in the Fields of Corrosion, Materials and Environmental Protection : proceedings / XIX YuCorr [Jugoslovenska korozija] Međunarodna konferencija = XIX YuCorr International Conference, September 12-15, 2017, Tara Mountain, Serbia ; [organizatori Udruženje inženjera Srbije za koroziju i zaštitu materijala ... [et al.] = [organized by] Serbian Society of Corrosion and Materials Protection ... [et al.] ; urednici, editors Miomir Pavlović, Miroslav Pavlović]. - Beograd : Udruženje inženjera Srbije za koroziju i zaštitu materijala UISKOZAM, 2017 (Beograd : Foto Futura). - 1 elektronski optički disk (CD-ROM) ; 12 cm

Sistemski zahtevi: Nisu navedeni. - Nasl. sa naslovne strane dokumenta. - Tiraž 200. - Bibliografija uz većinu radova. - Abstracts. - Registar.

ISBN 978-86-82343-25-7
a) Премази, антикорозиони - Зборници b) Превлаке, антикорозионе - Зборници c) Антикорозиона заштита - Зборници d) Животна средина - Заштита - Зборници e) Наука о материјалима - Зборници
COBISS.SR-ID 244324620

XIX YUCORR – Međunarodna konferencija | *International Conference*

IZDAVAČ | PUBLISHED BY
UDRUŽENJE INŽENJERA SRBIJE ZA KORZIJU I ZAŠTITU MATERIJALA (UISKOZAM),
SERBIAN SOCIETY OF CORROSION AND MATERIALS PROTECTION (UISKOZAM)
Kneza Miloša 7a/II, 11000 Beograd, Srebija, tel/fax: +381 11 3230 028, office@sitzam.org.rs; www.sitzam.org.rs

ZA IZDAVAČA | FOR PUBLISHER: *Prof. dr MIOMIR PAVLOVIĆ, predsednik UISKOZAM*

UREDNICI | *EDITORS:* *Prof. dr Miomir Pavlović, Dr Miroslav Pavlović*

OBLAST | *SCIENTIFIC AREA:* KOROZIJA I ZAŠTITA MATERIJALA / *CORROSION AND MATERIALS PROTECTION*

KOMPJUTERSKA OBRADA I SLOG | *PAGE LAYOUT:* *Dr Miroslav Pavlović*

TIRAŽ | *CIRCULATION:* *200 primeraka* **/** *copies*

ISBN 978-86-82343-25-7

ORGANIZATORI XIX YUCORR-a
XIX YUCORR IS ORGANIZED BY

UDRUŽENJE INŽENJERA SRBIJE ZA KOROZIJU
I ZAŠTITU MATERIJALA

Serbian Society of Corrosion and Materials Protection

INSTITUT ZA HEMIJU, TEHNOLOGIJU I METALURGIJU,
UNIVERZITET U BEOGRADU

Institute of Chemistry, Technology and Metallurgy,
University of Belgrade

SAVEZ INŽENJERA I TEHNIČARA SRBIJE

Union of Engineers and Tehnicians of Serbia, Belgrade

INŽENJERSKA AKADEMIJA SRBIJE

Engineering Academy of Serbia

EVROPSKA FEDERACIJA ZA KOROZIJU

European Federation of Corrosion

XIX YUCORR JE FINANSIJSKI POMOGLO
XIX YUCORR IS ORGANIZED UNDER THE AUSPICIES OF THE

MINISTARSTVO PROSVETE, NAUKE I TEHNOLOŠKOG RAZVOJA REPUBLIKE SRBIJE

MINISTRY OF EDUCATION, SCIENCE AND TECHNOLOGICAL DEVELOPMENT OF THE REPUBLIC OF SERBIA

GLAVNI SPONZOR | *MAIN SPONSOR*

ALFATERM d.o.o., Čačak

SPONZORI | *SPONSORS*

INTERNATIONAL SOCIETY OF ELECTROCHEMISTRY, Switzerland

PITURA d.o.o., Zemun

HELIOS SRBIJA, a.d., Gornji Milanovac

UNIPROMET d.o.o., Čačak

HEMIPRODUKT, Novi Sad

SAVEZ INŽENJERA I TEHNIČARA SRBIJE, Beograd

INSTITUT ZA PREVENTIVU, Novi Sad

SZR “GALVA“, Kragujevac

NOVOHEM d.o.o., Šabac

CONTENTS | *SADRŽAJ*

PLENARNA PREDAVANJA

PLENARY LECTURES

Controlled design of geopolymers'properties by the modification of microstructure

Mogućnost dizajniranja osobina geopolimera modifikovanjem mikrostrukture

Mira Vukčević[1], Ivana Bošković[1], Snežana Nenadović[2], Miljana Mirković[2], Marija Ivanović[2], Svetlana Ilić[2], Ljiljana Kljajević[2]

[1]University of Montenegro, Faculty of Metallurgy and Technology, Podgorica, Montenegro,

[2]University of Belgrade, Laboratory for Materials Sciences, Institute of Nuclear Sciences Vinča, Beograd, Serbia

Abstract

One of the key issues in geopolymer synthesis is the low level of ductility. It can often lead to the limited application possibilities, so the objective is to obtain the enhanced ductility, strength as well as decreased cracking tendency, by microstructure modification. By introducing of inorganic and organic modificators of microstructure (calcium hydroxide, bi-functional epoxy resins, or various types of alkoxylanes) during the process of geopolymer synthesis the enhanced values of ductility and hardness can be obtained.

Introduction of modificators, under the certain pH, synthesis and curing conditions, lead to the creation of homogenous inorganic or organic micro domains within the geopolymer matrix followed by the different types of processes with the same purpose to prevent the post-curing drying shrinkage:filling-the-pores process or „ swelling mechanism“ which generate accomodation of vast quantity of water during synthesis. All these mechanisms decrease the possibility of stress localization and cracking, increasing at the same time the potential use at elevated temperatures. The paper presents the influence of raw mixture, content of microstructure modificator, synthesis parameters (Si/Al, solid/liquid phase, pH, the conditions of alkali activation, modificators content, process of mixing) as well as the conditions of post-synthesis thermal treatment and aging of geopolymers on the mechanical properties of the final product.

Research was performed on alumosilicate raw material/alkali activator raw mixture with the added quantity of modificator.The best raw mixture composition, content of modificator, way of mixing , S/L ratio as well as pH conditions were defined. Characteristics of geopolymers were defined by measuring of compressive strength, ,as well as by SEM. The presence of amorphous phase as well as inorganic and organic domains was documented by using X-ray diffraction (XRD) and Fourier transform infra-red spectroscopy.

Key words: *geopolymers, modification of mictrostructure, ductility, strength*

Circular economy and challenges of waste-to-energy processes in EU

Cirkularna ekonomija i izazovi procesa energetskog iskorištavanja otpada u EU

Filip Kokalj

Faculty of Mechanical Engineering, University of Maribor, Smetanova 17, Maribor, Slovenia

Mašinski fakultet, Univerzitet u Mariboru, Smetanova 17, Maribor, Slovenija

Abstract

The EU action plan on the circular economy from the year 2015 highlights the need for a transition to a circular economy based on a different lifestyle and business style, including the cascading use of material and energy sources and an almost zero level of residual waste and energy. The introduction of this way of life must also be supported by the development of new innovative economic and financial systems.

Waste – to -energy is an integral part of the waste hierarchy and as such falls within the circular economy as the European Commission perceives. Of course, it should not negatively affect the reuse and recycling of waste, which are the preferred methods of waste management. The devices for waste – to – energy should be designed solely for material flows that can't be used otherwise.

Energy use of waste is, in most cases, considered as energy production partly or entirely from renewable energy sources, which means lowering greenhouse gas emissions. It also means the utilization of the domestic energy source and the reduction of domestic energy import dependence.

Proper introduction of circular economy systems, which also includes waste – to - energy, means sustainable economic growth, sustainable industrialization, green jobs and a contribution to achieving sustainable management of natural resources and their effective use.

Key words: *incineration, waste – to – energy, environment protection, circular economy, climate change, renewable energy sources*

Sažetak

Akcioni plan EU o kružnoj ekonomiji od 2015. godine naglašava potrebu za prelazak na cirkularnu ekonomiju zasnovanu na drugačijem načinu života i poslovnom stilu, uključujući kaskadnu upotrebu materijalnih i energetskih izvora i gotovo nultu stopu preostalog otpada i energije. Uvođenje ovog načina života mora biti podržano razvojem novih inovativnih ekonomskih i finansijskih sistema.

Iskorištavanje energije otpada je sastavni deo hijerarhije otpada i kao takav spada u cirkularno ekonomiju, kako to shvata Evropska komisija. Naravno, to ne bi trebalo negativno uticati na ponovnu upotrebu i recikliranje otpada, koje su poželjnije metode upravljanja otpadom. Uređaji za iskorištavanje energije otpada treba da budu projektovani samo za količine materijala koji se ne mogu koristiti na drugi način.

U najvećem broju slučajeva se iskorištavanje energije otpada smatra energetskom proizvodnjom delimično ili u potpunosti iz obnovljivih izvora energije, što znači smanjenje emisije gasova sa efektom staklene bašte. To podrazumeva i korištene domaćeg izvora energije i smanjenje zavisnosti od uvoza energije.

Pravilno uvođenje sistema cirkularne ekonomije, koji uključuje i energetsko iskorištavanje otpada, podrazumeva održivu ekonomsku rast, održivu industrijalizaciju, zelena radna mesta i doprinos postizanju održivog upravljanja prirodnim resursima i njihovom efikasnom korišćenju.

Ključne reči: *spaljivanje, iskorištavanje energije otpada, zaštita zivotne sredine, cirkularna ekonomija, klimatske promene, obnovljivi izvori energije*

1. Introduction

The transformation of our economy from linear to circular is a great opportunity for its thorough change and the increase of its sustainability and competitiveness. This stimulates investment and provides benefits for the economy, environment and citizens.

Countries in general have many opportunities, but it is also challenging to enter the circular economy. Countries of southeast Europe region are greatly forested with great natural capital, a high level of biodiversity and rich natural habitats. At the same time, they continue to cope with economic and systemic challenges that do not facilitate or encourage the transition to a circular economy.

Countries of southeast Europe region have mostly prepared agendas for the transition into circular economy. Slovenia for instance has adopted the Framework Program for the transition to the green economy in October 2015. It sets out strategic guidelines for the development of new environmental technologies and jobs and the marketing of Slovenian knowledge. Although the Slovenian government strongly supports the transition to the circular economy in its strategic documents, the implementation of this concept in practice is lurking.

Waste management is just one of many economic activities involved in the circular economy. Thus, the involvement of this sector is necessary, and in any case, this sector does not play a decisive role in the implementation of the new economy concept.

In general, ordinary population do not even think about the activities that take place before the waste is generated, but only deals with the waste itself. Substantial progress in terms of circular economy regarding waste management will be made when all previous options and methods are utilized to prevent waste from being created at all.

However, since the purpose of this paper is waste management and waste – to - energy, we will only focus on this topic in the future.

Waste must be considered as a material or energy source. To convert waste into a source, it is necessary to:

- reduce the amount of waste generated,
- to fully implement EU waste legislation, which includes a waste hierarchy,
- ensure an efficient separate collection of waste,
- limit the waste – to – energy process only to non-recyclable materials,
- redirect all material waste streams from landfills.

2. State of the art of European Union and Slovenian municipal solid waste management

Slovenia has made great progress in dealing with waste in recent years. According to Eurostat data for the year 2014 the level of municipal waste recycling in Slovenia is among the highest in the EU (61%), and has more than doubled since 2007. However, this rate is calculated on the basis of the amount of waste treated, while in Slovenia there is a significant gap between the amount of waste generated and the amount of waste treated (approximately 40% in 2014). The explanation for this should be in the incomplete coverage of the quantities of pre-treatment of waste.

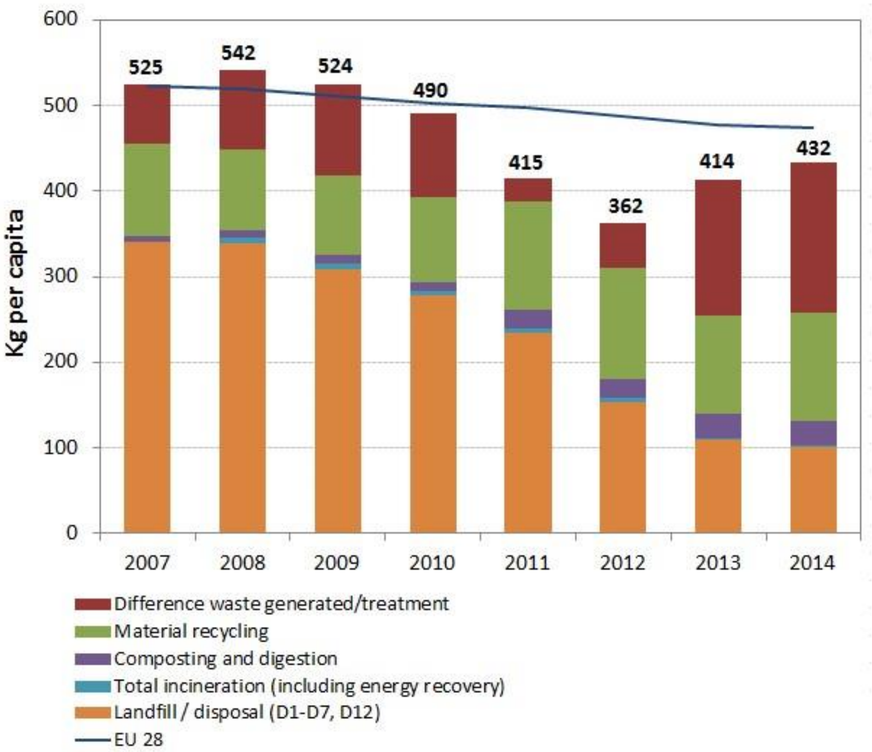


Figure 1: Quantities and management of municipal solid waste in the Republic of Slovenia [5]

Figure 1 shows the treatment of municipal solid waste in kilograms per inhabitant. The figure shows that the rates of recycling, composting and waste – to – energy are increasing, while landfilling is decreasing.

This was mainly due to the general efforts of the state and local communities to change their waste policy and ensure a shift from a society in which almost all waste is deposited in landfills (in 2007, the disposal rate was 75%), into a predominantly recycling society. According to Eurostat data for 2014, the rate of municipal waste disposal at landfills is 39 percent.

Figure 2 shows Slovenia's effort in material recycling in recent years. Material recycling rate in the year 2014 is 61% if waste treated is taken as denominator (49% if generation is taken as denominator). Slovenia is today well over the '2020' 50% recycling target, set by the latest Waste Framework Directive.

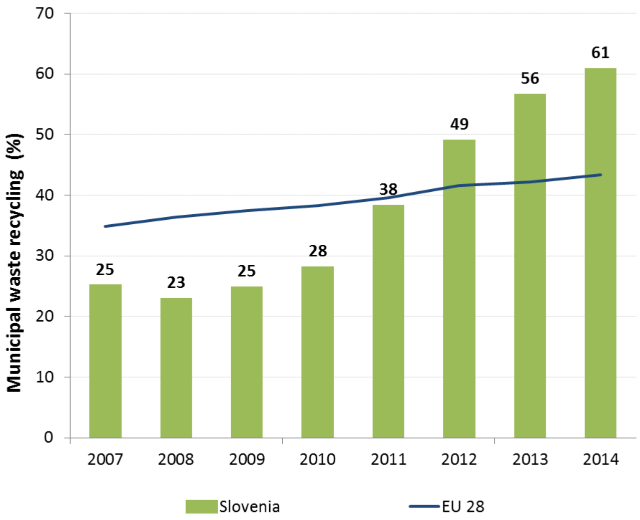


Figure 2: Recycling rates in Slovenia in recent years [5]

3. Waste management policy and legislation outlook

In EU countries, the amount of municipal solid waste increased in recent years at about 1% per year and it is foreseen to increase in future years at the rate of 0.5 to 1%. To handle this challenge ambitious circular economy package, which includes revised legislative proposals on waste was proposed by European Commission. The package should stimulate Europe's transition towards a circular economy which will boost global competitiveness, foster sustainable economic growth and generate new jobs.

The revised legislative proposal on waste sets clear targets for reduction of waste and establishes an ambitious and credible long-term path for waste management and recycling. To ensure effective implementation, the waste reduction targets in the new proposal are accompanied by concrete measures to address obstacles on the ground and the different situations across EU Member States.

Key elements of the revised waste proposal include:

- a common EU target for recycling 65% of municipal waste by 2030;
- a common EU target for recycling 75% of packaging waste by 2030;
- a binding landfill target to reduce landfill to maximum of 10% of municipal waste by 2030;
- a ban on landfilling of separately collected waste;
- promotion of economic instruments to discourage landfilling;
- simplified and improved definitions and harmonized calculation methods for recycling rates throughout the EU;
- concrete measures to promote re-use and stimulate industrial symbiosis – turning one industry's by-product into another industry's raw material;
- economic incentives for producers to put greener products on the market and support recovery and recycling schemes (e.g. for packaging, batteries, electric and electronic equipment, vehicles).

The following legislative proposals on waste have been adopted:

- Proposed Directive on Waste
- Annex to proposed Directive on Waste
- Proposed Directive on Packaging Waste
- Annex to proposed Directive on Packaging Waste
- Proposed Directive on Landfill
- Proposed Directive on electrical and electronic waste, on end-of-life vehicles, and batteries and accumulators and waste batteries and accumulators
- Analytical note on waste management targets
- Staff Working Document - Implementation Plan

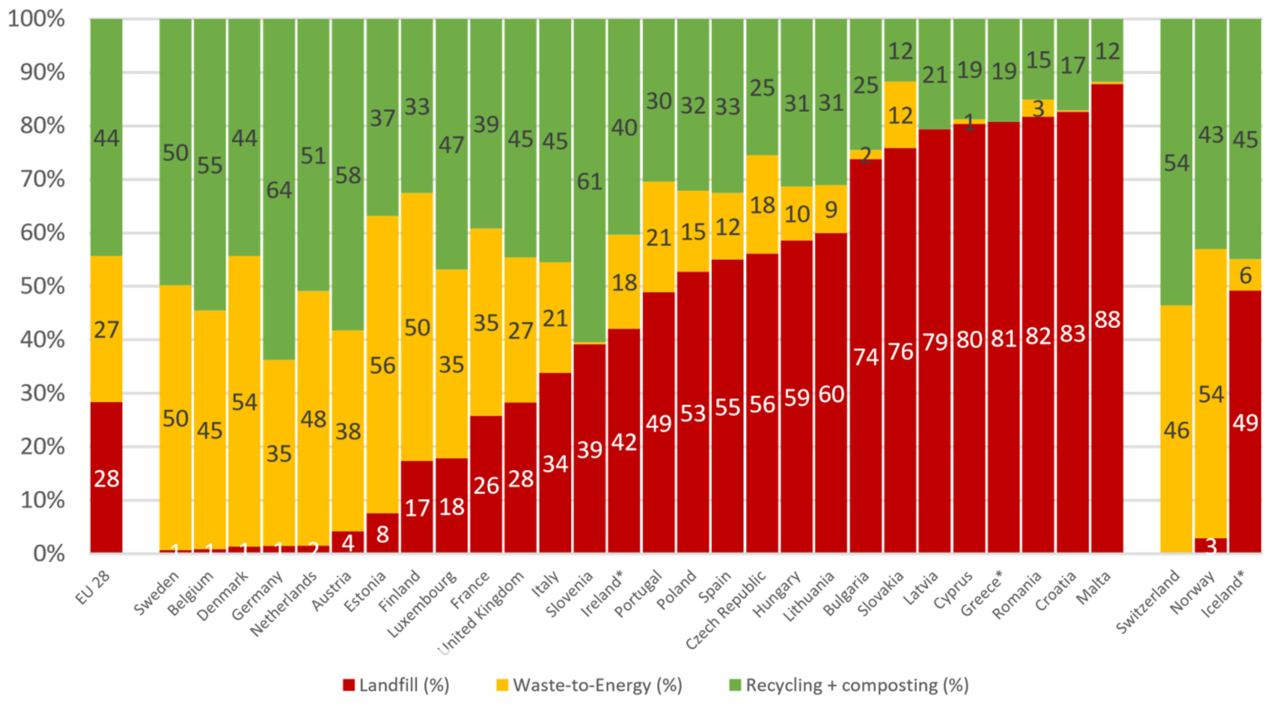


Figure 3: Waste management practice in EU countries in 2014 [3]

Figure 3 shows current waste management practice in EU countries. As it can be seen in the figure, the best performing countries in terms of recycling demonstrate that recycling goes hand in hand with both, the need for complementary energy recovery of the residual waste and the progressive diversion from landfilling.

13 EU countries still landfill more than 50% of their municipal waste. They have no or very little waste – to – energy capacity. These countries need responsible capacity planning, considering efforts of waste prevention and recycling and the need to treat rejects from recycling activities by waste – to – energy. Complementary, they can cooperate with countries with more waste – to – energy capacity to move up the waste hierarchy by recovering energy from waste which would otherwise be landfilled.

The circular economy targets proposed by the European Commission would by the year 2030:

- reduce landfilling to 10% (taking into account that some countries are already below 10% landfilling the average would be 7% (= 17 million tons landfilled);
- increase re-use and recycling to 65% (= 157 million tons), thereby increasing rejects from recycling activities going to waste – to - energy to about 13 million tons.

In order to fulfil the targets proposed for municipal waste, waste – to – energy capacity for 80 million tons would be necessary to treat the residual municipal waste and rejects from recycling processes.

In 2014, EU-28 produced 240.9 million tons of municipal waste of which 44% were recycled and 28% (more than 67 million tons) went to landfills. Waste-to-Energy plants treated 27% of this waste stream. This corresponds to 65 million tons.

In total, in EU-28, 435 waste – to – energy plants in EU treated 83 million tons in 2014.

In 2014 the EU-28 waste – to – energy capacity was over 8 million tons, so one could conclude that there is sufficient capacity to fulfil the municipal waste targets in line with the circular economy package. However, the input into waste – to – energy plants is not only municipal waste, but also industrial and commercial waste. In industrialized countries, the ratio is often 50/50.

With missing reliable EU-wide comparable data on how much commercial and industrial waste is landfilled and recycled it is difficult to estimate how many sorting residues and rejects from recycling facilities will go to waste – to – energy in the future as the targets set in the circular economy package focus mainly on municipal waste.

4. European Union policies and Waste – to – energy

Waste-to-energy can further contribute in meeting the objectives set out in the Energy Union Strategy, in particular with regard to the security of energy supply, the goals of the use of renewables and the EU's strategy on heating and cooling. Energy recovery of non-recyclable waste can not replace primary fuels, but waste can be a useful source of energy for the economy and society.

Energy recovery from waste has a place in a circular economy. Recovery of energy from waste is a broad concept, which involves more than just incineration of waste or thermal treatment. It covers various waste treatment processes for the purpose of obtaining energy (e.g. in the form of electricity / heat or fuel preparation from waste), each of which has an impact on the environment and opportunities in the circular economy.

The energy from waste process in the EU must be in line with the objectives of the circular action plan and have to fully match the waste hierarchy. Energy waste management processes plays an important role in meeting the objectives set out in the Energy Union Strategy and in the Paris Agreement.

Increasing the efficiency of energy recovery processes is linked to the integration of waste – to – energy plants with existing and the development of new district heating and cooling systems for heating of households and industry. Energy utilization with useful heat utilization is particularly present in processing of municipal solid waste, where plants are connected to the district heating network. Incineration that uses energy only for electricity production is relatively inefficient (approximately 20% efficiency) compared to the processes of combined of heat and power production (up to 85% efficiency). The development and broaden of efficient district heating and cooling systems provides unlimited possibilities for the efficient use of energy from waste, especially in connection with combined heat and power production.

Some EU Member States (e.g. Sweden and Denmark) have excess capacity for the waste – to – energy (mainly for municipal waste), while the south-eastern part of the EU is completely without capacities for waste – to – energy and shows a high level of waste disposal on landfills. Germany, France, the Netherlands, Sweden, Italy and the UK account for three quarters of the EU’s incineration capacity. Sweden and Denmark have the highest per capita incineration capacity with 591 kg/cap and 587 kg/cap respectively, followed by the Netherlands, Austria Finland and Belgium. This uneven plant capacity distribution is reflected in the shipment of waste (so called “waste tourism”) for waste – to – energy processing facilities throughout the EU. Taking into account the relevant provisions of EU waste legislation and the need to prevent illegal shipments of waste, steps should be made to move facilities to countries with under capacity and to limit capacities where they are already in excessive amount.

There are recent surveys of the European Commission, which identified about 20 different fuels produced from waste, which are found to be completely underestimated and / or under-utilized. The production of these fuels from certain types of waste has great potential for energy sector.

Although the EU issued guidelines explaining the waste hierarchy, it seems that Member States have different interpretations on the role of energy recovery from waste. The EU emphasizes that thermal treatment offers the best option for handling non-recyclable combustible wastes. In this context, the most efficient procedures for each individual waste stream should be created and implemented. Waste – to – energy contributes to the safe disposal of wastes containing dangerous substances that must be handled in such a way that they do not pose any significant risk to human health and the environment.

No sustainable circular economy, based on reducing waste disposal and promoting quality recycling, can not function well without waste – to –energy process. Thermal processing must be provided for residual waste, which is too polluted for quality recycling, while at the same time it produces safe and reliable energy.

Studies by the EU Commission show that energy from waste in the EU has an important energy potential, but unfortunately, this is often ignored. Exploiting synergies between energy use and district heating / cooling are important steps towards low-carbon energy systems and security of energy supply, which is one of the scopes of the EU energy union.

5. Waste – to – energy processes in relation to EU waste hierarchy

The waste hierarchy is the cornerstone of EU waste policy and legislation and is crucial for the transition to a circular economy. Its main purpose is to establish a priority order that reduces the negative effects on the environment and increases the efficiency of resources in the prevention and management of waste.

This contribution covers the following main waste – to- energy processes:

- co-incineration of waste in combustion plants (e.g. power plants) and in the production of cement and lime;
- incineration of waste in dedicated installations;
- anaerobic digestion of biodegradable waste;
- waste treatment and production of solid, liquid or gaseous fuels;
- other processes, including pyrolysis or gasification.

These processes have different environmental impacts and can be classified in a differentiated manner in the waste hierarchy. The fact is that the extraction of energy from waste covers very different waste treatment processes, ranging from disposal and recovery to recycling. For example, anaerobic digestion involving biogas and digestate production is considered as recycling under EU waste legislation. On the other hand, incineration of waste with limited energy use is considered as disposal. Figure 2 shows various processes of energy waste utilization in relation to the EU waste hierarchy.

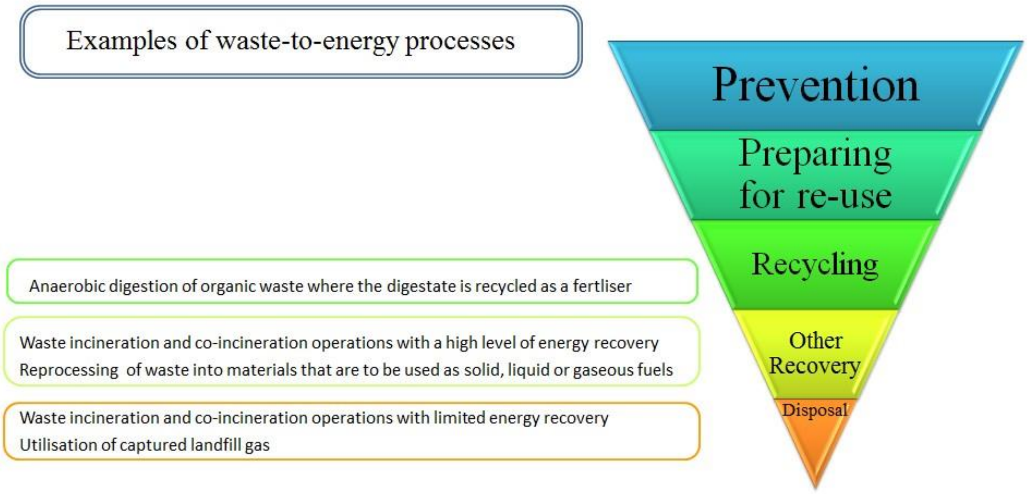


Figure 4: Examples of waste – to – energy processes in relation to waste hierarchy [7]

The waste hierarchy reflects the preferred environmental option from a climate perspective: disposal in landfills or through incineration with little or no energy recovery is usually the least favorable option for reducing greenhouse gas emissions. On other hand the waste prevention, reuse and recycling have the highest potential to reduce greenhouse gas emissions.

It should be stressed out that Member States have some flexibility in the application of the hierarchy, as the ultimate goal is to encourage those waste management options that deliver the best environmental outcome. For some specific waste streams, achieving the best environmental outcome may not be within the priority order of the hierarchy. The reasons can be technical feasibility, economic viability and environmental protection. This must be justified in line with the provisions of the Waste Framework Directive.

6. Waste – to – energy in relation to EU energy consumption

According to the Commission study [8], in 2014 approximately 1.5 % of the EU's total final energy consumption was generated by recovering energy from waste through incineration, co-incineration in cement kilns and anaerobic digestion (i.e. around 676 PJ/year). Whereas this percentage should not significantly increase in the future as more waste is directed to recycling, improving the energy efficiency of waste-to-energy processes and promoting those processes which combine material and energy recovery can contribute to decarbonising key sectors such as heating and cooling or transport and to reducing greenhouse gas emissions from the waste sector. For instance, diverting one ton of biodegradable waste from a landfill towards anaerobic digestion to produce biogas and fertilizers can prevent up to 2 ton of CO_2 equivalent emissions.

The overall technical potential for the improvement of energy recovery from waste – to – energy is presented in table 1. It is obvious that the biggest energy recovery is with waste incineration.

Table 1: EU waste – to - energy technical potential [8]

Scenario	**Energy recovered - Average (PJ)**	**Improvement potential (PJ)**	**Energy recovered - Optimised (PJ)**
waste incineration – electricity	110	71	181
waste incineration – heat	275	65	340
cement and lime plants	176	12	188
anaerobic digestion – electricity	70	-38	32
anaerobic digestion – heat	33	0	33
anaerobic digestion – fuel	12	86	98
Total	**676**	**173**	**872**

Where waste-to-energy processes are opted for, there is a need to ensure that the most efficient techniques are used: this maximizes their contribution to the EU's climate and energy objectives. The Commission study [8] estimates that if proven techniques and supporting measures are properly implemented, the amount of energy recovered from waste could rise by 29 % to 872 PJ/year, using exactly the same amount of waste as feedstock. This shows the potential for energy efficiency improvements.

The study [8] shows that between 2010 and 2014, the incineration capacity in the EU-28 countries (plus Switzerland and Norway) increased by 6 % to 83 Mt and that waste flows between some Member States for the incineration of municipal waste and RDF remained significant in some cases. In 2013, close to 2.5 Mt of waste (most of it RDF) was shipped for energy recovery.

In the period 2006 – 2013, the amount of energy recovered from waste increased by 39% for cement and lime plants, by 36% for electricity from waste incineration plants and by 53% for heat from waste incineration plants. The latter can be explained by the significant increase in the number of waste incineration plants providing combined heat and power.

Table 2 presents a summary overview of the amounts of waste-embedded energy going to either incineration or to landfill/disposal, for 15 out of the 18 waste types for which sufficient data was available (covering 93% of the embedded energy from all wastes sent for waste-to-energy processes). Analysis of the data presented for these wastes shows that:

- 6 types of waste (highlighted in blue in the table) together contain 83% of the total energy embedded in wastes sent to incineration and 93% of the total energy embedded in wastes sent to landfill;
- 3 waste streams only – household and similar wastes, sorting residues and wood waste – account for nearly two thirds of the energy contained in waste sent for incineration;
- 2 waste streams only – household and similar wastes and sorting residues – account for more than three quarters of the energy contained in landfilled waste.

Therefore, any changes in waste management practices for the six waste types highlighted in blue in the table, and in particular for household and similar wastes and sorting residues, would be likely to have the largest impacts on the waste – to – energy landscape in the EU-28.

Table 2 – Amounts of waste-embedded energy sent to incineration or to landfill/disposal in 2012 in the EU-28

	Incineration (D10+R1) (PJ)		Landfill/disposal (D1-D7-D12) (PJ)	
Wood wastes	375	21%	7	0%
Plastic wastes	61	3%	51	4%
Paper and cardboard wastes	6	0%	3	0%
Textile wastes	2	0%	3	0%
Waste tyres	35	2%	2	0%
Spent solvents	29	2%	0	0%
Waste oils	32	2%	0	0%
Chemical wastes	93	5%	31	2%
Household and similar wastes	470	26%	616	44%
Mixed and undifferentiated materials	149	8%	120	9%
Sorting residues	334	18%	489	35%
Animal and vegetal wastes[1]	70	4%	80	6%
Dried municipal sewage sludge[1]	22	1%	7	0%
Waste-derived biogas[2]	108	6%	0	0%
Waste-derived biodiesel[2]	19	1%	0	0%
Total	**1,805**	**100%**	**1,409**	**100%**

7. Conclusion

Energy recovery processes from waste will play an important role in the transition to a circular economy if the waste hierarchy is used as a guiding principle.

Energy recovery from waste must not prevent or compete with higher levels of waste handling, such as prevention, reuse and recycling processes. This is essential to ensure the necessary material flow potentials for the circular economy.

The use of energy from waste can add a contribution to the circular economy in terms of decarbonisation in line with the Union's energy strategy and the Paris agreement.

In the future, countries of southeast Europe will have to think more thoroughly about all the processes of energy utilization of waste. In particular, the process of anaerobic digestion of biodegradable waste, which can also mean a combined material recycling process (digestion residue), should be utilized more often.

In the case of the energy recovery of waste through the waste thermal treatment process, it is necessary to ensure that the recycling and reuse rates still increase. This can be achieved primarily by not imposing excess capacity for the treatment of residual waste. In planning future investments, it is therefore necessary in the long term to assess correctly the amount of waste that will be treated in waste –to – energy facilities. In addition, the potential of new and emerging technologies for waste management and recycling should be taken into account.

Literature

1. CEWEP, Waste – to – Energy Capacity Fact Sheet, www.cewep.eu.
2. Directive 2008/98/EC of the European Parliament and of the Council of 19 November 2008 on waste and repealing certain Directives; Official Journal L 312, 22/11/2008 P. 0003 – 0030.
3. Eurostat, http://ec.europa.eu/eurostat.
4. EXPLOITING THE POTENTIAL OF WASTE TO ENERGY UNDER THE ENERGY UNION FRAMEWORK STRATEGY AND THE CIRCULAR ECONOMY, A Communication from the Commission, 4. 2. 2016.
5. Pregled izvajanja okoljske politike EU, Poročilo za državo – SLOVENIJA, Sporočilo Komisije Evropskemu parlamentu, Svetu, Evropskemu ekonomsko-socialnemu odboru in Odboru regij, Pregled izvajanja okoljske politike EU: skupni izzivi in prizadevanja za boljše rezultate, Bruselj, 3. 2. 2017.
6. Statistical Yearbook, Statistical Office of the Republic of Slovenia, www.stat.si.
7. The role of waste-to-energy in the circular economy, COMMUNICATION FROM THE COMMISSION TO THE EUROPEAN PARLIAMENT, THE COUNCIL, THE EUROPEAN ECONOMIC AND SOCIAL COMMITTEE AND THE COMMITTEE OF THE REGIONS, Brussels, 26. 1. 2017.
8. Towards a better exploitation of the technical potential of waste-to-energy, European Commission, JRC Science for Policy Report, European Union, 2016.

Properties of Cu-Based Shape Memory Alloys

Svojstva legura s prisjetljivosti oblika na bazi bakra

Mirko Gojić[1], Stjepan Kožuh[1], Ladislav Vrsalović[2]

[1] University of Zagreb, Faculty of Metallurgy, Aleja narodnih heroja 3, Sisak, 44103, Croatia

[2] Univresity of Split, Faculty of Chemistry and Technology, Ruđera Boškovića 35, Split, 21000, Croatia

Abstract

Cupper based shape memory alloys (SMAs) are very important metallic materials for different application. The main advantage of Cu-based SMA are their low price in compared to other SMAs. Condition for memory effect is presence of phase transformation austenite to martensite. The comparison main properties of Cu-based shape memory alloys in relation to Ni-Ti shape memory alloys is given. Properties of Cu-Al-Ni alloys are superior to those of Cu-Zn-Al alloys. In the work results of investigation Cu-based shape memory alloys are presented with accent on metallography analysis, mechanical testing, thermal analysis and corrosion properties.

Key words: *shape memory alloys, martensite microstructure, corrosion*

1. Introduction

Shape memory alloys (SMA) are relatively a new class of advanced functional materials which are able to memorize and recover its original shape after being significantly deformed from heating over the phase transformation temperature. They are crystalline materials with entirely a new properties. The SMA was first found in Au-47.5 at.% Cd alloy (Swedish physicist Arne Olander in 1951.) and then in In-Ti alloy (1953.). However, the possibility for using of SMA in actual application was realized for Ti-Ni alloy in 1963. The TiNi alloys are commonly referred as Nitinol (derived from Ni-Ti Naval Ordinance Laboratories, part of the US Department of Defence). On the other hand Cu-based shape memory alloys were found to reveal the shape memory effect in 1964 [1].

The shape memory effect is the remembrance of the previously introduced material shape, and in physical aspect it is the consequence of martensite phase transformation in the structure of homogenous substance. Martensite transformation is a diffusionless phase transformation in the solid state. To enable memory effect in SMA, necessary condition is presence of reversible phase transformation of austenite to martensite. Such phase transformations can be obtained by mechanical (loading) or thermal methods (cooling and heating). Depending on the temperature of deformation the shape memory alloys demonstrate three different types of mechanical behavior: pseudo-elastic, pseudo-plastic (on way effect) and two way effect. The pseudoplastically deformed shape memory alloys can be completely recovered to their initial shape by heating. Numerous alloys [2-4] show shape memory effect (Ag-Cd, Au-Cd, Cu-Al-Ni, Cu-Sn, Cu-Zn, Cu-Zn-X, where X=Si, Sn, Al etc., In-Ti, Ni-Al, Ni-Ti, Fe-Pt, Mn-Cu, Fe-Mn-Si etc.). Among them the three most popular polycristalline shape memory alloys are: Ni-Ti, Cu-based (Cu-Zn-Al, Cu-Al-Ni etc.) and ferrous alloys (Fe-Pt, Fe-Mn-Si etc.).

Nitinol, as binary SMA, is very atractive for industrial and medical applications due to the important the shape memory effect, pseudoelasticity, corrosion resistance and biocompatibility. However most Ti-Ni-based alloys cannot be used at temparatures above 100 ^{o}C. In order to overcome this disadvantage, recent developments of ternary nitinol alloys including Ti-Ni-Nb, Ti-

Ni-Cu, Ti-Ni-Hf, Ti-Ni-RE (RE-reath elements) due to wider transformation temperature hysteresis [5]. Alloying by third elements influence not only the transformation temperatures than also have effect on strength, ductility, shape memory characteristics etc.

The main advantage of Cu-based SMA are their low price compared to other SMA. Properties of Cu-Al-Ni alloys are superior to those of Cu-Zn-Al alloys due to their wide range of useful transformation temperature and small hysteresis. Although Cu-Al-Ni alloys have a better thermal and electrical stability and a higher operating temperatures, their practical applications are sometimes restricted by very small shape changes due to their poor workability and susceptibility to brittle interganular cracks. Their very high elastic anistropy and large grain size cause brittle and poor mechanical properties owing to the high degree of order in the parent phase. Typically composition of Cu-Al-Ni SMA is in the range Cu-(13-15 wt. %) Al-(3-4.5 wt. %)Ni. Adding some alloying elements such as Mn, Fe, Ti, Zr, B etc. to the alloys can significantly improve their ductility and other properties modify their operating temperatures.

The technology of production of shape memory alloys are vacuum melting, induction melting followed by vacuum arc melting, hot working (forgeing, rolling) followed by cold working (wire drawing, rolling). These techniques combined with heat treatments finally lead to the required products. Also is interest microtechnology for production very thin shape memory alloys such as melt-spinning or research of thin film production by vapor deposition, magnetron sputtering etc. Other processing routes productions of SMA are powder metallurgy and combustion synthesis [6].

2. Properties and application of Cu-based shape memory alloys

Phase diagrams are important to understanding properties of shape memory alloys. By means of the phase diagram it is possible to determine stability of particular phases. Figure 1 shows the phase diagram for Cu-Al-Ni ternary alloy [7]. In an equilibrium state, at temperature of 565 ^{o}C and 11.8 wt. % Al, the β-phase with body centered cubic (BCC) structure decomposes into α-phase (primary solid solution of Al and Ni in Cu, FCC structure) and γ_2-phase. It is the eutectoid decomposition. Brittle phases such as γ_2 (cubic intermetallic phase Cu_9Al_4) and NiAl (ordered BCC structure) began to precipitate during exposure of alloy at temperature below eutectoid temperature. By rapidly quenching from single β-phase region, the eutectoid decomposed is suppressed. Then the martensite transformations (Figures 2 and 3) occur in the temperature range from M_s (martensite start temperature upon cooling) to M_f (martensite finish temperature upon cooling). Depends on temperature and stress condition the different types of martensite can be occurs [8,9]. Before martensite transformation, at aluminium concentration above 11 wt. %, the parent β-phase transform to ordered β_1-phase (DO_3-type superlattice). At concentration of aluminium from 11 to 13 wt. % the β'_1-martensite ($18R_1$-type structure) occurs, while at aluminium content above 13 wt. % the γ'_1-martensite (2H-type structure) prevails. By heating of product made from SMA from A_s (start temperature for austenite transformation on heating) to A_f (finish temperature for austenite transformation on heating) the product recovered its original shape. These temperatures (Figure 4) and hysteresis ($\Delta T=A_f-M_s$) determine the environment in which of SMA may be used. The transformation temperatures of Cu-Al-Ni alloys depend on their composition, quenching rate etc. Transformation temperature decreases with increasing both aluminium and nickel content [10]. The effect of aluminium content on transformation temperatures is much stronger than the effect of nickel. By increasing cooling rate results in increasing of M_s temperature. The effect of the cooling rate may be caused by variations in the aluminium content in the matrix due to the precipitation of the γ_2-phase, excess vacancies frozen in by quenching, variations in the degree of order or thermal induced during quenching [1].

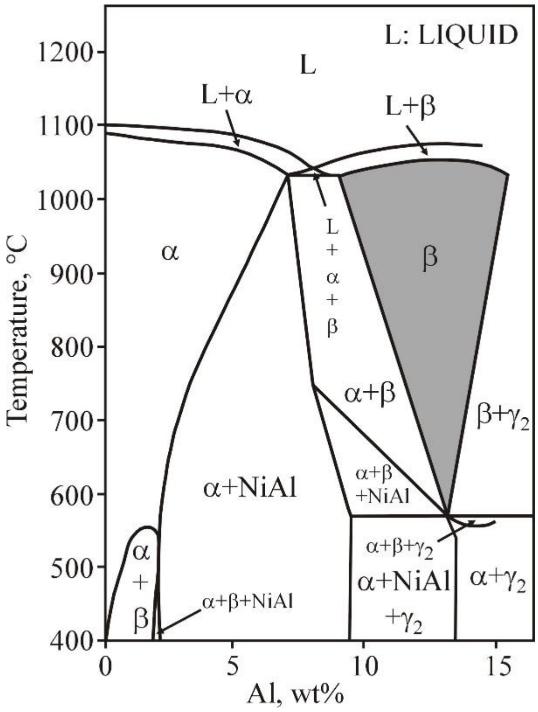


Figure 1. Phase diagram of Cu-Al-Ni alloy, vertical cross-section at 3 wt. % Ni [7]

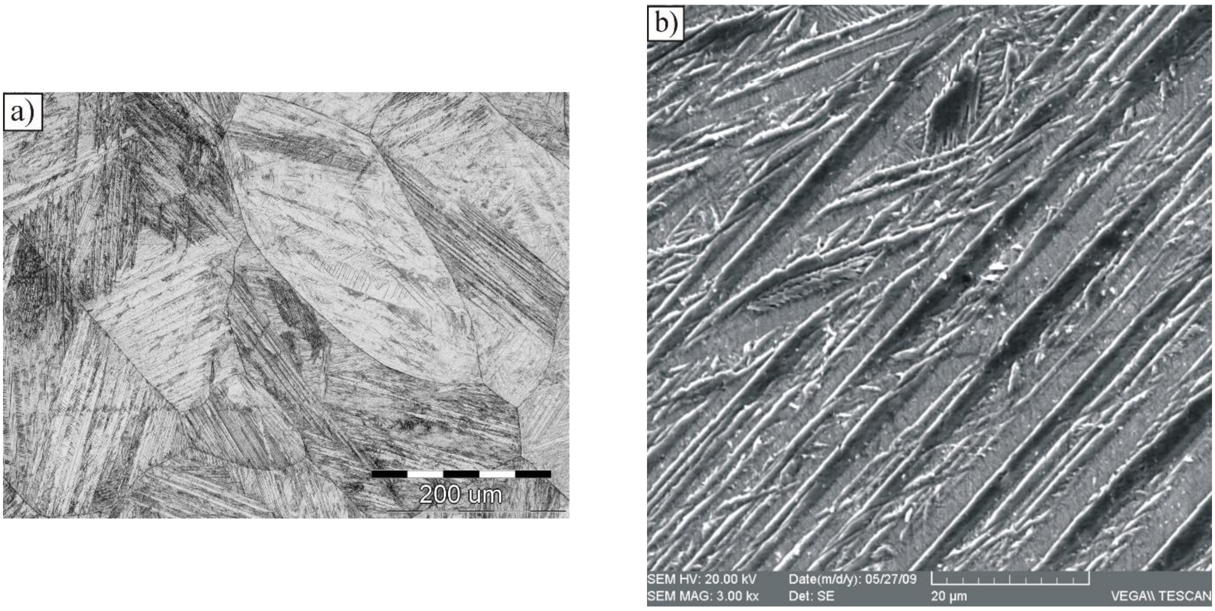
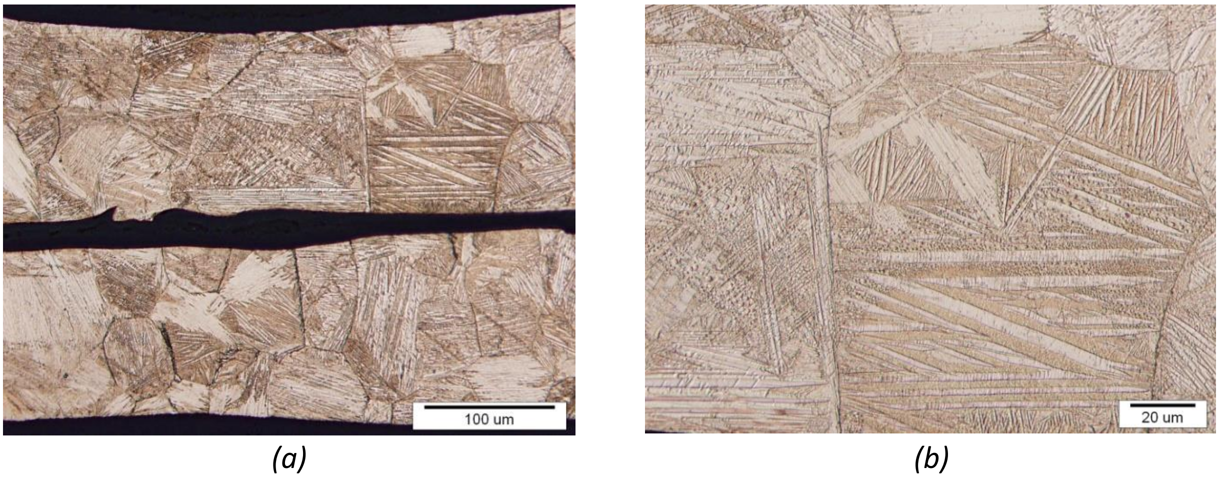


Figure 2. Optical (a) and scanning electron micrographies (b) of Cu-12.6Al-4.3Ni alloy [11]



(a) *(b)*

Figure 3. Optical micrographs of Cu-Al-Mn rapidly solidified ribbons at different magnifiations [12]

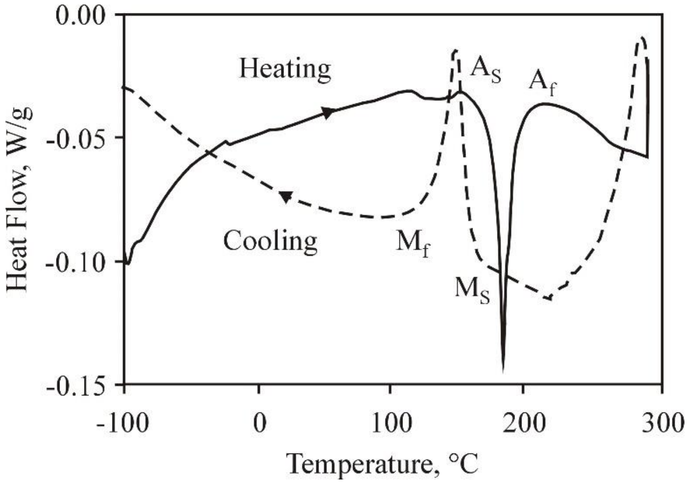


Figure 4. DSC curves of Cu-13Al-4Ni-0.035B shape memory alloy [13]

Cu-Al-Ni shape memory alloys are very sensitive to the exact composition, grain size, processing (including heat treatment), loading conditions etc. [14]. The inclusion of additional elements with a small quantity may change the properties of the alloys dramatically. Due to overcome the formation of coarse grains in Cu-Al-Ni alloys new processing techniques such as melt spinning, compustion synthesis sputtering are used. But these processes generally yield the material/alloys in small quantitivies. Copper based shape memory alloys are usually produced by conventional casting techniques. Products manufactured by this way have solidification related defects. Coarse grains (25-100 μm) formed during solidification and after subsequent betatizing treatment of Cu-Al-Ni alloys make them brittle and highly prone for intergranular cracking during working. From this reason their practical applications are sometimes restricted by very small shape changes due to their poor workability and susceptibility to brittle intergranular cracks. Cu-Al-Ni alloys have poor ductility due to the high degree of order and high elastic anisotropy in the parent β-phase. To improve the shape memory characteristics at high temperature there are following three methods: thermomechanical treatment (cold working followed by suitable annealing), precipitation hardening and addition of quaternary elements. Parent β-phase is the most stable for an electron to atom ratio e/a=1.48. Lower values of e/a will promote first the formation of the ductile α-phase during cooling, while higher values of e/a will promote the formation of the very brittle γ_2-phase. At smaller e/a values, the cold deformation of these alloys can be improved. Therefore, generally lower content of aluminium in Cu-Al-Ni SMA allows better cold deformation of the alloy. In order to improve the ductility of Cu-Al-Ni alloys manganese can be added [15], replacing partially the aluminium content due to manganese is a betastabilising element with e/a ratio equal to 1. In order to overcome the deleterious effect of coarse grains, grain-refining elements as Ti and B can be added to Cu-Al-Ni alloys [16,17]. Titanium as micro alloying elements have very low solubility in the β-matrix and tend to form fine precipitates such as the Cu_2AlTi. Also the addition of Ti and B can refine the grains by forming particles (TiB_2) which can hinder grain growth during annealing. Table 1 shows the comparison main properties of Cu-Al-Ni alloy in relation to Ni-Ti and Cu-Zn-Al shape memory alloys.

Table 1. Comparison main properties of Cu-Al-Ni alloy in relation to Ni-Ti and Cu-Zn-Al shape memory alloys [4, 18,19]

Properties of alloys	Cu-Al-Ni alloy	Ni-Ti alloy	Cu-Zn-Al alloy
Melting point, ^oC	1000-1050	1250	1020
Yield strength, MPa	400	580	80-200
Tensile strength, MPa	500-800	800-1000	500-600
Ductility, %	5-7	54	15
Fatigue strength (10^6), MPa	350	350	270
Specific heat, J/kg ^oC	373-574	450-620	390-400
Thermal conductivity at 20^oC,W/m K	30-75	8.6-18	84-120
Transformation enthalpy, kJ/kg	9	28	7
Density, kg/m^3	7100-7200	6400-6500	7540-8000
Latent heat, J/kg	7000-9000	19000-32000	7000-9000
Electrical resistivity, $10^6/\Omega$ m	0.1-0.14	0.5-1.1	0.07-0.12
Thermal expansion coefficient, 10^{-6}/K	17	6.6-11	17
Maximum recovery stress, MPa	300-600	500-900	400-700
Normal working stress, MPa	70	100-130	40
Max. transf. strain, % at $N = 1$	5-6	6-8	4-6
$N < 10^2$	4	6-8	4
$N < 10^5$		2-4(3)	
$N < 10^7$		0.5	
Normal number of thermal cycles	$> 5x10^3$	$> 10^5$	$> 10^4$
Young's modulus, GPa	80-100	28-83	70-100
Shape memory transf. temp., ^oC	-200 to 200	-200 to 110	-200 to 150
Hysteresis, ^oC	20-40	2-50	5-20
Max. one way memory, %	6	7	4
Normal two way memory, %	1	3.2	0.8
Maximum overheating temp., ^oC	300	400	150
Damping capacity, SDC %	10-20	15-20	30-85
Grain size, μm	25-100	1-100	50-150
Melting, casting and compos. control	Fair	Difficult	Fair
Forming (rolling, extrusion)	Difficult	Difficult	Easy
Cold working	Very difficult	Fair	Restricted
Machinability	Good	Difficult	Very good
Corrosion resistance	Good	Excellent	Fair

Biological compatibility	Bad	Excellent	Bad
Cost ratio	1.5-20	10-100	1-10

The development and applications of the shape memory alloys as the intelligent materials has attracted the worldwide attention. These alloys show very good potential in many real fields of applications. They are very favourable for a small and medium size companies. Because of their exceptional properties, shape memory alloys find their markets in a lot of industrial sectors, for example mechanical engineering, electrical engineering etc. (for example as sensors, actuators, detectors, absorbing component, superelastic elements, connectors, thermal security etc.). Nitinol alloys dominate on the commercial market, because of their larger shape memory effect, better pseudoelasticity, and superior properties with respect ductility, fatigue, corrosion resistance, biocompatibility and recoverable strain.

Cu-Al-Ni shape memory alloys are more cheaper than TiNi alloys. They are considered as one of the important functional materials to act as actuator or sensor is so-called smart or intelligent materials. The most important advantages to select these alloys as an actuation mechanism are: simplicity of mechanism, creation of clean, silent, spark-free and zero-gravity working conditions, high power/weight (power/volume) rations, low etc. [20]. Application of single-crystal Cu-Al-Ni alloys in aerospace field including hinges for development of booms, locking and latching devices, constant force fasteners and non-explosive separation devices [21]. Also these alloys can be used as connector pads in microelectronics chips.

In the Table 2 are shown the results of mechanical properties and microhardness measurements after tensile testing. As can bee seen the highest values of tensile strength were found after casting sample O) and after heat treatment at 780°C (sample 3). The elongation are very low. Fracture analysis of CuAlNi shape memory alloys shows two types fracture (Figure 5). Fracture surfaces indicates transgranular brittle fracture in the center samples where the equiaxial grains are found, while intergranular fracture was observed in the parts where the columnar grains appear.

Table 2. Results of mechanical testing and microhardness of CuAlNi shape memory alloys [22]

Properties/Sample	0	1	2	3
HV 10	305.3	239.4	252.4	242.7
Young's modulus / GPa	41.30	52.95	55.20	47.40
Yieldstrength / MPa	284.0	234.0	261.0	226.5
Tensilestrength / MPa	475.5	323.0	326.0	481.0
Elongation / %	3.95	1.35	1.15	4.00

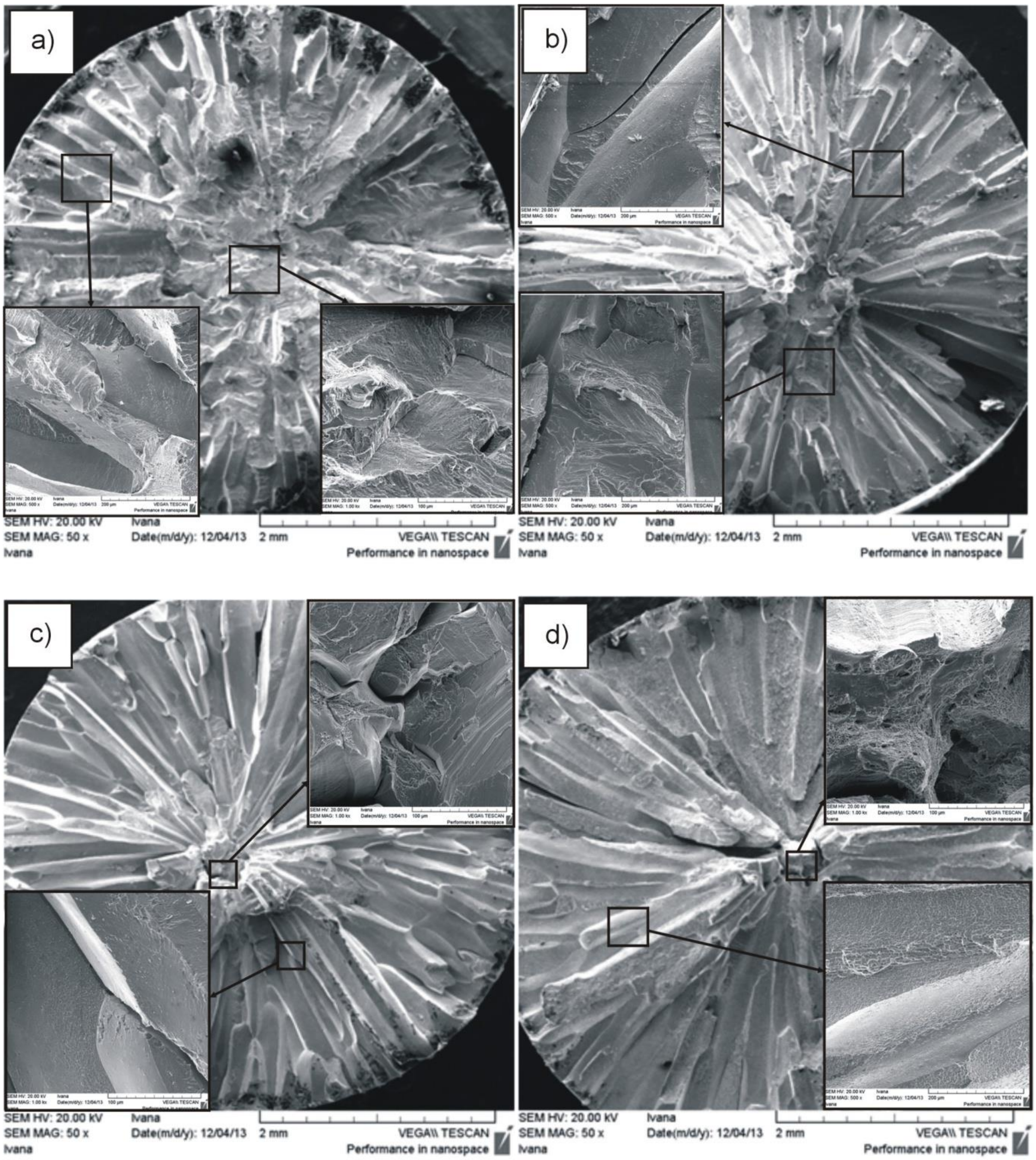


Figure 5. SEM fractography of CuAlNi SMA with marked magnified sections in as-cast state (a), heat treated at 700 °C/2'/WQ (b), heat treated at 740 °C/2'/WQ (c) and heat treated at 780 °C/2'/WQ (d) [22]

As the practical application of Cu-SMA is constantly increasing these alloys are exposed to different corrosion media for a longer period of time which could lead to appearance of corrosion damages on their surface, jeopardise their structural integrity and cause immense consequences if corrosion processes are not observed in time. Therefore it is important to evaluate the corrosion behaviour of Cu-based SMAs in different environments and also to improve their corrosion resistance before their industrial applications.

The good corrosion resistance of the Cu-Al-Ni alloys is due to the formation of the protective layer of alumina, which builds up quickly on the surface post-exposure to the corrosive environment. Aluminium has a higher affinity towards oxygen then copper and Al_2O_3 has better stability then

Cu_2O. Nickel enhance corrosion protection of alloy by its incorporation into corrosion product Cu(I) oxide which reduce the number of cation vacancies that normally exist in Cu(I) oxide.
Typical polarization behaviour of CuAlNi alloy in deaerated 0.5 mol dm^{-3} NaCl solution is presented on Figure 6.

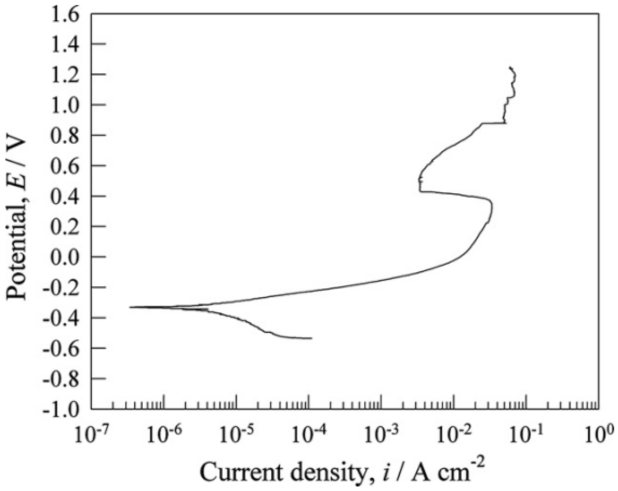
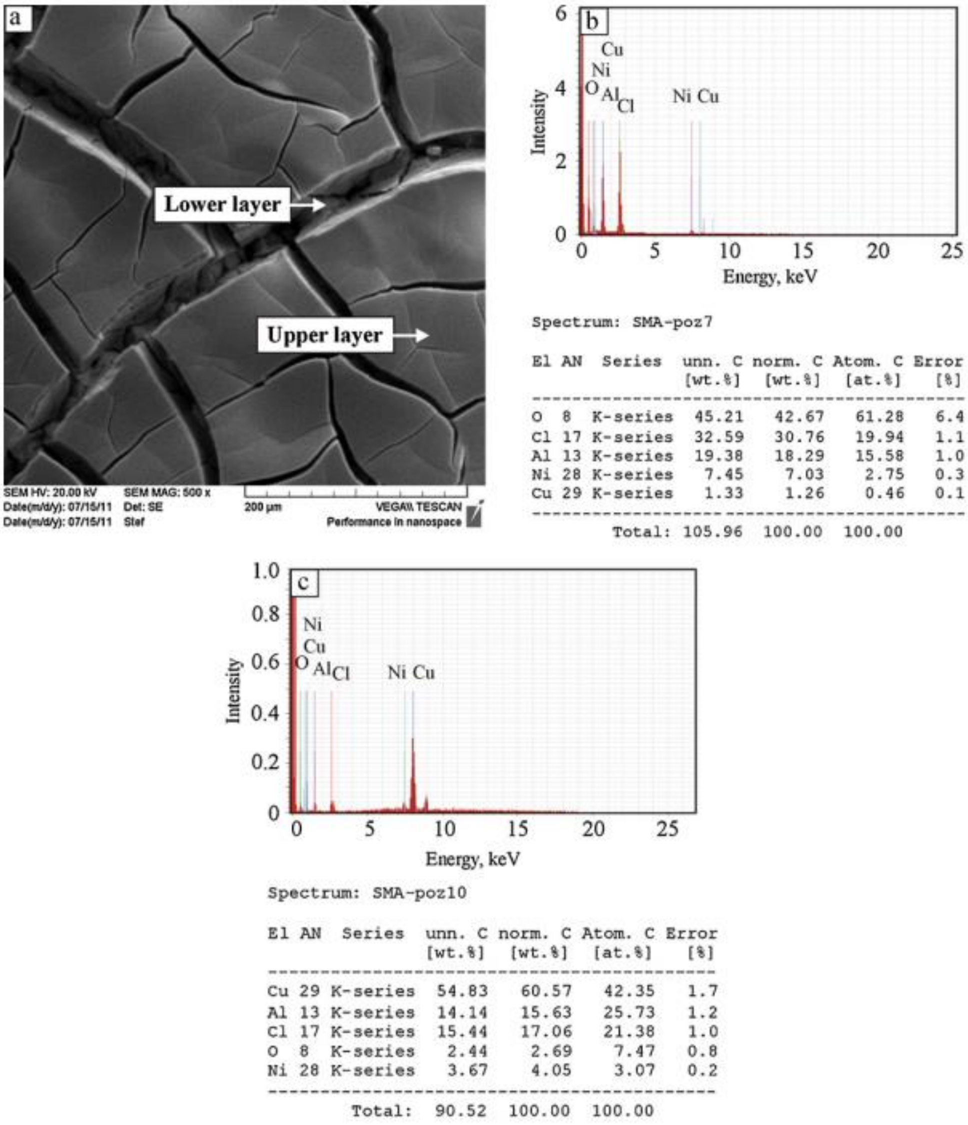


Figure 6. Potentiodynamic polarization curve for CuAlNi alloy in deaerated 0.5 mol dm^{-3} NaCl solution [11]

Composition of corrosion products were confirmed by SEM/EDX analysis which was performed on the Cu-Al-Ni alloy after potentiodynamic polarization interrupted at 0.4V (Figure 7). Two layers of corrosion products on the Cu-Al-Ni surface were observed, Fig. 7a. The upper layer of corrosion products consisted of: 42.7% oxygen, 18.3% aluminium, 7.0% nickel and 30.8% chlorine (wt. %), Fig. 7b. In contrast, the lower layer of corrosion products consisted of: 2.7% oxygen, 60.6% copper, 15.6% aluminium, 4.1% nickel and 17.1% chlorine (wt. %), Fig. 7c. It seems that the upper layer of corrosion products consists mainly of aluminium and nickel oxides and probably aluminium hydroxides and oxychloride complexes, while the inner layer also contains copper, probably in the form of chloride or oxide. In their corrosion research of Cu-Al-Ag alloy in NaCl solution.



```
Spectrum: SMA-poz7

El AN  Series   unn. C norm. C Atom. C Error
                [wt.%]  [wt.%]  [at.%]   [%]
---------------------------------------------
O   8  K-series  45.21   42.67   61.28   6.4
Cl 17  K-series  32.59   30.76   19.94   1.1
Al 13  K-series  19.38   18.29   15.58   1.0
Ni 28  K-series   7.45    7.03    2.75   0.3
Cu 29  K-series   1.33    1.26    0.46   0.1
---------------------------------------------
         Total: 105.96  100.00  100.00
```

```
Spectrum: SMA-poz10

El AN  Series   unn. C norm. C Atom. C Error
                [wt.%]  [wt.%]  [at.%]   [%]
---------------------------------------------
Cu 29  K-series  54.83   60.57   42.35   1.7
Al 13  K-series  14.14   15.63   25.73   1.2
Cl 17  K-series  15.44   17.06   21.38   1.0
O   8  K-series   2.44    2.69    7.47   0.8
Ni 28  K-series   3.67    4.05    3.07   0.2
---------------------------------------------
         Total:  90.52  100.00  100.00
```

Figure 7. a) SEM image of Cu-Al-Ni alloy surface after potentiodynamic polarization measurement which was interrupted at 0.4V. b) Results of EDX analysis for the upper layer of corrosion products. c) Results of EDX analysis for the lower layer of corrosion products [11].

3. Conclusion

Shape memory alloys are crystalline materials which are able to memorize and recover its original shape. The shape memory effect is the consequence of martensite phase transformation. By rapidly quenching from single β-phase region, the martensite transformations occur in the temperature range from M_s to M_f temperature. As the practical application of Cu-SMA is constantly increasing. Cu-Al-Ni shape memory alloys are considered as one of the important functional materials to act as actuator. The good corrosion resistance of the Cu-Al-Ni alloys is due to the formation of the protective layer of alumina, which builds up quickly on the surface post-exposure to the corrosive environment.

4. References

1. S. Miyazaki, K. Otsuka, Development of shape memory alloys, ISIJ International 29 (1989) 5, 353-377.
2. K. Otsuka, C. M. Wayman, Shape memory alloys, Cambridge University Press, Cambridge, 1998., 97-116.
3. D. Ćorić, M. Franz, Properties and application of shape memory alloys, Welding (in Croatien), 50 (2007) 5/6, 179-187.
4. M. Gojić, Alloys with the shape memory alloys, Metalurgija (in Croatien) 31 (1992) 2/3, 77-82.
5. W. Cai, X. L. Meng, L. C. Zhao, Recent development of TiNi-based shape memory alloys, Solid State and Materials Science 9 (2005) 296-302.
6. R. B. Pérez-Sáez, V. Recarte, M. L. Nó, O. A. Ruano, J. S. Juan, Advanced shape memory alloys processing by powder metallurgy, Advanced Engineering Materials 2 (2000) 1-2, 49-53.
7. G. Lojen, I. Anžel, A. Kneissl, A. Križman, E. Unterweger, B. Kosec, M. Bizjak, Microstructure of rapidly solidified Cu-Al-Ni shape memory alloy ribbons, Journal of Materials Processing Technology 162-163 (2005) 220-229.
8. U. Sari, I. Aksoy, Electron microscopy of 2H and 18R martensite in Cu-11.92 wt.%Al-3.78wt.%Ni shape memory alloys, Journal of Alloys and Compounds 417 (2006) 138-142.
9. J. I. Pérez-Landazábal, V. Recarte, V. Sánchez-Alarcos, M. L. Nó, J. S. Juan, Study of the stability and decomposition process of the β phase in Cu-Al-Ni shape memory alloys, Materials Science and Engineering A438-440 (2006) 734-737.
10. V. Recarte, R. B. Pérez-Sáez, E. H. Bocanegra, M. L. Nó, J. S. Juan, Influence of Al and Ni concentration on the martenitic transformation in Cu-Al-Ni shape memory alloys, Metallurgical and Materials Transactions 33A (2002) 8, 2581-2591.
11. M. Gojić, L. Vrsalović, S. Kožuh, A. Kneissl, I. Anžel, S. Gudić, B. Kosec, M. Kliškić, Electrochemical and microstructural study of Cu-Al-Ni shape memory alloy, Journal of Alloys and Compounds 509 (2011) 9782-9790.
12. S. Kožuh, I. Ivanić, M. Bizjak, B. Kosec, T. Holjevac Grgurić, I. Bogeljić, M. Gojić, Microstructure of Cu-Al-Mn shape memory ribbons casted by melt-spinner, Proceedings book of 15th International Foundrymen Conference, University of Zagreb Faculty of Metallurgy, Opatija, 11.-13-5.2016., 140-150.
13. M. Gojić, P. Matković, T. Matković, I. Anžel, A. C. Kneissl, M. Bizjak i B. Kosec, Characterization of Cu-Al-Ni Shape Memory Alloys, Proceedings of 7th Scientific/Research Symposium with International Participation: Metallic and Nonmetallic Materials: Production-Properties-Application, University of Zenica, Faculty of Metallurgy and Materials Science, Zenica, 15-16. may 2008. pp. 225-229.
14. A. Creuziger, W. C. Crone, Grain foundary fracture in CuAlNi shape memory alloys, Materials Science and Engineering A498 (2008) 4044-411.
15. T. Goryczka, Effect of wheel velocity on texture formation and shape memory in Cu-Al-Ni based melt-spun ribbons, Archives of Metallurgy and Materials 54 (2009) 3, 755-763.
16. H. Morawiec, J. Lelatko, D. Stróż, M. Gigla, Structure and properties of melt-spun Cu-Al-Ni shape memory alloys, Materials Science and Engineering A273-275 (1999) 708-712.
17. J. Dutkiewicz, T. Czeppe, J. Morgiel, Effect of titanium on structure and martensite transformation in rapidly solidified Cu-Al-Ni-Mn-Ti alloys, Materials Science and Engineering A273-275 (1999) 703-707.
18. W. Huang, On the selection of shape memory alloys for actuators, Materials and Design 23 (2002) 11-19
19. D. E. Hodgson, M. H. Wu, R. J. Bierman, Shape memory alloys, ASM Handbook, Volume 2: Properties and selection: non-ferrous alloys and special-purpose materials, ASM International, 1990., 897-902.
20. J. V. Humbeeck, Non-medical applications of shape memory alloys, Materials Science and Engineering A273-275 (1999) 134-148.
21. www.tinialloy.com
22. I. Ivanić, S. Kožuh, F. Kosel, B. Kosec, I. Anžel, M. Bizjak, M. Gojić, The influence of heat treatment on fracture surface morphology of the CuAlNi shape memory alloy, Engineering failure analysis 77 (2017), 85-92.

The impact of mining metallurgical copper production in Bor on the environment

Uticaj rudarsko metalurške proizvodnje bakra u Boru na životnu sredinu

Snežana Šerbula

University of Belgrade, Technical faculty in Bor, Vojske Jugoslavije 12, 19210 Bor, Serbia

Abstract

The mining-metallurgical process usually has an adverse effect on the environment. Levels of SO_2 *and metals/metalloids contaminants in the air from 2009 to 2015 were presented in this study. The annual levels of* SO_2 *were constantly above the proposed limit value (LV), except at the site Brezonik during 2009. Water washing significantly decreased Cu, As, and Pb contents in foliar parts of linden and elder. Compared with linden leaves and pine needles, unwashed and washed leaves of elder are better for biomonitoring of Cu, As, Cd and Pb in the conditions of high environmental pollution. According to bioconcentration factor, plant foliage were not enriched through soil at the sampling sites in the urban-industrial zone, suggesting absorption from the air. Translocation from roots to birch and spruce branches was noted at more polluted sites in the following order Pb >> Zn > Cu. Bioaccumulation coefficient showed that both species acted as excluders of Cu, Pb, Zn, and Mn. Regarding foliage, leaves were more enriched than needles with all metals, indicating better response of birch to airborne metal pollution compared to spruce, which could be applied in air biomonitoring surveys near copper smelters.*

Key words: *environment, mining-metallurgical process, air quality,* SO_2*, As, Pb, Cd*

1. Introduction

The mining and metallurgical production of metals is a significant source of particulate matter (PM) and waste gases [1]. The basic components of biosphere (air, water, soil and vegetation) are affected by atmosferic deposition of pollutants. Smelters, in which ores with a high content of sulfur are melted, emit SO_2 which is harmful to the environment in excessive concentrations [2]. Secondary sources of environmental pollution in the vicinity of the mining and metallurgical plants represent tailings from which the particles are distributed by wind [3]. Due to the increased air pollution close to mining and metallurgical complexes, different types of monitoring are implemented [4-7].

Particulate matter in the atmosphere, range from aggregates of a few molecules to pieces of dust readily visible to the naked eye. Airborne particles from anthropogenic and natural sources are the particles emitted directly from the pollution source into the atmosphere (primary particles) and the particles formed after the physical, chemical and photo-chemical reactions in the atmosphere (the secondary particles) [8]. Particles represent a mixture of different components, depending on the local and regional parameters and exist in the atmosphere in the form of the carbonate, sulphate and nitrate compounds, organic matters, ammonia etc. [4]. They can be classified not only based on their chemical structure but also based on the size of the particles. According to the size, they can be divided into: fine particles PM2.5 (2.5 μm in diameter), suspended particles PM2.5-10 (2.5-10 μm in diameter), and coarse particles (over 10 μm in diameter). There are also particles up to 1 μm in diameter (PM1), known as ultra-fine particles.

The time of particle detention in the lower layers of the troposphere is up to several days, whereas they can retain in the upper layers up to several weeks [9]. The industrial and urban-industrial environments are exposed to a higher level of pollution compared to the urban and rural environments, since the highest pollution level originates from industry-related activities, mining, metallurgy, burning of fossil fuels and wastes, and the traffic as well. The particle emission depends on the kind of the technological process and the chemical composition of the processed raw material. The concentration of PM varies due to different weather conditions and topography, as well as seasonal change (the concentration increases in autumn and winter). It even varies within a single day [10].

Air quality monitoring using biological material has been in use for over a century. Initially, biomonitoring was applied only for the porpose of analyzing the impact of SO_2 from the air (as the main air pollutant) on biomaterial. At the present time, biomonitoring is used to monitor a number of pollutants, since it is a reliable way to make a connection between air pollution in large areas and the temporal and spatial concepts at an affordable price [11,12]. Aboveground parts of vegetation are the first level of deposition of atmospheric pollutants which represent an aerosol filter. Diameter of most particles in the urban atmosphere is less than 0.1 μm, unlike the diameter of stomas (openings on the leaf surface), which is between 5 μm and 30 μm, so that the process of foliar absorption of pollutants from the air is undisturbed. As passive bioindicators of air pollution, the following species are the most commonly used: pine, spruce, birch, linden, oak, acacia, lichens, mosses, etc. Sulphur is an important nutrient. Plants compensate their need for sulphur, absorbing it from the soil in the form of sulphate ions, and partly by foliar absorption from the air, which is observed especially in industrial areas. According to, the amount of sulphur in the leaves reflects deposition of SO_2 from the atmosfere. Discarded parts of plants increase the concentration of S in the soil because they are subjected to decomposition and oxidation on the surface of the soil. During that process, sulphur gets transformed to a form acceptable to plants [13].

The aim of the survey was to assess which plant species is the best passive bioindicator of air pollution in the vicinity of the copper smelter in the studied zones. The concentration of substance in the leaves/needles, branches and roots of the plant species should indicate the areas with higher and lower levels of pollution than the dominant source of pollution. For comparison, the concentration of total sulphur content were determined in the samples of plants.

2. Methodology

2.1. The study area

The territory of Bor town and its surroundings, is located in the East Serbia and covers an area of 856 km^2. The population density is 67.2 inhabitants per square kilometer, which is below Serbian average amounting to 100 inhabitants/km^2. Geographic coordinates of the town of Bor are 44°25' N latitude and 22°06' E longitude. The territory of Bor and its surroundings is predominantly hilly and mountainous. This region belongs to the Danube river basin. The predominant economic activities in Bor are mining and metallurgy. Mining in Bor started in 1902. The first smelter started working back in 1906, whereas the present smelter was built during the 1961–1968 period and it is the biggest source of SO_2 and PM emissions in Serbia. Copper is derived by pyrometallurgical method from sulphide copper ores: chalcopyrite ($CuFeS_2$), chalcozine (Cu_2S), coveline (CuS), etc. The usual minor constituents of sulphide ores are: Fe and As (from arsenopyrite FeAsS), Cd, Pb, Ni, Zn, Mn, as well as precious metals.

After flotation, copper ore undergoes a roasting process. Roasting of sulphide concentrate is performed at 600-700^{o}C, which causes destroying and oxidation of sulphide (chalcopyrite, chalcozine, and coveline) and emission of waste gases with high content of SO_2. During the smelting process, from the roast, non-smelting components are removed from the roast in the form of slag, whereas matte is derived. Blister copper is further derived (98% purity), after refining in the converter, while the residues of sulphur oxidize. Sulphuric acid plant process 40% of waste gases, while the rest is discharged untreated into the atmosphere. At the same time, PM with high heavy metal content and atmospheric deposition are discharged into the atmosphere, in spite of dust removal from the waste gases. Around 2.25 kg of particles per ton of refined raw materials are emitted into the atmosphere. Every year the copper smelter emits: 5–8 kg of Zn, 6–25 kg of Pb and 5–20 kg of As per inhabitant of the Bor region, where emission depends on the production volume and the content of these metals in raw materials [14]. As a consequence of the stand-still in the sulphuric acid plant, the utilization of waste gases from the smelter is reduced, which causes a higher concentration of sulphur-dioxide, arsenic and other heavy metals in the atmosphere of Bor.

Besides production and processing of copper ore, pollution in the environment of Bor is also caused by ore waste heap from the open pit, as well as the flotation tailings resulting from the process of copper ore benefication [10].

2.2. Measuring and Sampling Sites

The measuring site Town Park (TP), is located in the urban-industrial area, 800 m southwest of the mining-metallurgical complex as the major pollution source. It is the oldest and most densely populated part of the town where the main business, commercial and administrative buildings are located. The urban-industrial (UI) area of Bor includes the old town core in the close vicinity of the industrial area and the mining-metallurgical complex itself .

The site of Mining and Metallurgy Institute (IN), is located 1900 m south of the urban-industrial area. The measuring site is located in a densely populated residential part of the town. In the close vicinity of the measuring site there are several schools and a recreational sports center.

The site Jugopetrol warehouse (JP), is located 2500 m southeast of the pollution source in the suburban zone. This area is poorly populated and is characterized by the highest frequency winds. Brezonik and Jugopetrol are suburban (S) sites.

Besides these three measuring sites, monitoring of the suspended particles concentration is performed at the Hospital (H) site and the sites Brezonik and Technical Faculty. The Technical Faculty (TF) site is 1000 m away from the pollution source in the west–northwest direction. It is located in the urban-industrial area next to the town hospital. The Brezonik (BR) site is located 2000 m north of the pollution source in the suburban area.

Less frequent measurements are performed in the rural (R) settlements of Slatina (SL), Oštrelj and Krivelj, whereas they are rarely performed in the tourist (T) areas of Brestovac Spa (9 km west of Bor) and Bor Lake (17 km west-nort-west of Bor) since the obtained concentrations are usually within the LV.

The position of the industrial plants, the volume and the character of the emission, the type of settlement, the map of the main traffic routes, the meteorological and topographic parameters are just a few factors which influence the selection and distribution of the representing sites for measuring the concentration of the pollutants [10].

2.3. Materials and Methods

All the used methods are in accordance with The Law on Environmental Protection of the Republic of Serbia and according with The Regulation on limit values, methods of concentration measurements, criteria for determining the measuring sites and data records.

Air quality monitoring includes measurements of: SO_2, suspended particles, soot and atmospheric deposition, continuously observing the meteorological data. The daily reports include data for wind speed and direction, air temperature, relative humidity, atmospheric pressure, etc.

The equipment for air monitoring consists of mobile measuring device and automatic stations. The concentrations of SO_2, as well as meteorological parameters, are measured by using a automatic station.

All the samples of fresh plant and soil material were dried at room temperature during a period of 15 days. The samples were then ground in a laboratory mill (Siebtechnik) and griddled through 0.2-mm sieve. The dried plant samples were measured in the quantity of 0.25 g (Precisa XR 125 SB semi-micro balance with a minimum 0.01 mg mass resolution). The samples were dissolved with acidic mixture concentrated HNO_3/30% H_2O_2/H_2O (3/2/5), using analytical grade reagents (Merck) and double-distilled water (MiliQ, 18.2 MΩ). Solutions were quantitatively transferred in 25 ml calibrated flasks, diluted with double-distilled water and analyzed by ICP-AES [10].

2.4. Meteorological parameters of the study area

The climate of the study area is moderately continental. During the studied period, the air temperature ranged from 10.6-11.7ºC; relative humidity from 68-75%; atmospheric pressure from 970.0-973.2 mbar. Long-term measurements indicate that there are no significant inter-annual variations of meteorological parameters in Bor, in spite of the trend of increasing average annual temperature. The Bor region is characterized by high wind frequency; however, these winds are of moderate intensity. The predominant winds in the study area are W, WNW, NW; less frequent winds are E, ENE, ESE, S. As a consequence of wind direction, the measuring sites Town Park, Hospital and Jugopetrol, as well as the rural settlements Oštrelj and Slatina, are the most endangered ones [10].

2.5. Biological Factors

For the obtained metal concentrations, the following biological factors were calculated; Bioconcentration factor (BCF), which represents the ratio of the element concentration in roots to its concentration in soil (Eq. 1), whereas BCF > 1 indicates accumulation in roots; Translocation factor (TF), which represents the ratio of the element concentration in shoots to its concentration in roots (Eq. 2), where TF > 1 indicates efficient translocation of elements from roots to shoots (branches); Bioaccumulation coefficient (BAC), which represents the ratio of element concentration in aboveground plant parts (foliage) to its concentration in soil (Eq. 3). The value of BAC > 1 shows that the plant is enriched with element (plant is an accumulator); BAC ≈ 1 internal metal concentration indicates the external levels (indicator), and BAC < 1 shows that the plant excludes elements from uptake (excluder) [15-17]. According to Kabata-Pendias and Mukherjee, when BAC surpasses 10, those plants have the ability to hyperaccumulate elements [18].

$$BCF = C_{root}/C_{soil} \tag{1}$$

$$TF = C_{shoot}/C_{root} \tag{2}$$

$$BAC = C_{foliage}/C_{soil} \tag{3}$$

3. Results and discussion

3.1. Air pollution data

Pollution roses based on annual SO_2 concentrations at the six measuring sites in the urban-industrial zone of Bor in the period from 2009 to 2015 are given in Figure 1. At the measuring sites Town Park (TP) and Jugopetrol (JP), SO_2 concentrations were higher compared to the concentrations at the sites Insitute (IN) and Brezonik (BR) [19,20].

During the 7-year period, SO_2 concentrations at the most polluted sites were above the EU limit value (LV), the Serbian LV and the US National Ambient Air Quality Standards (NAAQS) [21-23]. According to the detected exceedances of LVs it could be concluded that plants in Bor and its surroundings grow in the environment which is toxic for plants [24]. Šerbula et al. [6] showed that SO_2 concentrations mostly followed the anode copper production in the period from 2005 to 2008. In some cases, the trend was not present and increasing production was accompanied by decreasing SO_2 concentrations and vice versa, due to the irregularities during the operation of the sulphuric acid plant. This is the consequence of frequent stoppages of the smelter and difficulties in operation due to limited capacities of the sulphuric acid plant [20].

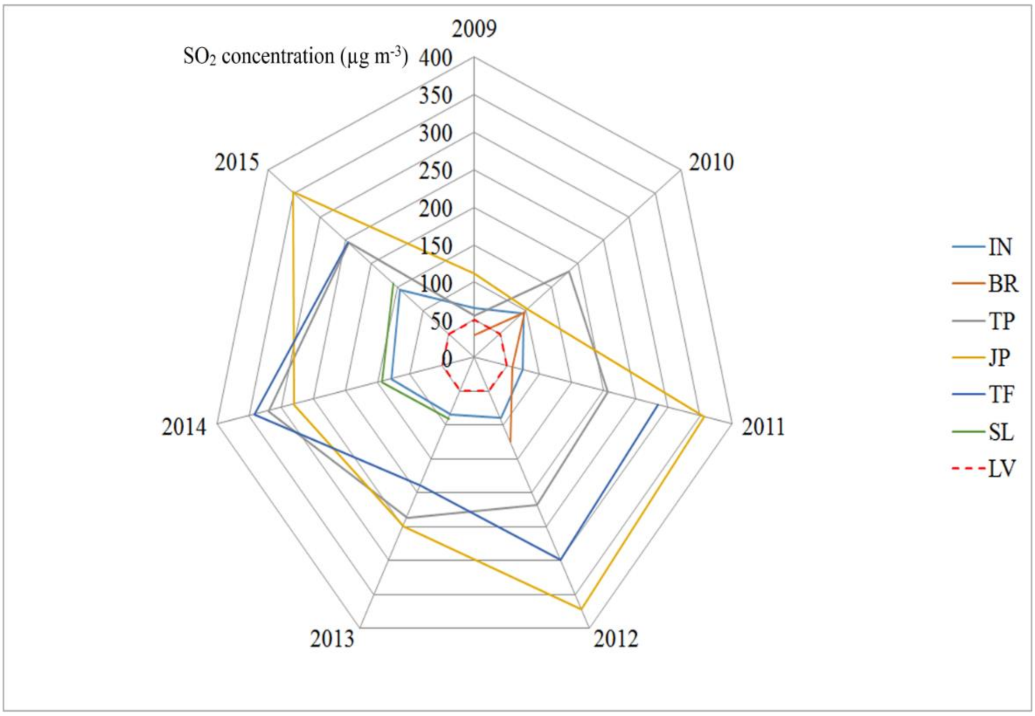


Figure 1. The annual SO2 concentrations in the air at six measuring sites, in regard to the annual limit value (LV) for SO2 concentration, which is 50 µg m-3 [20]

3.2. Soil

The maximum allowable concentration (MAC) of heavy metals in soils has been enacted by the Regulation about allowable quantities of hazardous and harmful substances in soil [24]. In Table 1 concentrations of As, Cu, Zn, Pb, Cd and Hg in top soil of *Robinia pseudoacacia L.* are presented at all the sampling sites compared to the MAC [5].

The terrestrial abundance of As is around 1.5 to 3 mg kg^{-1} [25]. Concentrations of As in soil in all the zones, except in the C zone and at the sampling site Krivelj, considerably surpasses the MAC (25 mg kg^{-1}). The highest concentrations of As are at the sampling site Institute in the UI zone. The reason of the increased concentrations of As in the UI zone is the vicinity of the pollution source. The higher level of As in the T zone (site Bor lake) is due to a negative influence of dominant winds, which transport pollution from the industrial zone. Another possibility could be naturally higher level of As in soil in the T zone. Arsenic is present in copper ores as an accompanying element in the form of arsenopyrite mineral (FeAsS). It is also present in high concentrations in PM in the urban-industrial and suburban zones of Bor [4].

Table 1. Concentrations of As, Cu, Zn, Pb, Cd and Hg (mg kg-1 dry wt) in soil samples compared to the maximum allowed concentration (MAC) and soil pH at ten sampling sites distributed in five zones [5]

Metal	**MAC[a] (mg kg^{-1})**	**UI**			**S**		**R**		**T**		**C**
		Hospital	**Institute**	**Town park**	**Jugopetrol**	**Brezonik**	**Oštrelj**	**Krivelj**	**Brestovac spa**	**Bor lake**	**Sumrakovac**
As	25	51.7±3.9	95.5±9.5	74.7±5.9	43.1±3.8	60.9±5.2	44.5±4.2	16.8±1.1	27.1±2.3	81.8±5.7	9±0.4
Cu	100	470.3±30.5	569.9±43.0	817.3±51.0	266.1±19.5	903.3±51.7	462.4±39.3	67.8±4.7	123.2±9.4	281.4±21.2	59.1±2.3
Zn	300	310.3±26.8	260.2±22.8	330.1±30.1	141±12.2	200±15.4	260±25.3	130.1±6.3	138.1±10.2	220.1±15.1	130.7±5.8
Pb	100	69.9±6.1	96.5±7.6	86.1±3.9	46.5±3.3	52.2±3.8	70.5±5.9	29.6±2.6	40.1±3.2	69.7±5.1	32.3±0.9
Cd	3	0.72±0.05	0.86±0.07	0.64±0.06	<0.5	<0.5	<0.5	<0.5	<0.5	0.52±0.04	<0.5
Hg	2	<0.1	<0.1	<0.1	<0.1	0.3±0.01	<0.1	<0.1	<0.1	<0.1	<0.1
pH		7.5±0.4	7.5±0.3	7.9±0.6	7.3±0.8	7.4±0.5	5.3±0.7	7.8±0.4	5.6±0.2	7.3±0.3	6.0±0.1

All metal concentrations and soil pH shown as Mean±SD
UI–urban-industrial zone, S–suburban zone, R–rural zone, T–tourist zone, C–control zone
[a] *The Official Gazette of Republic Serbia*, No. 23/94

The terrestrial abundance of As is around 1.5 to 3 mg kg^{-1} [25]. Concentrations of As in soil in all the zones, except in the C zone and at the sampling site Krivelj, considerably surpasses the MAC (25 mg kg^{-1}). The highest concentrations of As are at the sampling site Institute in the UI zone. The reason of the increased concentrations of As in the UI zone is the vicinity of the pollution source. The higher level of As in the T zone (site Bor lake) is due to a negative influence of dominant winds, which transport pollution from the industrial zone. Another possibility could be naturally higher level of As in soil in the T zone. Arsenic is present in copper ores as an accompanying element in the form of arsenopyrite mineral (FeAsS). It is also present in high concentrations in PM in the urban-industrial and suburban zones of Bor [4].

The mean levels for Cu in soils vary from 13 to 24 mg kg^{-1}. The common characteristic of Cu distribution in soil profiles is its accumulation in the top horizons [26]. The determined concentrations of Cu in soil are considerably higher than the MAC (100 mg kg^{-1}) in the UI, S, R (site Oštrelj) and the T zone. In the EU, the limit value for Cu in soil is 50-140 mg kg^{-1} of dry weight [27]. The high level of Cu, in all the zones, is a consequence of long-term influence of mining and pyrometallurgical production of copper in the examined area [14].

The Zn soil levels usually fall in the range of 10-300 mg kg^{-1} [26]. A higher level of Zn was recorded in the UI zone at the sampling sites Hospital and Town park. However, exceedance was not significant. At the other sites, the concentrations of Zn were present within the MAC (300 mg kg^{-1}). In the EU the limit value for Zn in soil is from 150-300 mg kg^{-1} of dry weight [27]. The smelter and refinery have the biggest influence on the concentrations of Zn in soil in the Bor suroundings, since Zn is an accompanying element of copper ores [14].

Not at any sampling site do the concentrations of Pb, Cd and Hg in soil exceed the MAC (100 mg kg^{-1}, 3 mg kg^{-1} and 2 mg kg^{-1}, respectively). Higher concentrations of Pb at the site Institute can be a result of traffic pollution [28]. According to annual reports from the Mining and Methalurgy Institute in Bor [19], Cd and Hg are present in small concentrations in PM, which can be the reason of their low concentrations in the soil samples. The limit values in the EU are: for Pb from 50-300 mg kg^{-1}, for Cd from 1-3 mg kg^{-1} and for Hg from 1-1.5 mg kg^{-1} dry weight [27]. The mean Pb concentration for surface soils on the world scale is estimated at 25 mg kg^{-1}; the average contents of Cd in soils are between 0.06 and 1.1 mg kg^{-1}; for various soils on a world level, mean concentrations of Hg in surface soils do not exceed 0.4 mg kg^{-1} [26]. All three metals are in the range of global average concentrations in the soil in our research.

Regarding the zone distribution of pollutants, it can be observed that the highest metal concentrations are in the UI and the S, with certain variations, and the lowest are in the C zone. Higher concentrations of metals at the sampling site Krivelj (R zone) are the consequence of pollution from the open pit near the settlement.

The fate of trace metals in soils depends upon many soil processes. All these processes such as dissolution, complexation, migration, precipitation, diffusion, absorption, etc. are governed by several soil properties, of which soil pH is very important. Changes in the pH of the root ambient solution may play an especially significant role in the rate of availability of certain trace elements [26].

Soil at the examined sampling sites is moderately acid up to mildly alkiline (Table 1). The lowest pH values were measured in the R zone (site Oštrelj), whereas the highest pH value was recorded in the UI zone (site Town park). The analysis of pH soil of Samecka-Cymermana et al. [28] shows slightly lower values (pH 4.1-6.7) than in our research. Mobility of metal ions, according to Kabata-Pendias and Pendias [26], decreases with the increase of pH and is the highest for most metals in acid media (pH<5). At pH>7 the mobility of ions is very weak, therefore rather foliar than absorption through root system can be expected [5].

3.3. Element concentrations in unwashed and washed leaves/needles

Concentrations of Cu, As, Cd and Pb in the unwashed (UL) and washed (WL) leaves sampled in the background zone and in the zones affected with copper production activities are given in Fig. 2. Water washing could have an effect of wind or rain, removing loosely adhering coarse impurities from the leaves [29].

Copper

From Fig. 2a) it can be seen that unwashed leaves of elder have higher Cu concentrations than the linden leaves and the pine needles in the R2, SU and UI zones. In the other areas where foliar Cu contents were lower, the elder and linden leaves had similar Cu concentrations. It is evident that washed elder leaves contained higher Cu concentrations than the other two plants in the R2, SU and UI zone. This difference is less noticeable in the other zones. Unwashed and washed pine needles contained the lowest Cu concentrations in all the zones, except the washed needles from the UI zone. Foliar parts of all the three species sampled in the B zone, and in the area around the tailings ponds of the Krivelj and Cerovo copper mines (I1 and I2 zone), have the lowest, while the R2, SU and UI zones have the highest Cu concentrations. Cu contents in the washed linden leaves from the urban-industrial and rural zone from our previous research [7] were higher than in this study. It can be concluded that that a decreasing pollution trend with Cu has existed during a four year period (2009-2013), which may be regulated with the preventive stoppages of the processes in the copper smelter due to the prediction of unfavorable weather conditions. It should be noted that critical Cu concentrations in leaf tissues that affected growth in most species (15-20 µg/g) (Påhlsson 1989; Rademacher 2001) exceeded in all the three species (WL) in almost all the zones, except in the B and in several cases in the I1 and I2 zone. Critical heavy metal value for copper in plants (100 µg/g) [30] was exceeded to a great extent in the pine, linden, and elder washed leaves/needles in the UI zone. The other exceedances were mostly in the washed elder leaves from the R2 and SU zone. Washed and unwashed pine needles sampled in the polluted zones of Bor and the surroundings have a higher Cu content than in the papers of Dogan et al. [31], Rucandio et al. [32], Samecka-Cymerman et al. [33], Sawidis et al. [34] and Sun et al. [35]. Tomašević et al. [36] obtained Cu concentrations in washed linden leaves of an urban area, which were in the rank with the urban zone of the town of Bor. Washed elder leaves from the surroundings of Pb-Zn mine [37] have Cu, in similar contents as the elder leaves collected in the vicinity of the tailings ponds of the Cerovo and Veliki Krivelj copper mines [29].

Arsenic

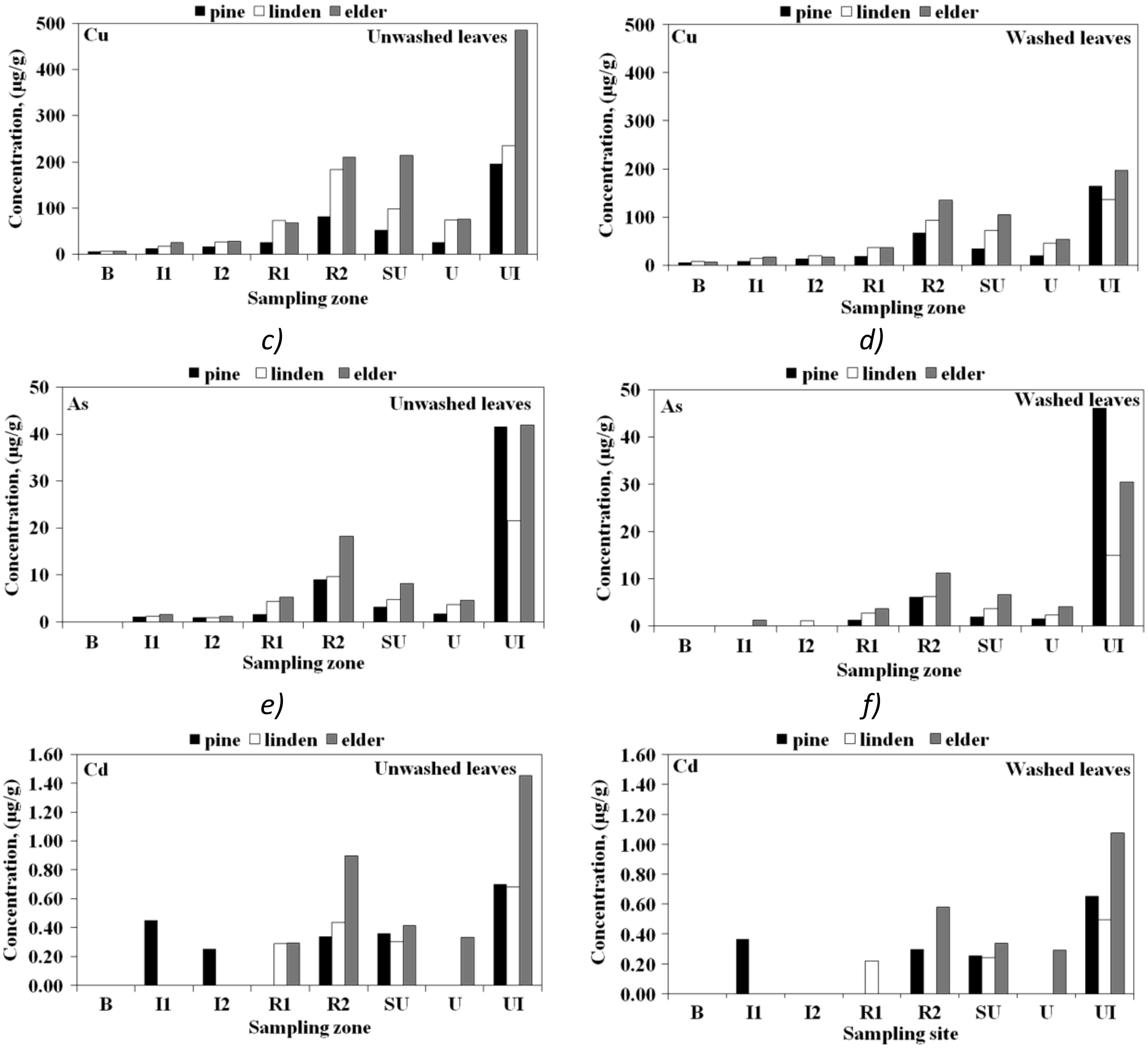
From Fig. 2c) and 2d) it can be seen that elder leaves (UL and WL) have higher As concentrations than linden and pine leaves/needles in the R1, R2, SU and U zone. At the same time, linden leaves were more efficient in As accumulation than pine needles. In the conditions of the increased environmental pollution with As (UI zone), unwashed pine needles and elder leaves showed similar As contents, 41.60 µg/g and 41.94 µg/g, respectively. In the UI zone, washed pine needles had higher As content than washed elder leaves. This difference occurred because after washing of pine needles, As concentrations remained almost the same, which is not the case with elder leaves, whose contents significantly decreased ($P<0.05$) after washing. Fig. 2c) and 2d) show that washed foliar parts of the three plant species collected in the B zone, and from the area around the tailings ponds of Veliki Krivelj and Cerovo copper mines (I1 and I2 zone), had the lowest As concentrations, which were in the range of tolerable As concentrations (up to 2 µg/g) [26]. The most endangered zones, in this regard, are the R2, SU and UI, which are along transects of the predominant wind directions from the smelter. Similar to the case of Cu, foliar parts of all the three species sampled in the B zone, and in the area around the tailings ponds (I1 and I2 zone) have the lowest, while the SU, R2 and UI zones have the highest As concentrations. This is related to the same anthropogenic origin of As and Cu in the examined area, which is the copper smelter. High arsenic concentrations of soil and plants from the rural zones are of big concern, due to the possibility that this carcinogenic may enter the food chain. Arsenic toxicity threshold (~20 µg/g) for plant tissue [38] was exceeded in the washed pine needles and elder leaves sampled in the UI zone. According to the higher As contents in unwashed and washed linden leaves in this study compared to the leaves concentrations in the [39], it can be concluded that As concentrations in the environment of Bor and the surroundings have increased over the years. Foliar As concentrations from the R, U and UI zones in Bor are several times higher, compared to the literature data on the As contents in the current year pine needles and linden leaves from the urban, traffic and rural sites [37]. Arsenic concentrations in washed elder leaves from the polluted sampling sites in this study, are higher than in the paper of Madejón and Lepp [40], where this plant is suggested for phytostabilisation of As contaminated soil [29].

Cadmium

Unwashed and washed leaves of elder contain higher Cd concentrations compared to linden and pine leaves/needles in the R2, SU, U and UI zone. Foliar parts of plants sampled from the B zone have the lowest Cd contents. Cadmium concentrations in the foliar parts of the three examined plant species are the highest in the UI zone. Nevertheless, Cd contents in washed leaves/needles in this zone are below the 5 µg/g, which is considered as a lower limit of critical heavy metal value in plants [30]. Similar as for As, Cd concentrations in the leaves of linden sampled in the vicinity of the copper smelter have increased over the years, compared with the data from the study of Alagić et al. [39]. The unwashed pine needles sampled in the vicinity of the copper smelter have slightly higher Cd contents than the pine needles collected near the iron and steel company [35] and metal smelter in the paper of Samecka-Cymerman et al. [33]. Washed and unwashed linden leaves from the urban sites in an area of heavy traffic of Belgrade [36] have lower Cd concentrations than in urban area of the Bor region. All the determined Cd concentrations in linden leaves from the current investigation have shown to be lower than in the paper of Piczak et al. [41]. Cd contents in washed elder leaves collected around the lead–zinc mine in China [37] are higher than in our examined area, possibly due to the different ore composition [29].

Lead

In Fig. 2g) it can be seen that unwashed foliar parts of pine, linden and elder, sampled in the B, I1 and I2 zone, have almost the same Pb contents. In the R2, SU, U and UI zone, elder leaves have different highest Pb concentrations. Similar pattern is observed for washed leaves/needles, except in the UI zone where pine needles and elder leaves have similar Pb contents. Similar to the case of As and Cu, Pb contents in the unwashed foliar parts of pine, linden and elder from the B zone, and in the area around the Krivelj and Cerovo tailings ponds (I1 and I2 zone), have the lowest, while the SU, R2 and UI zones have the highest Pb concentrations. The washed leaves/needles show the highest Pb concentrations in the R2 and UI zone. Compared to our previous study [7], it could be said that there has been a decreasing trend of Pb concentrations in linden leaves sampled in the R1, R2 and UI zone of Bor. Pb concentration in leaves (35 µg/g) which causes damage to plants according to Rademacher [42], has exceeded in the washed pine needles and elder leaves from the UI zone. Pine needles (WL, UL) collected from the vicinity of iron and steel smelting plants [35] contained about severalfold lower Pb concentrations than the needles sampled in the vicinity of the copper smelter in Bor. Washed linden leaves collected near high traffic street [41] have higher Pb concentrations than the leaves from all the examined zones except the UI zone in this study [29].



a) *b)*

c) *d)*

e) *f)*

g) *h)*

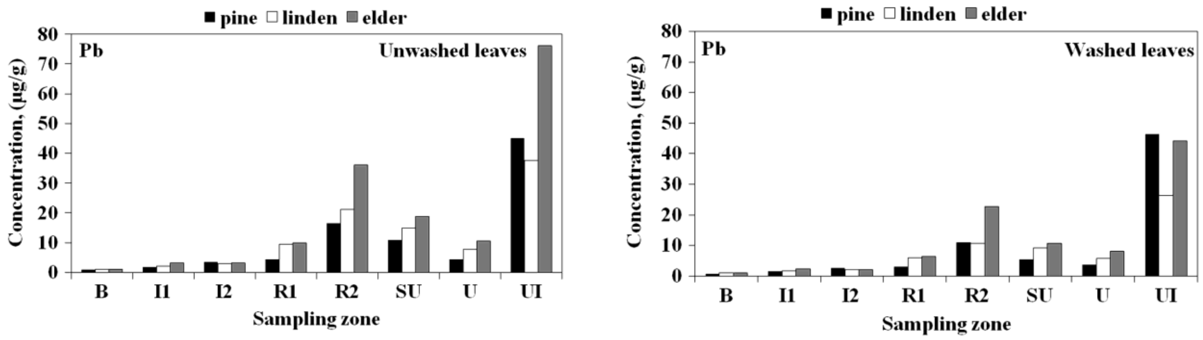


Figure 2. Concentrations of elements Cu, As, Cd and Pb in the unwashed and washed foliar parts of pine, linden and elder: a) Cu (UL); b) Cu (WL); c) As (UL); d) As (WL); e) Cd (UL); f) Cd (WL); g) Pb (UL); h) Pb (WL). Bars are missing in the cases of the concentrations below the lower limits of determination ([As]<1 µg/g; [Cd]<0.2 µg/g) [29]

3.4. Biological Factor Analysis

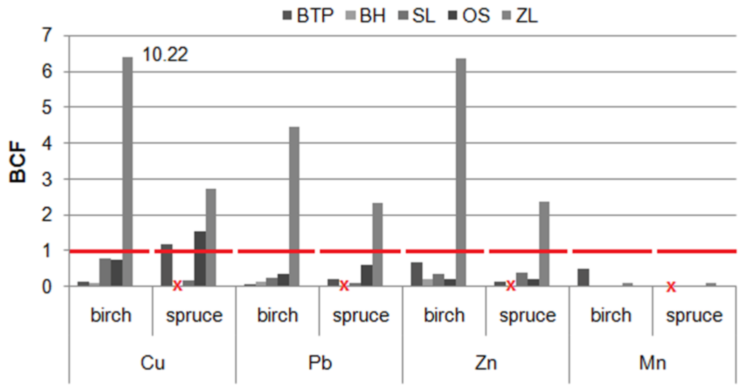
Due to different patterns of behaviour and mobility within trees and limited uptake and translocation of metals [43], contamination of soil above a certain level does not always result in an increased metal uptake via roots [44]. Based on a different capacity for metal uptake from soil, plant species can be used in phytoextraction or phytostabilisation. Plants which are able to accumulate relatively high metal content from soil into aboveground parts and translocate metals efficiently from roots to aboveground parts (BCF > 1, TF > 1) have the potential to be used in phytoextraction. On the other hand, plants with high capacity of accumulation from soil and low translocation of metals to aboveground parts (BCF > 1, TF < 1) have the potential in phytostabilisation [15].

Data on the BCFs per site (Fig. 3.a)) show that birch and spruce roots were most efficient in take up Cu, Pb and Zn from soil at the background site (BCFs were in the range of 2.32–10.22). Additionally, accumulation of Cu is observed in spruce roots at the sites BTP and OS (BCF amounted 1.18 and 1.55, respectively). Neither of the species was efficient in take up Mn from soil (BCFs were from 0.02 to 0.52) at any of the sampling sites. At the sites closest to the copper smelter, the BCFs were very low for all four metals, thus suggesting foliar absorption (with an exception of spruce at the BTP site).

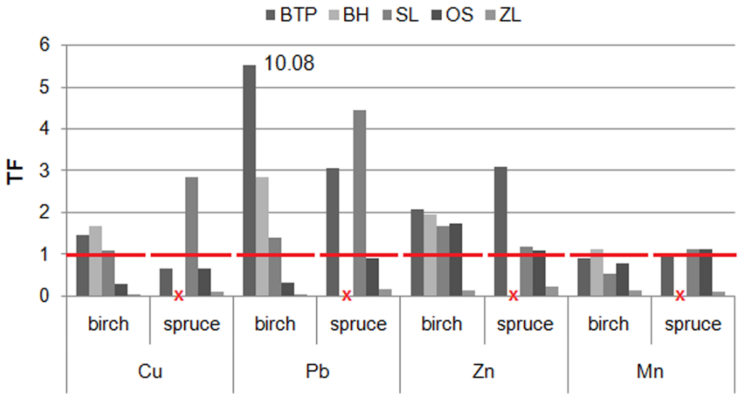
Similarities between the TFs per sampling site were also observed (Fig. 3.b)). Both of the species translocated at least one of the studied metals from roots to branches. Based on the average TF values at the sites in urban-industrial and rural zone, birch was most efficient in translocating Pb >> Zn > Cu, but with lower rate for Mn (TF = 0.83), while spruce showed the translocation of Mn too. Both of the species retained Cu, Pb, Zn and Mn in roots at the background site (TFs in the range of 0.04–0.23), contrary to the results for BCFs. Kopponen et al. (2001) reported translocation of Zn and Cu from roots to birch leaves and stems at higher soil concentrations, which is in agreement with our results. Overall, the different behaviour of both species at the sites with higher and lower load of air pollution is noted. Regarding the potential use in phytoextraction (BCF > 1, TF > 1), neither of the species showed good results for the studied metals, while phytostabilisation (BCF > 1, TF < 1) of Cu, Pb and Zn showed both species at the background site and further research is needed to confirm this potential. Rosselli et al. [46] studied the ability of five woody species to extract Zn from the polluted soil to their aboveground tissues, and found that birch transfers reasonably high concentrations of Zn to their leaves and twigs and may be useful for phytoextraction, which is contrary to our results.

In Fig. 4.c), the BAC values for leaves/needles per site are shown. According to the results, both species mainly behaved as excluders (BACs < 1). However, there are some possibilities for indication and accumulation of airborne heavy metal pollution. Birch leaves prove to be good indicators of Zn (average BACs = 1.33), while the BACs > 1 for Zn and Mn at the BTP site suggest accumulation of these metals in birch leaves at the more polluted site. Regarding spruce in biomonitoring surveys, needles have potential ability for hyperaccumulation of Pb, since the BAC surpassed 10 [18] at the background site. In Rosselli et al. [46], the BACs in birch leaves were very low for Cu, Zn and Cd, ranging from 0.02 for Cu to 0.37 for Zn, which is far lower than our study results. Moreover, the BAC was calculated for leaves/needles, which could be a good sign of foliar absorption of Cu and Pb rather than the absorption from soil or metal exclusion by both species [45].

a)



b)



c)

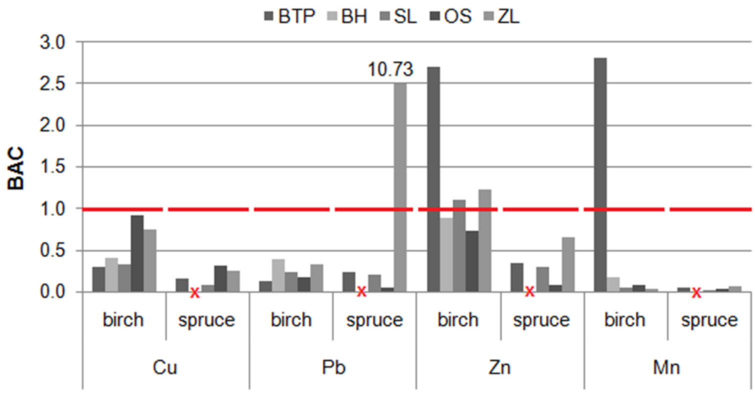


Figure 3. Biological factors per site for Cu, Pb, Zn and Mn (a) Bioconcentration factor (BCF); (b) Translocation factor (TF); (c) Bioaccumulation coefficient (BAC) (dashed line shows effective translocation/accumulation of metals) [45]

4. Conclusion

Long-term monitoring of air-quality parameters in this area, and scientific studies as well, prove that the mining-metallurgical complex, is the major pollution source emitting particulate matter and sulphur-dioxide into the atmosphere.

Airborne PM with high content of heavy metals, pollute not only the urban parts of the town in the close vicinity of the mining-metallurgical complex, but also the suburban and distant rural zones. The predominant winds in the study area are WNW, NW and W. Data analysis shows a direct influence of the wind direction on the pollutants transported to the particular measuring sites. Due to unfavourable wind conditions, the areas around the measuring sites Town park and Hospital (E and ESE wind direction) are considered to be pollution risk areas. As far as suburban settlements are concerned, the areas around the measuring sites Jugopetrol and Brezonik are the endangered areas.

Long-term measurements of the content of heavy metals: Cd, Pb, and As in PM has showed permanent exceedance of the LV for As concentrations, while the increased Cd concentrations appeared occasionally in the urban-industrial, and the suburban zones. The average annual Pb concentrations were within the LV, where the highest concentrations were in the urban-industrial zone (the measuring site Hospital) and the lowest ones in the rural zone. With the increase of the number of vehicles, there was no proportional increase of Pb concentration in the air, which means that the primary source of air pollution by lead is the mining-metallurgical complex. The greatest danger for the environment and all the living organisms are the high concentrations of arsenic in PM. Over 50% of the arsenic concentration value at all the sites in the examined period by far exceeded the allowed values. Arsenic is also a carcinogenic matter, so that this state of matter is troublesome. The immediate vicinity of the measuring site Town park to the pollution source, as well as the position of the measuring site Jugopetrol along the prevailing wind direction caused high As air pollution levels.

The presence of SO_2 in the air is very high, forming acid rain and sulphates in atmospheric deposition.

Concentrations of heavy metals in plant material, confirm results of the analysis performed at the measuring sites in the urban-industrial, suburban and rural zones by the automatic and mobile stations. These concentrations were higher at the sampling sites closer to the mining-metallurgical complex than to the rural zone. According to the accumulated quantities of the polluting matters in the plant material, it can be concluded that mining and metallurgy present large emitters of hazardous matters, as well as a big risk for the environment.

The high concentrations of heavy metals in plants, from the Bor region, represent a serious danger for human health, as it is very easy for them to enter the human digestive tract, through the food chain or by direct consummation.

Acknowledgments

The authors are grateful to the Ministry of Science of Serbia for financial support (Project No. 46010 and 33038). Our thanks go to Proffesor Mara Manzalović from Technical Faculty in Bor (University of Belgrade) for providing language help.

5. References

1. Boyd, R.; Barnes, S. J.; De Caritat, P.; Chekushin, V. A.; Melezhik, V. A., Reimann, C. & Zientek, M. L., Emissions from the copper–nickel industry on the Kola Peninsula and at Noril'sk, Russia. Atmospheric Environment. 2009, 43 (7), 1474–1480.
2. Koptsik, G. & Alewell, C. (2007). Sulphur behaviour in forest soils near the largest SO2 emitter in northern Europe. Applied Geochemistry, 22 (6), 1095–1104.
3. Csavina, J.; Landázuri, A.; Wonaschütz, A.; Rine, K.; Rheinheimer, P.; Barbaris, B.; Conant, W.; Sáez, A. E. & Betterton, E. A., Metal and metalloid contaminants in atmospheric aerosols from mining operations. Water, Air, and Soil Pollution, 2011, 221 (1–4), 145–157.
4. Šerbula, S. M.; Antonijević, M. M.; Milosević, N. M.; Milić, S. M. & Ilić A. A. (2010). Concentrations of particulate matter and arsenic in Bor (Serbia). Journal of Hazardous Materials, 181 (1–3), 43–51.
5. Serbula, S. M.; Miljkovic, D. Dj.; Kovacevic, R. M. & Ilic, A. A. (2012a). Assessment of airborne heavy metal pollution using plant parts and topsoil. Ecotoxicology and Environmental Safety, 76 (1), 209–214.
6. Serbula, S. M.; Kalinovic, T. S.; Kalinovic, J. V. & Ilic, A. A. (2013a). Exceedance of air quality standards resulting from pyro-metallurgical production of copper: a case study, Bor (Eastern Serbia). Environmental Earth Sciences, 68 (7), 1989-1998.
7. Serbula, S. M.; Kalinovic, T. S.; Ilic, A. A. & Kalinovic, J. V. & Steharnik, M. M. (2013). Assessment of airborne heavy metal pollution using Pinus spp. and Tilia spp. Aerosol and Air Quality Research, 13 (2) 563–573.
8. Šerbula, SM; Stevanović, J.; Trujić, V. Title: Arsenic, Heavy Metals and SO2 Derived in a Mining-Metallurgical Production Process. In: Brar SK editor. Title: Hazardous Materials: Types, Risks and Control. New York: Nova Science Publishers US; 2011; 187–223.
9. Toledo, V. E., Almeida, P. B., Quiterio, S. L., Arbilla, G., Moreira, A., Escaleira, V., Moreir, J. C. (2008). Evaluation of levels, sources and distribution of toxic elements in PM10 in a suburban industrial region, Rio de Janeiro, Brazil. Environmental Monitoring Assessment, 139, 49-59.
10. Serbula, S. M.; Alagic, S. C; Ilic, A. A.; Kalinovic, T. S. & Strojic, J. V. Title: Particulate Matter Originated From Mining-Metallurgical Processes. In: Knudsen H, Rasmussen N. editors. Title: Particulate Matter: Sources, Emission Rates and Health Effects. New York: Nova Science Publishers US; (2012b); 9–116.
11. Falla, J.; Laval-Gilly, P.; Henryon, M.; Morlot, D. & Ferard, J.-F. (2000). Biological air quality monitoring: A review. Environmental Monitoring and Assessment, 64 (3), 627–644.
12. Wolterbeek, B. (2002). Biomonitoring of trace element air pollution: principles, possibilities and perspectives. Environmental Pollution, 120 (1), 11–21.
13. Serbula S. M., Kalinović T. S.,. Ilic A. A, Kalinovic J. V., Bugarski B. M., The Impact of Air Pollution from the Mining-Metallurgical Complex on the Content of Total Sulfur in Plant Material and Soil, chapter in Air Quality: Environmental Indicators, Monitoring and Health Implications, Editors: Arthur Hermans,Nova Science Publishers, US, New York. (2013), pp. 73-98
14. Local Environmental Action Plan of Municipality of Bor 2003. Marjanovic, T., Trumic M., Markovic, Lj., Bor (in Serbian).
15. Yoon, J., Cao, X., Zhou, Q. and Ma, L.Q. (2006). Accumulation of Pb, Cu, and Zn in native plants growing on a contaminated Florida site. Sci Total Environ. 368: 456–464.

16. Malik, R.N., Husain, S.Z. and Nazir, I. (2010). Heavy metal contamination and accumulation in soil and wild plant species from industrial area of Islamabad, Pakistan. Pakistan J Bot. 42: 291–301.
17. Zhang, X., Zhang, S., Xu, X., Li, T., Gong, G., Jia, Y., Li, Y. and Deng, L. (2010). Tolerance and accumulation characteristics of cadmium in Amaranthus hybridus L. J Hazard Mater. 180: 303–308.
18. Kabata-Pendias, A. and Mukherjee, A.B. (2007). Trace Elements from Soil to Human. Berlin, Springer.
19. Mining and Metallurgy Institute Bor, Annual reports about quality of ambient air in Bor from 2005 to 2016. Group for measuring and control of gaseous and dust parameters, Department for Chemical-Technical Control (in Serbian).
20. Serbula S. M., Milosavljevic J. S., Radojevic A. A, Kalinovic J. V., Kalinović T. S. (2017). Extreme air pollution with contaminants originating from the mining–metallurgical processes. Science of the total enviroment, 586, 1066-1075.
21. Directive 2008/50/EC of the European Parliament and of the Council of 21 May 2008 on Ambient Air Quality and Cleaner Air for Europe, Official Journal of the European Union, L152, 11 June 2008, p. 1–44.
22. The Official Gazette of Republic of Serbia, 2013. Regulation on the conditions for monitoring and requirements of the air quality. No 11/10, 75/10, 63/13 (in Serbian).
23. U.S. Environmental Protection Agency (2010). National Ambient Air Quality Standards (NAAQS) USA.
24. The Official Gazette of Republic Serbia, No. 23/94. Regulation about allowable quantities of hazardous and harmful substances in the soil and methods for their investigation (in Serbian).
25. Mandal, B.K., Suzuki, K.T., 2002. Arsenic round the world: a review. Talanta. 58, 201–235.
26. Kabata-Pendias, A., Pendias, H., 2001. Trace Elements in Soils and Plants, third ed. CRC Press, Boca Raton.
27. Council Directive 86/278/EEC on the protection of the environment, and in particular of the soil, when sewage sludge is used in agriculture. Official Journal of the European Communities, L 181/6.
28. Samecka-Cymerman, A., Stankiewicz, A., Kolon, K., Kempers, A.J., 2009. Self-organizing feature map (neutral networks) as a tool to select the best indicator of a road traffic pollution (soil, leaves or bark of Robinia pseudoacacia L.). Environ. Pollut. 157, 2061–2065.
29. Kalinović T. S., Serbula S. M., Radojevic A. A, Kalinovic J. V., Steharnik M. M., Petrovic J.V.(2016). Elder, linden and pine biomonitoring ability of pollution emitted from the copper smelter and the tailings ponds. Geoderma, 262, 266-275.
30. Cicek, A., Koparal, A.S., Accumulation of sulphur and heavy metals in soil and tree leaves sampled from the surroundings of Tunçbilek Thermal Power Plant. Chemosphere. 2004, 57, 1031–1036.
31. Dogan, Y., Ugulu, I., Baslar, S., 2010. Turkish Red Pine as a biomonitor: A comparative study of the accumulation of trace elements in the needles and bark. Ekoloji 19 (75), 88–96.
32. Rucandio, M.I., Petit–Domínguez, M.D., Fidalgo-Hijano, C., García-Giménez, R., 2011. Biomonitoring of chemical elements in an urban environment using arboreal and bush plant species. Environ. Sci. Pollut. Res. 18, 51–63.
33. Samecka-Cymerman, A., Kosior, G., Kempers, A.J., 2006. Comparison of the moss Pleurozium schreberi with needles and bark of Pinus sylvestris as biomonitors of pollution by industry in Stalowa Wola (southeast Poland). Ecotox. Environ. Safe. 65, 108–117.
34. Sawidis, T., Breuste, J., Mitrovic, M., Pavlovic, P., Tsigaridas, K., 2011. Trees as bioindicator of heavy metal pollution in three European cities. Environ. Pollut. 159, 3560–3570.
35. Sun, F., Wen, D., Kuang, Y., Li, J., Li, J., Zuo, W., 2010. Concentrations of heavy metals and polycyclic aromatic hydrocarbons in needles of masson pine (Pinus Massoniana L.) growing nearby different industrial sources. J. Environ. Sci. 22, 1006–1013.
36. Tomašević, M., Aničić, M., Jovanović, Lj., Perić-Grujić, A., Ristić, M., 2011. Deciduous tree leaves in trace elements biomonitoring: A contribution to methodology. Ecol. Indic. 11, 1689–1695.
37. Yanqun, Z., Yuan, L., Schvartz, C., Langlade, L., Fan, L., 2004. Accumulation of Pb, Cd, Cu and Zn in plants and hyperaccumulator choice in Lanping lead–zinc mine area, China. Environ. Int. 30, 567–576.
38. Vamerali, T., Bandiera, M., Mosca, G., 2010. Field crops for phytoremediation of metal–contaminated land–A review. Environ. Chem. Lett. 8, 1–17.
39. Alagić, S.Č, Šerbula, S.S., Tošić, S.B., Pavlović, A.N., Petrovic, J.V., Bioaccumulation of arsenic and cadmium in birch and lime from the Bor region. Arch. Environ. Contam. Toxicol. 2013, 65, 671–682.

40. Madejón, P., Lepp, N.W., 2007. Arsenic in soils and plants of woodland regenerated on an arsenic-contaminated substrate: A sustainable natural remediation? Sci. Total Environ. 379, 256–262.
41. Piczak, K., Leśniewicz, A., Żyrnicki, W., 2003. Metal concentrations in deciduous tree leaves from urban areas in Poland. Environ. Monit. Assess. 86, 273–287.
42. Rademacher, P., 2001. Atmospheric heavy metals and forest ecosystems, Federal Research Centre for Forestry and Forest Products (BFH), CLRTAP. http://literatur.ti.bund.de/digbib_extern/dk040080.pdf
43. Pulford, I.D. and Watson, C. (2003). Phytoremediation of heavy metal-contaminated land by trees-a review. Environ Int. 29: 529–540.
44. Kozlov, M.V. (2005). Sources of variation in concentrations of nickel and copper in mountain birch foliage near a nickel-copper smelter at Monchegorsk, north-western Russia: results of long-term monitoring. Environ Pollut. 135: 91–99.
45. Serbula S. M., Radojevic A. A., Kalinovic J. V., Kalinovic T. S., Indication of airborne pollution by birch and spruce in the vicinity of copper smelter, Environmental Science and Pollution Research, 21, (19) (2014), 11510-11520
46. Rosselli, W., Keller, C. and Boschi, K. (2003). Phytoextraction capacity of trees growing on a metal contaminated soil. Plant Soil 256: 265–272.

Stabilization of waste mud from flotation process

Stabilizacija otpadnog mulja nakon flotacionog procesa

Miladin Gligorić[1], Dragana Tomašević Pilipović[2], Aleksandar Došić[1], Nataša Slijepčević[2]

[1]University of East Sarajevo, Faculty of Technology, Karakaj 34a, 75400 Zvornik, RS, Bosnia and Herzegovina

[2]University of Novi Sad, Faculty of Science, Trg Dositeja Obradovića 3, 21000 Novi Sad, Serbia

[1]Univerzitet u Istočnom Sarajevu, Tehnološki fakultet, Karakaj 34a, 75400 Zvornik, RS, Bosna i Hercegovina

[2]Univerzitet u Novom Sadu, Prirodno-matematički fakultet, Trg Dositeja Obradovića 3, 21000 Novi Sad, Srbija

Izvod

Stabilizacija otpadnog mulja nakon flotacionog procesa, koji je opterećen toksičnim metalima, vršena je tehnikama stabilizacije i solidifikacije. Korišten je otpadni mulj Rudnika olova i cinka Sase, Srebrenica, RS, Bosna i Hercegovina. Toksični metali su imobilisani kompaktiranjem sa lebdećim pepelom i crvenim muljem u monolite različitih proporcija. Efikasnost imobilizacionih postupaka praćena je korišćenjem difuzionog testa izluživanja (ANS 16.1). Takođe su, određeni i parametri (koeficijenti difuzije, indeksi izlužljivosti) koji su poslužili za ocjenu efikasnosti prethodno primjenjenih imobilizacionih tehnika, te dominantni mehanizam izluživanja metala iz solidifikata.

Lebdeći pepeo i crveni mulj su se pokazali kao dobri imobilizacioni agensi za većinu toksičnih metala. Može se zaključiti da je dominantan mehanizam izluživanja za većinu metala difuzija, a za olovo površinsko spiranje do koga dolazi u inicijalnoj fazi eksperimenta.

Stabilizovana i solidifikovana jalovina se može na kraju upotrijebiti u određene svrhe ili odložiti.

Ključne riječi: *lebdeći pepeo, crveni mulj, stabilizacija/solidifikacija, toksični metali, test izluživanja.*

Abstract

The stabilization of the waste mud after the flotation process, which was loaded with toxic metals, was performed by stabilization and solidification techniques. Waste mud of lead and zinc mines Sase, Srebrenica, RS, Bosnia and Herzegovina was used. Toxic metals were immobilized by compacting with fly ash and red mud in monoliths of various proportions. The efficacy of immobilization procedures was monitored using a leaching test (ANS 16.1). Also, certain parameters (diffusion coefficients, leaching index) used to evaluate the efficiency of previously applied immobilization techniques, and the dominant mechanism of leaching of metals it's determined.

Fly ash and red mud proved to be a good immobilization agents for most toxic metals. It can be concluded that the dominant leaching mechanism for most metals is diffusion, for lead is surface flushing which it comes in the initial phase of the experiment.

Stabilized and solidified waste mud finally can be used for specific purposes or postponed.

Key words: *fly ash, red mud, stabilization/solidification, toxic metals, leaching test.*

Uvod

Procesi i tehnike stabilizacije i solidifikacije (S/S) se sve više koriste u oblasti zaštite životne sredine. Zato mnoge metode S/S se promovišu i nude za tretman opasnog i drugog otpada iz industrije i komunalnih izvora. Ova tehnologija, koja uključuje mješanje vezivnog materijala sa kontaminiranim materijalom, štiti životnu sredinu imobilišući štetne komponente. Vezivni materijal reaguje hemijski sa vodom iz materijala koji je tretiran, izazivajući promjene u fizičkim i hemijskim osobinama i stabilizuje štetne konstituente i tako spriječava njihov dalji transport u životnoj sredini [1].

U ovom radu primjenjen je modifikovani test izluživanja sa ciljem što bolje simulacije realnih uslova. Rezultati dobijeni simulacijom ovih uslova i daljom karakterizacijom smješa omogućuje izradu modela ponašanja metala u smislu dugoročnog "izluživanja" iz tretirane (stabilizovane) jalovine kao i procjenu koji materijali su bolji za imobilizaciju toksičnih metala u jalovini Rudnika Sase Srebrenica.

U Rudniku olova i cinka Sase Srebrenica, ruda nakon jamskog iskopavanja ide na postupak redukcije prečnika i koncentrisanje korisne komponente galenitnog koncentrata sa najvećim udjelom PbS i svaleritnog koncentrata sa najvećim udjelom ZnS. Postupak smanjenja prečnika u osnovi se sastoji iz dvije faze. Prva faza je postupak drobljenja na čeljusnoj i konusnoj drobilici do 30 mm. Ova frakcija nakon konusne drobilice se odlaže putem trakastih transportera u bunkere rude. Iz bunkera ruda putem trakastih dozatora i magnetnih separatora odlazi u mlin sa šipkama na postupak mokrog mljevenja. Nakon mlina sa šipkama nastala suspenzija ide u mlin sa kuglama, a odatle na hidrociklon. Preliv sa hidrociklona ide na flotiranje, a ostatak se ponovo vraća na domeljavanje u mlinu sa kuglama. Nakon linije za flotiranje preostala jalovina se skuplja u privremeni spremnik jalovine odakle se kontinuirano putem cenrifugalnih pumpi šalje na hidrociklon koji se nalazi na brani (odlagalištu) jalovine [2]. Nastala jalovina u sebi sadrži toksične metale kao što su: Pb, Zn, Cr, Ni, Cu, Cd, As i drugi.

Imobilizacija metala uz dodatak lebdećeg pepela i crvenog mulja

Pozolaničke supstance (pozolani) su silikatni ili aluminozni materijali. To su supstance koje se pojavljuju u prirodi ili nastaju kao industrijski sporedni proizvodi, a koje dobijaju cementne osobine kada se aktiviraju kalcijum-hidroksidom. Zbog toga je korišćenje ovih aditiva isplativo pošto nije potreban nikakav poseban postupak za njihovo dobijanje.

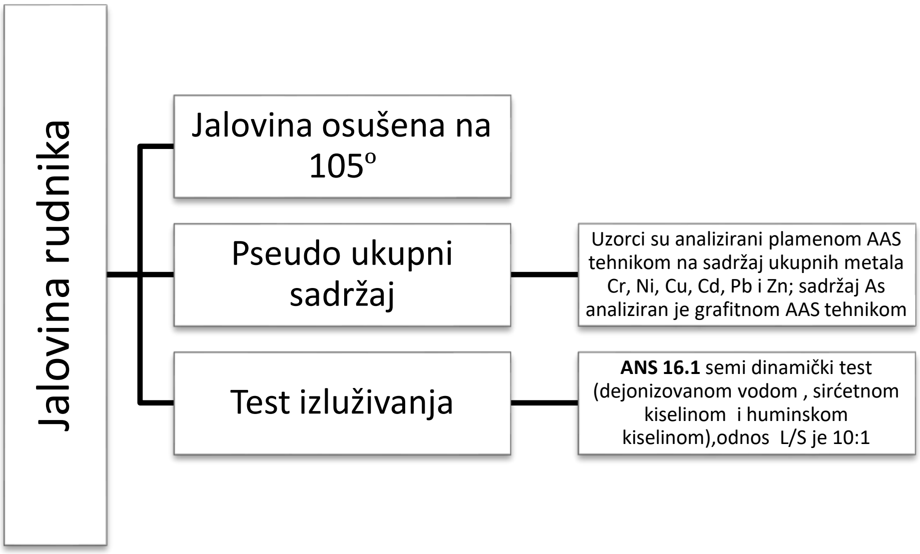
Lebdeći pepeo nastao pri sagorjevanju uglja i drugi pozolani sadrže staklastu silikatnu fazu koja reaguje sa $Ca(OH)_2$ iz cementa i formira gel kalcijum-silikat-hidrata (CSH) koji je primarni agens stezanja cementa. Lebdeći pepeo obično sadrži i sulfide koji reaguju sa mnogim teškim metalima u otpadu i smanjuju njihovu rastvorljivost [3].

Crveni mulj je otpadni materijal koji se formira prilikom proizvodnje aluminijuma kada je boksitna ruda podvrgnuta kaustičnom luženju. Za svaku tonu proizvedenog aluminijuma, nastaje 0,5-2 tona crvenog mulja. Crveni mulj se predlaže kao adsorbent za uklanjanje teških metala, glina, fosfata, nitrata, fluorida i arsena zbog visokog sadržaja aluminijuma, gvožđa i kalcijuma [4].

Prosječna pH vrijednost za crveni mulj je od 11,3 ± 1,0. Razlog tome je što su u prosjek uključene i pH vrijednosti starih crvenih muljeva koji su djelimično neutralisani atmosferskim CO_2 [5]. Pokazano da crveni mulj ima sposobnost da neutrališe kiseline, kao i da se uspješno može koristiti za neutralizaciju kiselih otpadnih i procjednih voda iz rudnika [6]. pH vrijednost uslovljena je prvenstveno prisustvom kalcijum karbonata, trikalcijum aluminata i hidrokalumita. Pored toga, postoji niz drugih reakcija koje se javljaju tokom i pre digestije. Jedna od najvažnijih je solubilizacija filosilikatnih minerala (gline), npr. kaolinita. Rastvaranje ovih minerala rezultira aluminatnim i silikatnim jonima u rastvoru [7]. Pozolanična svojstva pečenog crvenog mulja su ispitivana monitoringom primjene različitih mješavina portland cementa i crvenog mulja. Glavni proizvodi hidratacije su C-S-H i mono-karboaluminat (C_4ACH_{11}). Zbog metode boksit-kalcinacije, crveni mulj sadrži određene količine amorfnog aluminijum-silikatnog materijala i $Al(OH)_3$ [8]. Oni mogu da se modifikuju u reaktivni silicijum i glinicu usljed procesa kalcinacije, dobijajući pozolanična svojstva. Kalcinacija ispod 600-700°C može značajno da poboljša aktivnost crvenog mulja zbog raspadanja glinenih materijala tako da se formiraju aktivni silicijum i glinica [9, 10]. Osim toga, dodatkom CaO ili nekog drugog izvora kalcijuma tokom kalcinacije, može se dodatno poboljšati aktivnost crvenog mulja [11, 12]. S obzirom da usljed metode boksit-kalcinacije crveni mulj sadrži veliku količinu CaO u svom hemijskom sastavu, ovu metodu koristimo kao izvor kalcijuma kako bi se poboljšala aktivnost jalovine kroz aktivaciju jedinjenja [9].

Eksperimentalni dio

Cilj istraživanja bio je ispitivanje mogućnosti stabilizacije otpadnog mulja sa jalovišta Rudnika Sase Srebrenica primjenom lebdećeg pepela i crvenog mulja kao imobilizacionih agenasa.
Prvo su određivane početne koncentracije toksičnih metala u jalovini. Odmjeren je 1g jalovine koji je potom podvrgnut metodi digestije EPA 3051a (Mikrotalasna digestija Milestone, star E). Za digestiju je korišćeno 9±0,1mL HNO_3 i 3±0,1mL HCl. Korištene su koncentrovane kiseline. Zatim su uzorci analizirani plamenom AAS tehnikom (Perkin Elmer AAnalyst™ 700) na sadržaj ukupnih metala Cr, Ni, Cu, Cd, Pb i Zn u skladu sa procedurom EPA 7000B, sadržaj As analiziran je grafitnom AAS tehnikom (Perkin Elmer AAnalyst™ 700) u skladu sa procedurom EPA 7010.
Jalovina, lebdeći pepeo i crveni mulj su prvo osušeni na 105 °C, a zatim je jalovina mješana (slika 1) sa imobilizacionim agensima prema šemi predstavljenoj u tabeli 1., (J-jalovina, F-lebdeći pepeo, R-crveni mulj).



Uzorci su analizirani plamenom AAS tehnikom na sadržaj ukupnih metala Cr, Ni, Cu, Cd, Pb i Zn; sadržaj As analiziran je grafitnom AAS tehnikom

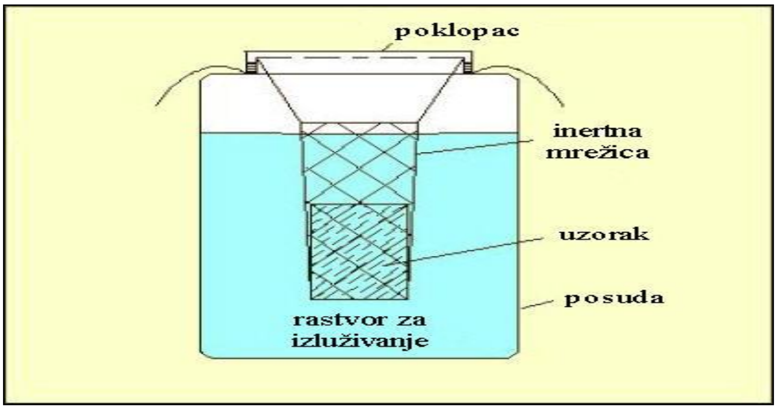
ANS 16.1 semi dinamički test (dejonizovanom vodom , sirćetnom kiselinom i huminskom kiselinom),odnos L/S je 10:1

Slika 1. Blok šema pripreme smješa i testova izluživanja

Tabela 1. Sastav smješa jalovine, lebdećeg pepela i crvenog mulja

Smješe	**Masa (g)**		
	Lebdeći pepeo	**Crveni mulj**	**Jalovina**
F10R10J80	60	60	480
F10R20J70	60	120	420
F10R30J60	60	180	360

Efikasnost primjenjenih imobilizacionih agenasa u S/S tretmanu vršena je primjenom semi-dinamičkog ANS 16.1 testa izluživanja [13]. Takođe su određeni i parametri (koeficijenti difuzije, indeksi izluživanja) koji su poslužili za ocjenu efikasnosti primjenjenog imobilizacionog agensa. Primjenjen je modifikovani ANS 16.1 test izluživanja sa ciljem što bolje simulacije realnih uslova. U modifikovanom ANS 16.1 testu izluživanja korišćen je rastvor sirćetne kiseline sa pH 3,25 da bi se simulirali uslovi koji oponašaju kisele kiše, odnosno uslove u realnom sistemu. Takođe je korišćen i rastvor huminskih materija sa ciljem simulacije uslova velikog organskog opterećenja do kojeg bi moglo doći u slučaju akcidentnih situacija (na primjer poplava) i generalno uslova koji se stvaraju u prirodi pri raspadanju organskog materijala (lišće, trava, itd.).
Ovaj test je izveden na sobnoj temperaturi sa dejonizovanom vodom (DI), sirćetnom kiselinom (AA) i huminskom kiselinom (HA) kao agensima za izluživanje. Uzorci su smješteni u inertne plastične mrežice i postavljeni u visećem položaju u plastične posude sa navedenim rastvorima za izluživanje pri čemu je odnos tečnost/čvrsto (L/S) bio 10:1 (L kg^{-1}) (slika 2). Test je rađen pod semidinamičkim uslovima pri čemu je monolit potapan u svjež rastvor destilovane vode, sirćetne i huminske kiseline nakon 2, 7, 24, 48, 72, 96, 120, 456, 1128 i 2160 sati, a iz rastvora nakon izluživanja i filtriranja na membranskom filteru (0,45 μm) određena je koncentracija metala AAS tehnikom.



Slika 2. Semi dinamički test izluživanja

Koeficijenti difuzije i indeksi izluživanja

ANS 16.1 model izluživanja koristi Fikovu difuzionu teoriju i gdje se praćenjem brzine vrši procjena efikasnosti tretmana [13-18]. Jedanačine za određivanje koeficijenata difuzije (De) i indeksa izluživanja (LX) su prikazani obrascima (1) i (2). Srednje vrijednosti koeficijenata difuzije $\overline{De}$ izračunate su i prikazane u tabeli 3, a srednje vrijednosti indeksa izluživanja $\overline{LX}$ na slici 3.

$$De = \pi \left[\frac{\frac{a_n}{A_0}}{(\Delta t)_n} \right]^2 \left[\frac{V}{S} \right]^2 T_n \qquad (1)$$

gdje je: a_n gubitak kontaminanta (mg) tokom određenog perioda izluživanja sa indeksom n; A_0 je početna koncentracija kontaminanta u uzorku (mg); $(\Delta t)_n$ vremensko trajanje n-tog intervala izluživanja (s); V je zapremina uzorka (cm^3); S je geometrijska površina uzorka izračunata iz dimenzija (cm^2); T_n je vrijeme u sredini perioda izluživanja (s); De je stvarni difuzioni koeficijent (cm^2/s).

$$LX = \frac{1}{m}\sum_{n=1}^{m}\left[-\log(De)\right]_n \qquad (2)$$

gdje je: n broj određenih perioda izluživanja m je ukupan broj pojedinačnih perioda izluživanja [19-21].

Mehanizam koji kontroliše izluživanje metala

Mehanizam koji kontroliše izluživanje metala iz S/S smješa određuje se modelom difuzione teorije [22]. U ovom modelu, kumulativni izluženi maksimum komponente B_t (mg/m^2) izražava se kao:

$$\log(B_t) = \frac{1}{2}\log(t) + \log\left[U_{\max} d\sqrt{\left(\frac{De}{\pi}\right)}\right] \qquad (3)$$

gdje je: De stvarni difuzioni koeficijent u cm^2/s za komponentu x; t je vrijeme kontakta u sekundama; U_{max} je maksimalna izlužena količina izražena u mg/kg; d je gustina uzorka u kg/m^3.

Tri mehanizma koji potencijalno kontrolišu izluživanje metala (spiranje, difuzija, i rastvaranje) se mogu odrediti na osnovu procjene nagiba krive zavisnosti kumulativne izlužene frakcije metala i vremena koji su definisani u jednačini (3).

Prema vrijednosti nagiba iz zavisnosti kumulativne izlužene frakcije metala B_t (mg m^{-2}) i vremena može se odrediti mehanizam izluživanja: manje od 0,4 mehanizam površinsko spiranje; 0,4-0,6 – mehanizam difuzije i veće od 0,6 - mehanizam rastvaranja.

Rezultati i diskusija

Sastav jalovine rudnika, korištenog lebdećeg pepela i crvenog mulja

Jalovina korišćena u ogledima potiče iz Rudnika olova i cinka Sase, opština Srebrenica, Republika Srpska, Bosna i Hercegovina. Sastav upotrebljene jalovine bio je sljedeći: (% maseni): SiO_2 (73,98), Al_2O_3 (11,5), Fe_2O_3 (25,9), MgO (0,33), CaO (2,57), TiO_2 (0,56), S (4,4), MnO (4,5) i gubitak žarenjem (4,9).

Sastav lebdećeg pepela (TE Ugljevik) bio je sljedeći (% maseni): SiO_2 (26,24), Al_2O_3 (6,66), Fe_2O_3 (13,97), CaO (19,74), MgO (5,21), Na_2O (0,68), K_2O(1,08), P_2O_5 (0,11), TiO_2 (1,21) i SO_3 (25,07).

Sastav crvenog mulja (Alumina d.o.o. Zvornik) bio je sljedeći (% maseni): CaO (4,12), SiO_2 (9,04), Al_2O_3 (19,62), Fe_2O_3 (48,97), TiO_2 (5,21), Na_2O ukupni (5,68), Na_2O vezani (5,44), i gubitak žarenjem 6,23.

Pseudo-ukupni sadržaj metala u početnom uzorku jalovine prikazan je u tabeli 2. i upoređen sa graničnim vrijednostima za klasifikaciju otpada.

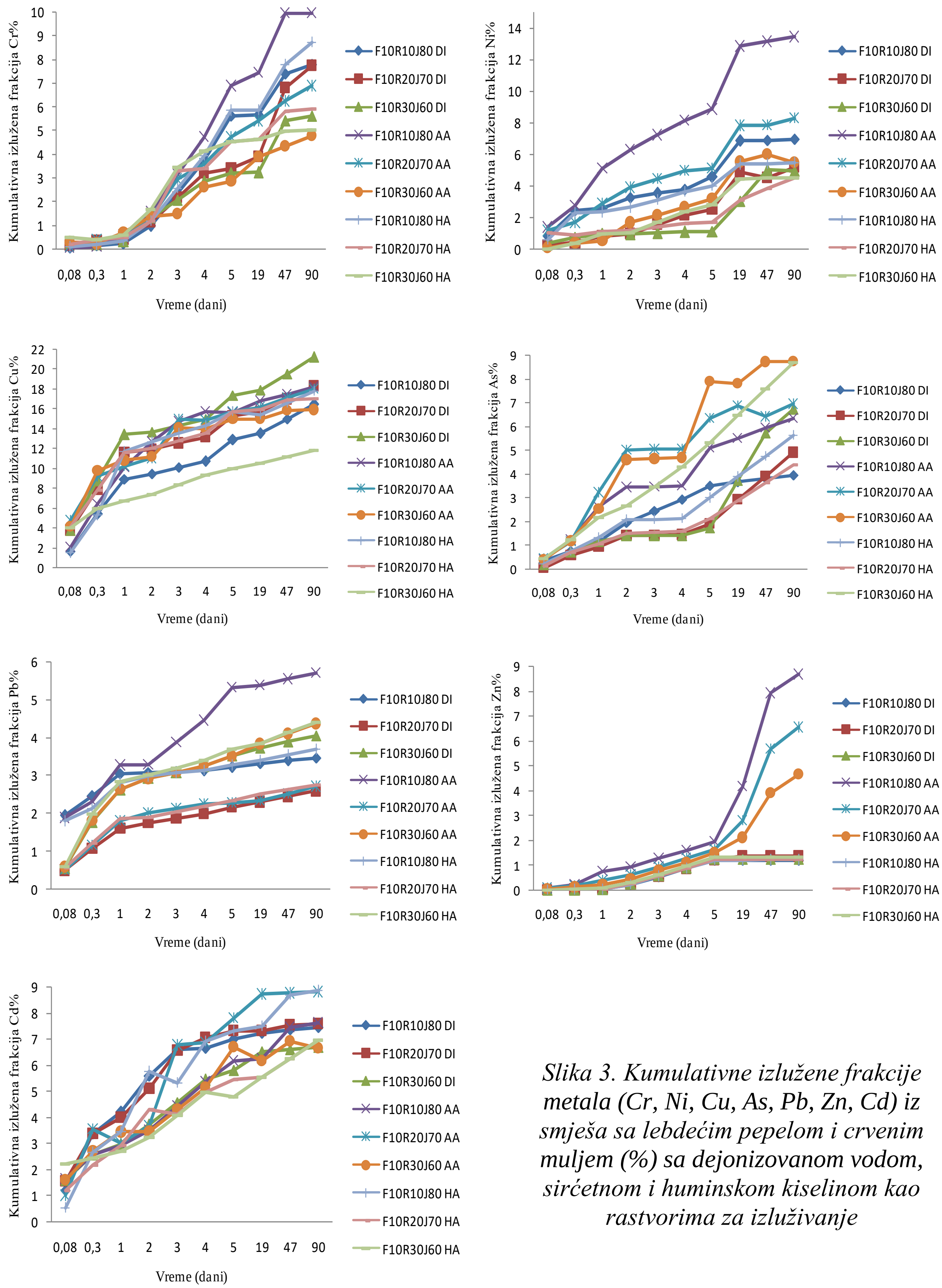
Tabela 2. Pseudo-ukupni sadržaj metala u početnom uzorku jalovine (mg/kg)

Parametar	Vrijednost	Granična vrijednost[1]	Granična vrijednost[2]
Cr (mg/kg)	7,47	-	-
Ni (mg/kg)	9,81	60	160
Cu (mg/kg)	406,92	60	-
As (mg/kg)	44,79	20	400
Pb (mg/kg)	1313,25	300	400
Zn (mg/kg)	740,04	200	-
Cd (mg/kg)	15,14	3	80

[1] Solid waste disposal, EPA 658/09, 2009

[2] Waste classification guidelines, Part 1, Department of Environment, Climate Change and Water NSW, 2009

Iz tabele 2. se može zaključiti da koncentracija Pb, Cu i Zn u značajnoj mjeri prelaze obe granične vrijednosti, dok vrijednosti za Cd i As prelaze granične vrijednosti prema EPA 658/09 direktivi, ali su ispod graničnih vrijednosti za klasifikaciju otpada prema Department of Environment, Climate Change and Water NSW (2009). Sadržaj Ni je zanemarljiv, jer je ispod graničnih vrijednosti po EPA 658/09 direktivi.



Slika 3. Kumulativne izlužene frakcije metala (Cr, Ni, Cu, As, Pb, Zn, Cd) iz smješa sa lebdećim pepelom i crvenim muljem (%) sa dejonizovanom vodom, sirćetnom i huminskom kiselinom kao rastvorima za izluživanje

Kumulativno izluženi metali

Kada kumulativne izlužene koncentracije metala (slika 3) poredimo sa koncentracijama koje za otpad propisuje Evropska Unija (*2003/33/EC*), dolazimo do zaključka da se neopasnim otpadom mogu smatrati sve ispitivane smješe u sva tri rastvora za izluživanje u pogledu koncentracija Cu i Cd. U slučaju Cr sve smješe se smatraju neopasnim otpadom, osim smješe sa 10% lebdećeg pepela i 20% crvenog mulja u dejonizovanoj vodi čije vrijednosti prelaze propisane i spada u opasan otpad. U pogledu Ni sve smješe u dejonizovanoj vodi i huminskoj kiselini se mogu smatrati neopasnim otpadom, dok smješa sa najmanje imobilizacionog agensa i smješa sa 10% lebdećeg pepela i 20% crvenog mulja predstavljaju opasan otpad u sirćetnoj kiselini sa aspekta Ni. Opasnim otpadom se smatraju sve smješe u sirćetnoj kiselini, kao i smješe sa najviše imobilizacionog agensa u dejonizovanoj vodi i huminskoj kiselini sa aspekta As, dok se ostale smješe u ova dva rastvora za izluživanje smatraju neopasnim otpadom. U pogledu Pb sve smješe u sva tri rastvora za izluživanje ne zadovoljavaju koncentracije koje za otpad propisuje Evropska Unija (*2003/33/EC*) i predstavljaju opasan otpad. Smješa sa najmanje imobilizacionog agensa u sirćetnoj kiselini prekoračuje dozvoljene koncentracije za Zn, dok se ostale smješe u sva tri rastvora za izluživanje smatraju neopasnim otpadom. Ukoliko kumulativne izlužene koncentracije metala poredimo sa koncentracijama koje za otpad propisuje *Pravilnik o kategorijama, ispitivanju i klasifikaciji otpada (Službeni glasnik Republike Srpske, br. 19/2015*), dolazimo do zaključka da sve smješe u sva tri rastvora za izluživanje zadovoljavaju propisane koncentracije za sve ispitivanne metale.

Na osnovu upoređivanja rezultata sa regulativama dolazi se do zaključka da se smješa jalovine sa lebdećim pepelom i crvenim muljem pokazala kao dobar imobilizacioni agens u pogledu Zn, jer dobijene vrijednosti zadovoljavaju propisane koncentracije koje za otpad propisuje Pravinik u Republici Srpskoj i koncentracije koje za otpad propisuje Evropska Unija (*2003/33/EC*). Sa aspekta Pb ova smješa jalovine sa lebdećim pepelom i crvenim muljem se nije pokazala u potpunosti kao dobar imobilizacioni agens, jer vrijednosti prelaze dozvoljene koncentracije metala koje za otpad propisuje Evropska Unija (*2003/33/EC*). Prema Pravilniku u Republici Srpskoj sve smješe u sva tri rastvora za izluživanje zadovoljavaju propisane vrijednosti za olovo.

Koeficijenti difuzije i indeksi izluživanja

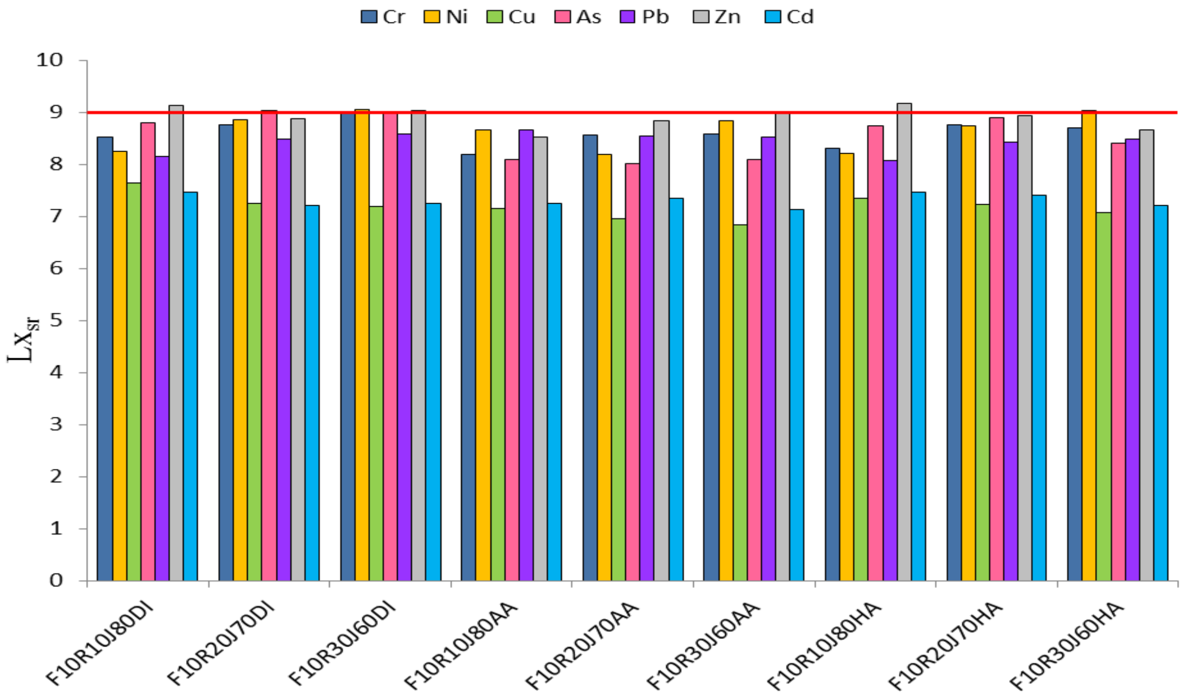
Srednje vrijednosti koeficijenata difuzije $\overline{De}$ i indeksa izluživanja $\overline{LX}$ u tretiranim uzorcima jalovine sa lebdećim pepelom i crvenim muljem izračunate su i prikazane u tabeli 3. i na slici 4.

Srednje vrijednosti koeficijenata difuzije za tretirane uzorke su se kretale od 1,10E-07 cm^{2}s^{-1} do 9,79E-09 cm^{2}s^{-1}. Svi metali u rastvoru dejonizovane vode, kao i rastvorima sirćetne i huminske kiseline su umjereno mobilni.

Ako efikasnost tretmana posmatramo sa aspekta LX vrijednosti (slika 4), tretman se može smatrati uspješnim u slučaju smješa sa 10 i 30% crvenog mulja u dejonizovanoj vodi sa aspekata Zn, jer su srednje LX vrijednosti za ove smješe veće od 9 i mogu se koristiti za kontrolisanu upotrebu. Takođe, smješa sa 10% crvenog mulja u huminskoj kiselini ima srednju LX vrednost preko 9, pa se tretman za tu smješu smatra uspješnim. Ostale smješe sa aspekta Zn imaju vrijednosti preko 8 i mogu se bezbjedno odlagati na deponije. Sve smješe za Cr i Pb u sva tri rastvora za izluživanje pokazuje srednje LX vrijednosti preko 8 i takve smješe se mogu bezbjedno odlagati na deponije. Sa apekta Ni srednje LX vrijednosti u pogledu smješe jalovine i 30% crvenog mulja u dejonizovanoj vodi i huminskoj kiselini su veće od 9, tako da u potpunosti zadovoljavju ovaj kriterijum i mogu se kontrolisano upotrebljavati. U slučaju As, smješe sa 20 i 30% crvenog mulja u dejonizovanoj vodi imaju srednju LX vrijednosti preko 9, pa se tretman za te smješe smatraju uspešnim, dok su vrijednosti za LX za ostale smješe preko 8 i mogu se bezbjedno odlagati na deponije. Sa aspekta bakra i kadmijuma sve smješe u svim rastvorima za izluživanje apsolutno ne zadovoljavaju ovaj kriterijum i smatraju se neadekvatnim za odlaganje.

Tabela 3. Srednji difuzioni koeficijenti $\overline{De}$ *u smješama jalovine sa lebdećim pepelom* *i crvenim muljem*

$\overline{De}$ (cm^2/s)				
		F10R10J80	F10R20J70	F10R30J60
DI	Cr	2,64E-08	1,46E-08	9,34E-09
	Ni	8,01E-09	3,10E-09	1,15E-09
	Cu	5,29E-08	1,24E-07	1,37E-07
	As	4,78E-09	2,51E-09	1,36E-09
	Pb	1,61E-08	7,31E-09	5,88E-09
	Zn	1,32E-08	2,11E-08	1,78E-08
	Cd	1,60E-07	2,68E-07	3,08E-07
AA	Cr	5,26E-08	2,04E-08	1,97E-08
	Ni	3,49E-08	1,05E-08	4,71E-09
	Cu	1,51E-07	2,19E-07	2,98E-07
	As	1,43E-08	2,06E-08	1,88E-08
	Pb	3,52E-08	6,40E-09	6,52E-09
	Zn	7,20E-08	3,89E-08	3,40E-08
	Cd	2,47E-07	2,23E-07	4,19E-07
HA	Cr	3,65E-08	1,37E-08	1,16E-08
	Ni	9,10E-09	2,64E-09	3,45E-09
	Cu	1,10E-07	1,18E-07	1,72E-07
	As	4,38E-09	2,74E-09	9,79E-09
	Pb	1,87E-08	8,04E-09	7,18E-09
	Zn	1,69E-08	1,98E-08	2,22E-08
	Cd	2,02E-07	2,03E-07	3,26E-07



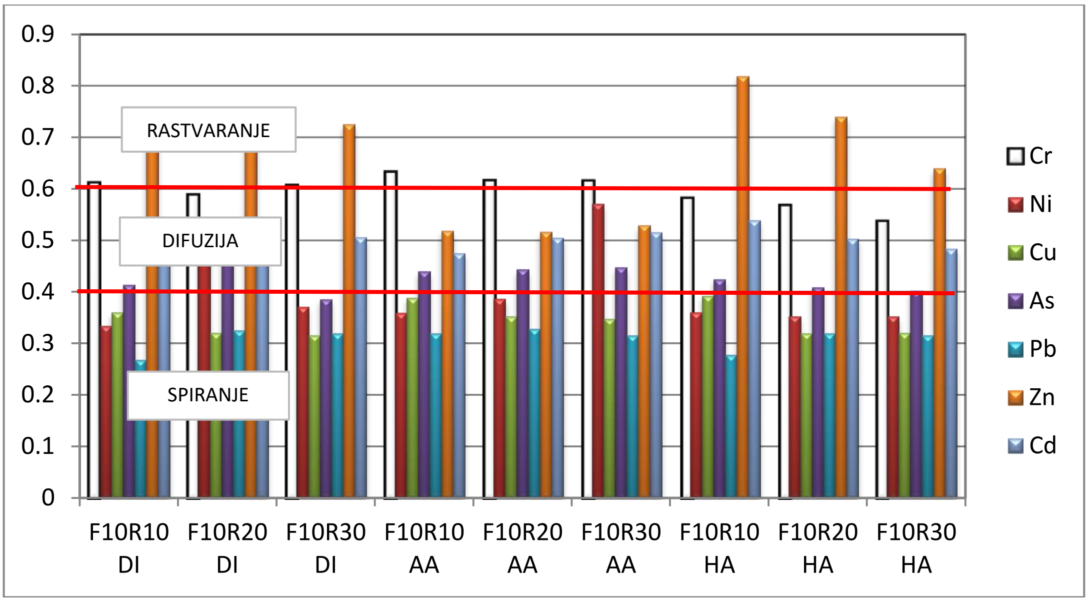
Slika 4. Srednji indeksi izluživanja ($\overline{LX}$ *) u smješama jalovine sa lebdećim pepelom i crvenim muljem*

Kumulativno izluženi metali

Kada kumulativne izlužene koncentracije metala (slika 3) poredimo sa koncentracijama koje za otpad propisuje Evropska Unija (*2003/33/EC*), dolazimo do zaključka da se neopasnim

Mehanizam koji kontroliše izluživanje

Na osnovu vrijednosti nagiba, iz grafika zavisnosti kumulativne izlužene frakcije metala (mg m^{-2}) i vremena (slika 5), za smješe jalovine sa crvenim muljem i lebdećim pepelom, vidimo da je za hrom, arsen i kadmijum dominantan mehanizam difuzije.



Slika 5. Mehanizam izluživanja određen na osnovu vrijednosti nagiba iz grafika zavisnosti kumulativne izlužene frakcije metala i vremena za smješe jalovine, crvenog mulja i lebdećeg pepela

Sa aspekta cinka dominantan mehanizam izluživanja je difuzija kada je sredstvo izluživanja sirćetna kiselina, a kod dejonizovane vode i huminske kiseline dolazi se do zaključka da je glavni mehanizam izluživanja rastvaranje. Za bakar i olovo površinsko spiranje je dominantan mehanizam izluživanja, do koga dolazi u inicijalnoj fazi eksperimenta. Kod nikla difuzija kao mehanizam izluživanja se javlja kada se sirćetna kiselina koristi za izluživanje, u drugim slučajevima to je spiranje.

Zaključak

Rezultati pseudo-ukupnog sadržaja metala u početnom uzorku jalovine ukazuju da koncentracije Pb, Cu i Zn u značajnoj mjeri prelaze granične vrijednosti prema EPA 658/09 direktivi i prema Department of Environment, Climate Change and Water NSW (2009), dok vrijednosti za Cd i As prelaze granične vrijednosti prema EPA 658/09 direktivi, ali su ispod graničnih vrijednosti za klasifikaciju otpada prema Department of Environment, Climate Change and Water NSW (2009). Sadržaj Ni je zanemarljiv, jer je ispod graničnih vrijednosti po EPA 658/09 direktivi.

Pri tretmanu jalovne sa lebdećim pepelom i crvenim muljem može se zaključiti da sa porastom udjela crvenog mulja u smješi opada mobilnost metala: Cr, Ni, Cu, Zn i Cd, dok kod As i Pb dolazi do odstupanja. Smješa jalovine sa lebdećim pepelom i crvenim muljem se pokazala kao dobar imobilizacioni agens za: Cr, Ni, Cu, As, Cd i Zn, jer vrijednosti ne prelaze propisane vrijednosti regulativa sa kojima su poređene. U pogledu Pb sve smješe u sva tri rastvora za izluživanje ne zadovoljavaju koncentracije koje za otpad propisuje Evropska Unija (*2003/33/EC*) i predstavljaju opasan otpad. Srednje vrijednosti koeficijenata difuzije za tretirane uzorke su se kretale od 1,10E-07 cm^2s^{-1} do 9,79E-09 cm^2s^{-1} što znači da su svi metali umjereno mobilni. Ako efikasnost tretmana posmatramo sa aspekta LX vrijednosti, tretman se može smatrati uspješnim u slučaju Zn, Ni i As za pojedine smješe jer imaju srednje LX vrijednosti preko 9, pa se tretman za te smješe smatra uspješnim i mogu se koristiti za kontrolisanu upotrebu. Ostale smješe za ova tri metala se mogu bezbjedno odlagati na deponije. Takođe, sve smješe za Cr i Pb u sva tri rastvora za izluživanje se mogu bezbjedno odlagati na deponije. Sa aspekta Cu i Cd sve smješe u svim rastvorima za izluživanje ne zadovoljavaju ovaj kriterijum i smatraju se neadekvatnim za odlaganje.

Može se zaključiti da je dominantan mehanizam izluživanja za većinu metala difuzija. Za olovo površinsko spiranje je dominantan mehanizam izluživanja, do koga dolazi u inicijalnoj fazi eksperimenta. Za nikl takođe, površinsko spiranje je dominantno, osim kada se sirćetna kiselina koristi za izluživanje kada difuzija postaje dominantan mehanizam

Iz istraživanja možemo zaključiti da je tehnika solidifikacije i stabilizacije jalovine iz Rudnika olova i cinka Sase Srebrenica, pomoću lebdećeg pepela i crvenog mulja, dala generalno uspješne rezultate za većinu metala na osnovu kojih možemo zaključiti da se korišteni imobilizacioni agens može koristiti u pogledu rješavanja problema jalovine koja je zagađena metalima. Takođe zaključujemo da se za neke metale, prije svega Pb, jer ga ima najviše u netretiranoj jalovini, ovaj imobilizacioni agens treba koristiti u kombinaciji sa drugim primarnim i sekundarnim imobilizacionim agensima.

Ovi rezultati se mogu upotrebiti za projektovanje i izgradnju pilot postrojenja na kome bi se ispitala efikasnost ovih agensa za remedijaciju jalovine u realnim uslovima.

Zahvalnica

Autori se zahvaljuju Ministarstvu nauke i tehnologije Republike Srpske za finansijsku podršku ovom radu čiji rezultati proizilaze iz projekta *Remedijacija otpadnih muljeva neorganskim imobilizacionim agensima.*

Literatura

1. Langton, C.A., (2001) Chemical Fixation and Stabilization, In: Chang H.O., Hazardous and Radioactive Waste Treatment Technologies Handbook, Boca-Raton, FL: CRC Press.
2. Došić, A., (2016) Primjena neorganskih imobilizacionih agenasa u remedijaciji otpadnog mulja, Doktorska disertacija, Tehnološki fakultet, Zvornik.
3. Maio, V.C., (2001) Overview of Mixed Waste Solidification and Stabilization Methods, in: Oh, Chang H., Hazardous and Radioactive Waste Treatment Technologies Handbook, CRC Press.
4. Coruh, S., Ergun, O. N., (2010) Use of fly ash, phosphogypsum and red mud as a liner material for the disposal of hazardous zinc leach residue waste, Journal of Hazardous Materials 173, 468–473.
5. Liu Y., Lin C., Wu Y., (2007) Characterization of red mud derived from a combined Bayer process and bauxite calcination method, J. Hazard. Mater. 146, 255–261.
6. Paradis, M., Duchesne, J., Lamontagne, A., Isabel, D., (2006) Using red mud bauxite for the neutralization of acid mine tailings: a column leaching test, Can. Geotech. J. 43, 1167–1179.
7. Smiljanić, S., (2013) Proučavanje tretmana, fizičko-hemijskih svojstava crvenog mulja i parametara sorpcije na efikasnost uklanjanja jona nikla iz vodenih rastvora, Doktorska disertacija, Tehnološko-metalurški fakultet, Beograd.
8. Pera, J., Boumaza, R., Ambroise, J., (1997) Development of a pozzolanic pigment from red mud Cement and Concrete Research, Vol. 27, No. 10, 1513-1522.
9. Zhang, J., Sun, H., Sun, Y., Zhang, N. (2009) Correlation between ^{29}Si polymerization and cementitious activity of coal gangue, J. Zhejiang Univ. Sci. 10, 1334–1340.

10. Song, X., Gong, C., Li, D., (2004) Study on structural characteristic and mechanical property of coal gangue in the activation process, J. Chin. Ceram. Soc. 32 (3) 358–363.
11. Li D., Song X., Gong C. , Pan Z., (2006) Research on cementitious behavior and mechanism of pozzolanic cement with coal gangue, Cem. Concr. Res. 36, 1752–1759.
12. Li C., Wan J., Sun H., Li L., (2010) Investigation on the activation of coal gangue by a new compound method, J. Hazard. Mater. 179, 515–520.
13. ANS (American National Standard) ANSI/ANS-16.1. (1986) American National Standard for the Measurement of the Leachability of Solidified Low-Level Radioactive Wastes by a Short-Term Tests Procedure. ANSI/ANS-16.1. American National Standards Institute, New York, NY.
14. Dermatas, D., Meng, X., (2003) Utilisation of fly ash for stabilization/solidification of heavy metal contaminated soils, Engineering Geology 70, 377-394.
15. Dermatas, D., Moon, D.H., Menounou, N., Meng, X., Hires, R. (2004) An evaluation of arsenic release from monolithic solids using a modified semi-dynamic leaching test, Journal of Hazardous Materials B116, 25-38.
16. Moon, D.H., Dermatas, D., Menounou, N., (2004) Arsenic immobilization by calcium–arsenic precipitates in lime treated soils. Science of the Total Environment 330, 171–185.
17. Moon, D.H., Dermatas, D., (2006) An evaluation of lead leachability from stabilized /solidified soils under modified semi-dynamic leaching conditions. Engineering Geology 85, 67–74.
18. Kundu, S., Gupta, A.K. (2008) Immobilization and leaching characteristics of arsenic from cement and/or lime solidified/stabilized spent adsorbent containing arsenic, Journal of Hazardous Materials 153, 434–443.
19. Godbee, H. & Joy, D. (1974) Assessment of the Loss of Radioactive Isotopes from Waste Solids to the Environment: Part I. Background and Theory. ORNL-TM-4333. Oak Ridge National Laboratory, Oak Ridge, TN.
20. Nathwani, J.S., Phillips, C.R. (1980) Leachability of Ra-226 from uranium mill tailings consolidated with naturally occurring materials and/or cement: analysis based on mass transport equation. Water Air Soil Pollut. 14, 389–402.
21. Environment Canada (1991) Proposed Evaluation Protocol for Cement-Based Solidified Wastes. Environmental Protection Series. Report No. EPS 3/HA/9.
22. De Groot, G.J., Van der Sloot, H.A., (1992) Determination of leaching characteristics of waste materials leading to environmental product certification, in: Gilliam, T.M., Wiles C.C. (Eds.), Stabilization and Solidification of Hazardous, Radioactive, and Mixed Wastes, ASTMSTP 1123, vol. 2, American Society for Testing Materials, Philadelphia, PA, 149–170.

Hydrophobic surfaces

Regina Fuchs–Godec

University of Maribor, Faculty of Chemistry and Chemical Engineering, Maribor, Slovenia

Abstract

Superhydrophobic surfaces have received significant attention because of their extraordinary surface properties. It is well known that superhydrophobic surfaces have many potential industrial applications, such as reduction of ice and snow adhesion, surface self-cleaning, stain resistant textiles, corrosion prevention and antibiofouling surfaces. Superhydrophobic surfaces can be achieved by a combination of low surface energy materials, and surface micro- and nanostructures. The majority of these approaches start by creating roughness on the surface, by chemical etching, plasma treatment, the electrochemical method, the template method, vapour deposition and the sol-gel method and end with the deposition of low surface energy materials on the roughened surfaces. The development of methods for preparing super-hydrophobic surfaces via a simple, fast and economic process is highly desirable. For this reason, our research has focused on a solution immersion method, which is a time-saving procedure and needs cheap reagents. The approach is fairly simple to operate, and no special technique or equipment is required. An aerated ethanol solution of stearic acid (SA) ($CH_3(CH_2)_{16}COOH$) at room temperature with and without the addition of fat-soluble Vitamins (E and K_3) was used in the procedure for fabricating a super-hydrophobic surface on Cu and stainless steel.

Introduction

Wettability is an important property of solid surfaces from both the theoretical and technological points of view. A surface which is easily wet by the application of water is referred to as hydrophilic, while a surface which is unwettable is considered to be hydrophobic. These different behaviours can be correlated to the surface energies of both the water and the solid material. Other factors that may influence wetting behaviour are the parameters of the surface structure, such as porosity, roughness, chemical heterogeneity or reactivity [1]. Furthermore, superhydrophobic surfaces have evoked great interest among researchers both for pure academic interest and in terms of industrial applications. Superhydrophobic surfaces are generally defined as surfaces that have water contact angles (WCA) greater than 150°. These surfaces have received continual attention because of their broad applications, such as self-cleaning, antifogging and frosting, and drag reduction. Given the unique water-repellent properties of these surfaces, they are also capable of reducing deterioration of metal surfaces caused by corrosion in aqueous media [2-5].

Regarding its definition (ISO 8044-1986), “corrosion is the physic-chemical interaction between a metal and its environment, which results in changes in the properties of the metal and which may often lead to impairment of the function of the metal, the environment, or the technical system of which these form a part”.

The cost of corrosion has been reported by a variety of sources to be in the order of 3 to 6% of GDP, or more than $1 trillion per year. The economic impact of corrosion is more than "lost metal": it also includes lost production from unscheduled outages and potential risks to health, safety and the environment. Corrosion knows no national boundaries. Acid rain or toxic materials released from corroded equipment generated in one country pollutes the environment and can cause corrosion damage far beyond that country’s borders, and even beyond the borders of its neighbours. Corrosion never stops, but its scope and severity can be lessened. Therefore, inhibition of corrosion is clearly very important.

Generally, corrosion prevention technology uses one or more of the following methods: i.) adopting metals with elements that enrich the surface with a corrosion-resistant component during the corrosion process; ii.) addition of aqueous inhibitors, which adsorb strongly on the metal surface and prevent the reaction with the oxidizing agent; and iii.) deposition of protective coatings. The choice of the most effective method is not always simple or easy. This choice is partly governed by the actual environmental conditions and partly by economic considerations.

The corrosion protective mechanism of an organic coating system can roughly be divided into three groups: the electrochemical effect, the physicochemical effect and adhesion to the substrate. The adhesion is very important, since the protective effect of the coating will completely fail in areas where delamination occurs, creating easy access to areas where corrosion can proceed without restriction [6].

In recent years, improving the corrosion resistance of metallic materials by surface superhydrophobisation has become one of the most interesting research areas in corrosion and protection. Corrosion protection by hydrophobic and superhydrophobic coatings belongs to the interdisciplinary field between classical corrosion science and wetting. As has been established, superhydrophobic surfaces, because of their extraordinary surface properties (WCA>150°), have many potential industrial applications (stain resistant textiles, reduction of ice and snow adhesion, corrosion prevention etc.). It is well known that the maximum contact angle that can be attained on a flat surface by lowering the surface energy does not exceed 120° [7, 8].

However, the addition of roughness to the surface can increase the contact angle of water without altering the surface chemistry [9]. Superhydrophobic surfaces can be achieved by a combination of low surface energy materials, and surface micro-nanostructures.

Generally, the wetting state of water droplets on a solid surface can be classified into two categories, namely, the Cassie-Baxter state and the Wenzel state, in which the water either sits upon the surface protrusions or penetrates into the surface porosity, respectively (Fig.1). Superhydrophobicity can usually be explained by the Cassie-Baxter model [10]. In this model, a large amount of air is trapped in the microgrooves of a rough surface, and the water droplets rest on a composite surface comprising air and the tops of the micro-protrusions. The importance of the fractal dimensions of the rough surfaces is well recognized, and many approaches have been based on the fractal contribution. Suitable roughness in combination with low surface energy is required to construct artificial superhydrophobic surfaces. Therefore, altering one or both of these factors will change the surface wettability state.

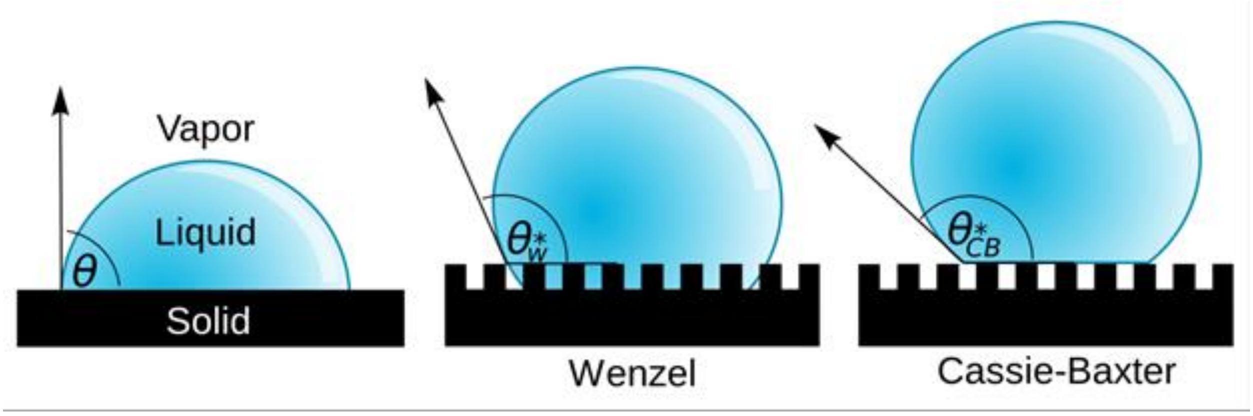


Figure 1: Schematic illustration of the wetting states of surfaces with different contact angles (https://commons.wikimedia.org/wiki/File:Contact_angle_microstates.svg)

The majority of these approaches begin by creating the roughness on the surface. For this purpose, chemical etching, plasma treatment, the electrochemical method, the template method, vapour deposition and the sol-gel method can be used, and ends up with the deposition of low surface energy materials on the roughened surfaces [11-16]. The commonly used reactive molecules for low surface-energy modification are mainly long alkyl chain thiols, alkyl or fluorinated organic silanes, perfluorinated alkyl agents, long alkyl chain fatty acids, polydimethylsiloxane-based polymers or other polymers, or their combinations. However, most of the chemical materials used for hydrophobisation are non-biodegradable, expensive and potentially harmful to human health and the environment, a factor which limits their potential applications [17]. Therefore, developing a simple, inexpensive approach to obtaining an industrially feasible superhydrophobic surface is important and necessary [18, 19].

The present study investigates a very simple, one-step and low-cost superhydrophobic coating prepared by a solution immersion method, which is a time-saving procedure and requires cheap reagents. The approach is fairly straightforward to operate, and no special technique or equipment is required. This simple chemical method was used for the fabrication of the super-hydrophobic surface on stainless-steel (SS) X4Cr13, copper and copper alloys. For this purpose, fat-soluble Vitamins E and K_3, as types of green inhibitors, were used. After chemical etching in 10% HNO_3, the specimens were immediately immersed in a non-stirred, aerated ethanol solution of stearic acid ($CH_3(CH_2)_{16}COOH$) at room temperature with and without addition of the chosen fat-soluble Vitamin (E or K_3).

The immersion time was constant, one hour, as well as the concentration of stearic acid, c = 0.05 M (M = mol L^{-1}). The chosen concentrations of added Vitamin E were 0.5%, 1.0%, and 2.0 %. For vitamin K_3 as a preliminary concentration the value of c = 2.0 % was chosen. The corrosion medium in use was 3% NaCl solution and simulated urban rain at pH = 3, 4, and 5. Moreover, this research demonstrates the long-term stability and effectiveness of those as-prepared hydrophobic layers on the (SS) X4Cr13 within artificial acid rain (pH = 3.0) and 3% NaCl at 25 °C.

Potentiodynamic polarization and electrochemical impedance spectroscopy techniques were performed, in order to examine the corrosion-inhibition process of the chosen system. A scanning electron microscope (SEM) was used to characterise the surface morphology of the self-assembled layers, and a commercial goniometer for testing the wettability of the copper and brass surfaces with and without self-assembled layers. In addition, the infrared (ATR-FTIR) spectroscopy technique was used to gain insight into the potential corrosion inhibition mechanism. The corrosive resistances of the layers were tested. Two different electrochemical methods were used for this purpose: the classic potentiodynamic measurement and electrochemical impedance spectroscopy (EIS).

Experimental

The conventional three-electrode configuration was applied in order to conduct the potentiodynamic studies. All the potentials were measured against the saturated calomel electrode (SCE), and the counter electrode was made from Pt. The potentiodynamic current-potential curves were recorded by automatically changing the electrode potential from -0.7 to not more than 0.5V, with a scanning-rate of $1mVs^{-1}$. EIS measurements were carried out within the 100 kHz –1 mHz frequency range at a steady open circuit potential (OCP) disturbed by an amplitude of 10 mV. Nyquist and polarization plots were obtained from the results of these experiments 30 mins after the working electrode had been immersed in the solution, in order to allow stabilization of the stationary potential. All the experiments were carried at 25°C ± 1°C. The measurements were performed using the Solartron 1287 Electrochemical interface and the Solartron 1250 Frequency response analyser. Data were collected and analysed using CorrView, CorrWare, Zplot, and ZView software, as developed by Scribner Associates Inc. A scanning electron microscope (SEM) (XL FEG/SFEG/SIRION) was used to characterise the surface morphology of the self-assembled layers and a commercial goniometer (Data Physics OCA 35, Germany) for testing the wettability of the copper and brass surfaces with and without self-assembled layers. ATR-FTIR analysis by Fourier transform infrared

(SHIMADZU-IRAffinity-1) analysis was utilised to confirm the presence of some functional groups in the as-prepared hydrophobic layer on the metal surface.

Copper:

Copper and its alloys are commonly used within many application and environmental fields (industrial equipment, building construction, electricity and electronics, coinage and ornamental parts, etc.) on account of its good electrical and thermal properties, excellent corrosion resistance, good castability and low price. Despite excellent corrosive resistance in many environments, copper and its alloys corrode under certain circumstances. This fact limits their application. In widespread usage of these, protection for copper and its alloys against corrosion plays an important role. The section below presents the stability and efficiency of the as-prepared hydrophobic layer on copper surfaces within the simulated urban rain solution at pH 5.0.

Fat-soluble Vitamins (E and K_3) were used as types of green inhibitors. After chemical etching in 15% HNO_3, the specimens were immediately immersed within a non-stirred, aerated ethanol solution of stearic acid (SA) ($CH_3(CH_2)_{16}COOH$) at room temperature with and without the addition of the chosen fat-soluble Vitamins. The immersion time was constant at one hour, as well as the concentration of stearic acid at c = 0.05 M (M = mol L^{-1}). The chosen concentrations of added Vitamin E were 0.5 wt%, 1.0 wt%, and 2.0 wt%, while the concentration of Vitamin K_3 was constant; c = 2.0 wt%.

Wettability of a high-level hydrophobic surface (contact angle measurements)

Typical SEM images of copper surfaces are presented in Figure 2 - (a) the untreated Cu substrate, whilst images (b) and (c) show the modified surfaces of the metal used in SA solution for one hour and in SA solution, with the addition of 2.0 wt% of Vitamin E, for one hour. The images of water droplets on the modified surfaces, given within rectangles, indicate the hydrophobicity of the modified surfaces, with values of CA very close to those of super-hydrophobic surfaces (CA ≥150°). It can be seen that the surface shown in Fig.2b is rather rough and looks as though it is covered by ridge-like structures. The modified surface became more uniformly covered (Fig.2c) with the addition of Vitamin E to the ethanolic SA-solution. It was reported that such regularly-ordered ridge-like structures (or flower-like structures, as reported by some authors [20-23], can trap a large amount of air, which is expected when revealing this high a level of hydrophobicity on the surface [22,24,25].

SEM images of Vitamin K_3–SA composites show the formation of tube like structures. The dimensions of the resulting tubes (in diameter) are in the range from several micrometres to several hundred nanometres. It could be speculated that some of these are nanostructured (Fig 3).

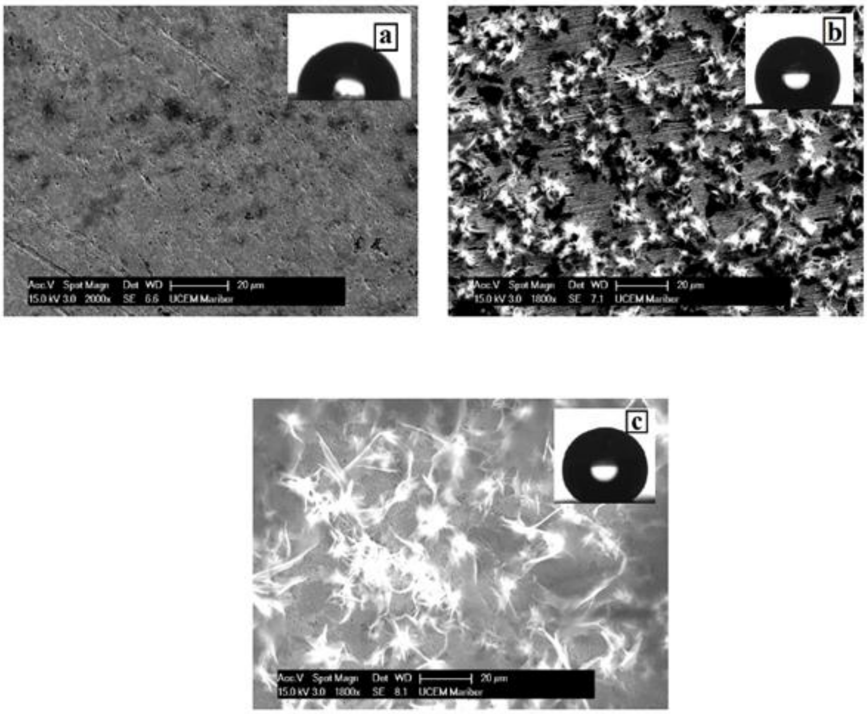


Figure 2: SEM of the untreated and modified surface of Cu (a) untreated and etched surface (CA=64°±2), (b) modified surface in SA solution for one hour (CA=138.8°±1) and (c) modified surface in SA solution with the addition of 2% Vitamin E for one hour (CA=143.0°±2).

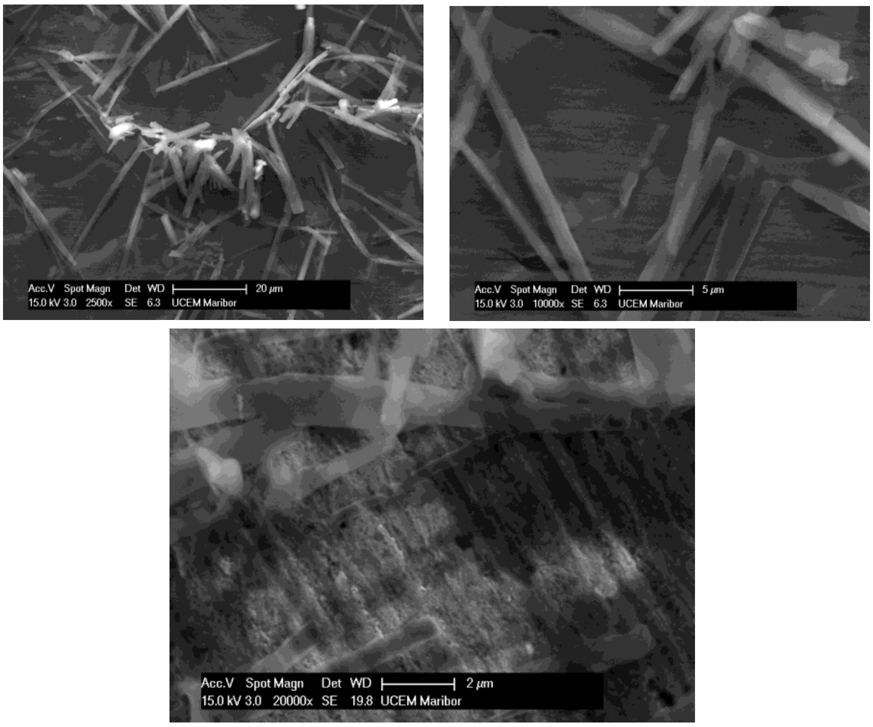
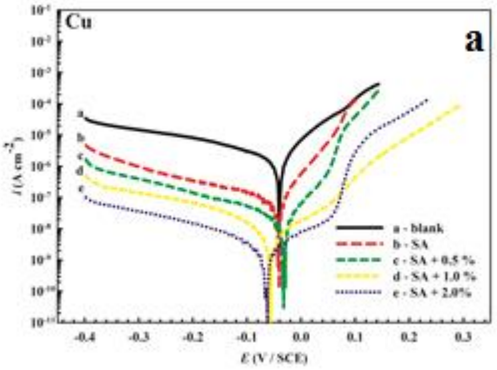


Figure 3: SEM of modified surface of Cu (modified surface in SA solution with the addition of 2% Vitamin K3 for one hour.

Corrosion resistance of the as-prepared hydrophobic layers

The potentiodynamic curves for the ‘acid rain’ solution for bare Cu and for those surfaces modified by immersion in SA with and without the addition of Vitamin E are shown in Figure 4. Compared to the bare Cu, the modified surfaces of Cu showed a decrease in the current densities in the cathodic and anodic directions. Furthermore, reduction of the corrosion current was noticeable and, up to a third order of magnitude lower icorr was observed for the chosen ‘mixtures’ with respect to the blank solution. Electrochemical measurements indicated that Vitamin E additionally improved the inhibitory properties of the as-prepared hydrophobic layer against corrosion. The inhibitive effectiveness increased to more than 99–%. This result seems to suggest that the formed film completely stops the corrosion until degradation of the film begins [26].



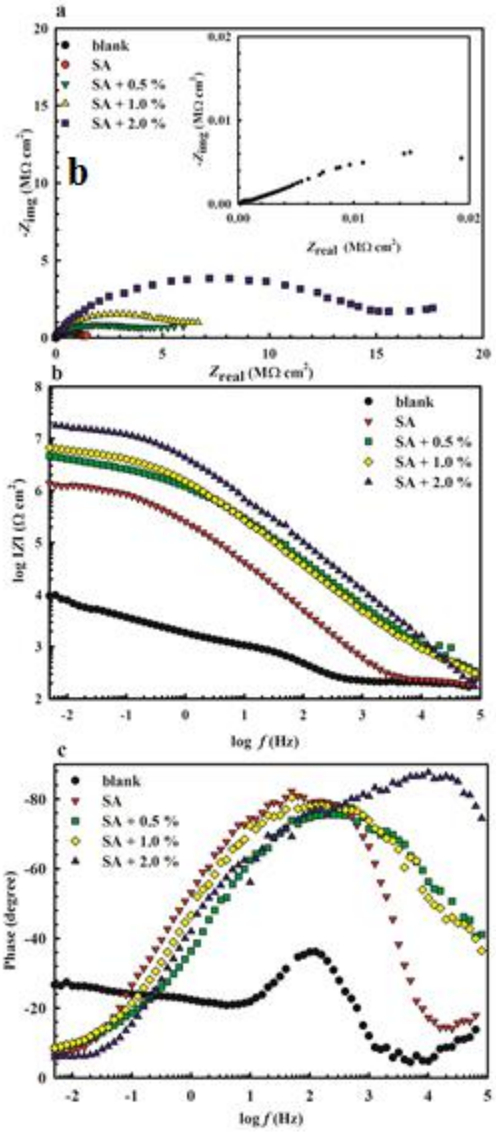


Figure 4: a) Potentiodynamic polarisation curves (1 mVs-1), b) EIS Nyquist plots and Bode plots —of Cu for the bare and modified surfaces of the 'acid rain' solutions (pH =5) at 25ºC. The modified surface was prepared by the immersion of the sample in 0.05 M stearic acid in ethanol with and without the addition of Vitamin E.

Vitamin K3 was the next fat-soluble vitamin used in this research as a corrosion inhibitor within a solution of simulated urban rain with a pH of 5.0. EIS measurements of pure Cu for bare and modified surfaces were performed after 1, 15, 25 h, and after 2, 3, 4, and 6 days of immersion at its open-circuit potential in selected corrosion media (Figs. 5). Surfaces were treated through the same procedure as in the case of Vitamin E. The concentration of added Vitamin K3 was fixed at 2%.

The inhibition effectiveness showed an increase, and after 25 hours it reached a value of 99.9%. After two days the inhibition effectiveness began to decrease slightly, and after six days it seemed that degradation of the protective hydrophobic film had started.

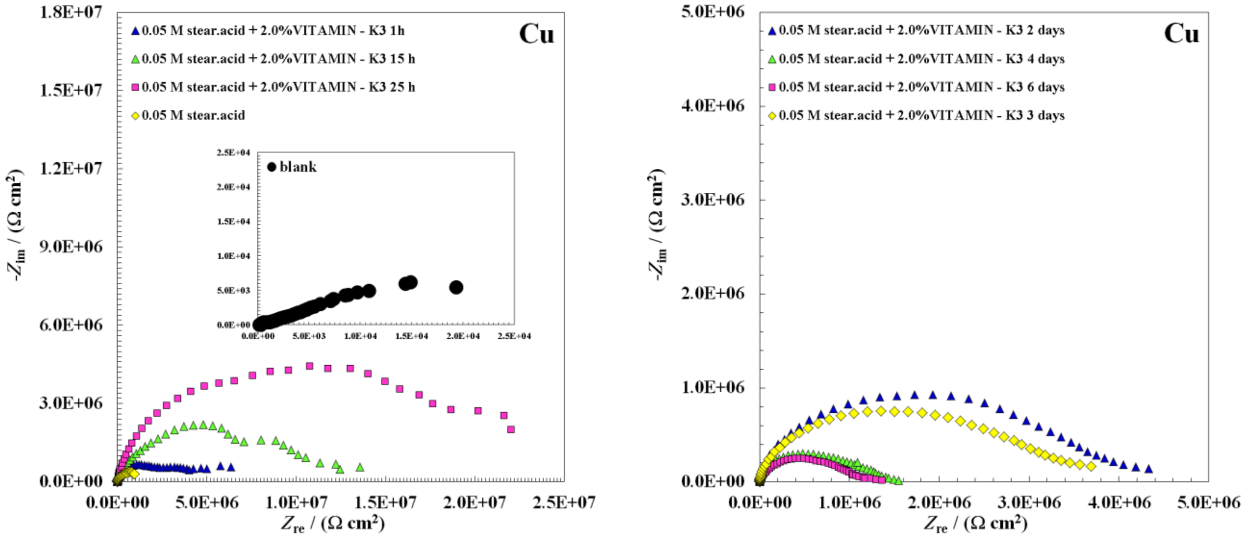


Figure 5: EIS Nyquist plots for pure Cu samples for bare and modified surfaces in urban acid rain (pH=5) measured after 1, 15, 25 h, and after 2, 3, 4, and 6 days of immersion at its open-circuit potential. (The modified surfaces were prepared by immersion of Cu in 0.05 M stearic acid in ethanol with and without the addition of 2% Vitamin K3).

Potentiodynamic curves within the artificial acid rain solution after 1, 4, 6, and 7 days duration test for the bare Cu surface and the surface modified by immersion in stearic acid with and without the addition of 2% Vitamin K are shown in the Figure 6. The values for the inhibition effectiveness obtained on the basis of potentiodynamic measurements (i_{corr}) are in good agreement with those obtained from the total polarisation resistance (R_p) obtained from the Nyquist plots (EIS measurements), i.e. after six days the protective hydrophobic film began to perforate.

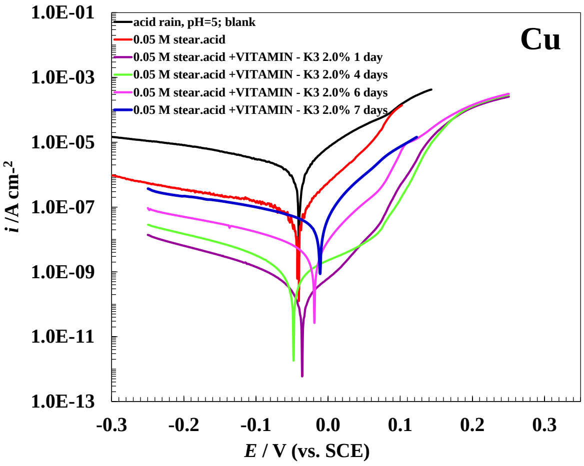


Figure 6: Potentiodynamic polarisation curves (1 mVs-1) of pure Cu for bare and modified surfaces in the 'acid rain' solution (pH =5) at 25ºC measured after 1, 4, 6, and 7 days of immersion in the corrosion medium. (The modified surfaces were prepared by immersion of Cu in 0.05 M stearic acid in ethanol with and without the addition of 2% Vitamin K3).

The next figure (Fig.7) gives the potentiodynamic polarisation curves of modified Cu surfaces within solutions of simulated urban rain, where the pH values of these solutions have been changed (pH =3, 4, and 5). These results unambiguously show the high inhibition ability of the as-prepared hydrophobic layer at pH = 5. The contrary effect was achieved at pH = 3 and 4; icorr up to a third order of magnitude higher was observed for both pH values with respect to the solution with a value of pH =5.

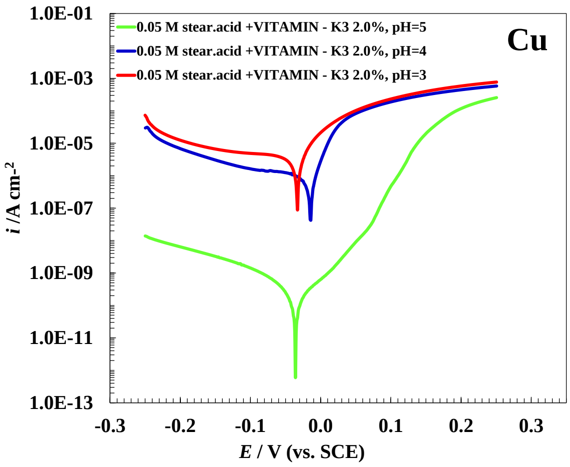


Figure 7: Potentiodynamic polarisation curves (1 mVs-1) of pure Cu for the bare and modified surfaces in the 'acid rain' solutions (pH =3, 4 and 5) at 25°C (The modified surfaces were prepared by immersion of Cu in 0.05 M stearic acid in ethanol with and without the addition of 2% Vitamin K3).

Stainless steel (X4Cr13)

Wettability of a high-level hydrophobic surface (contact angle measurements)

Figure 8 shows the surface microstructures of the bare and hydrophobic samples for SS type X4Cr13, as observed by SEM. The images of the water droplets on the modified surfaces, given within rectangles, indicate the hydrophobicity of the modified surfaces, with values of CA very close to those of super-hydrophobic surfaces (CA ≥150°). It can be seen that the surfaces are rather rough and look as though they are covered by flower-like clusters where a large amount of air can be trapped, and high level of surface hydrophobicity can be expected.

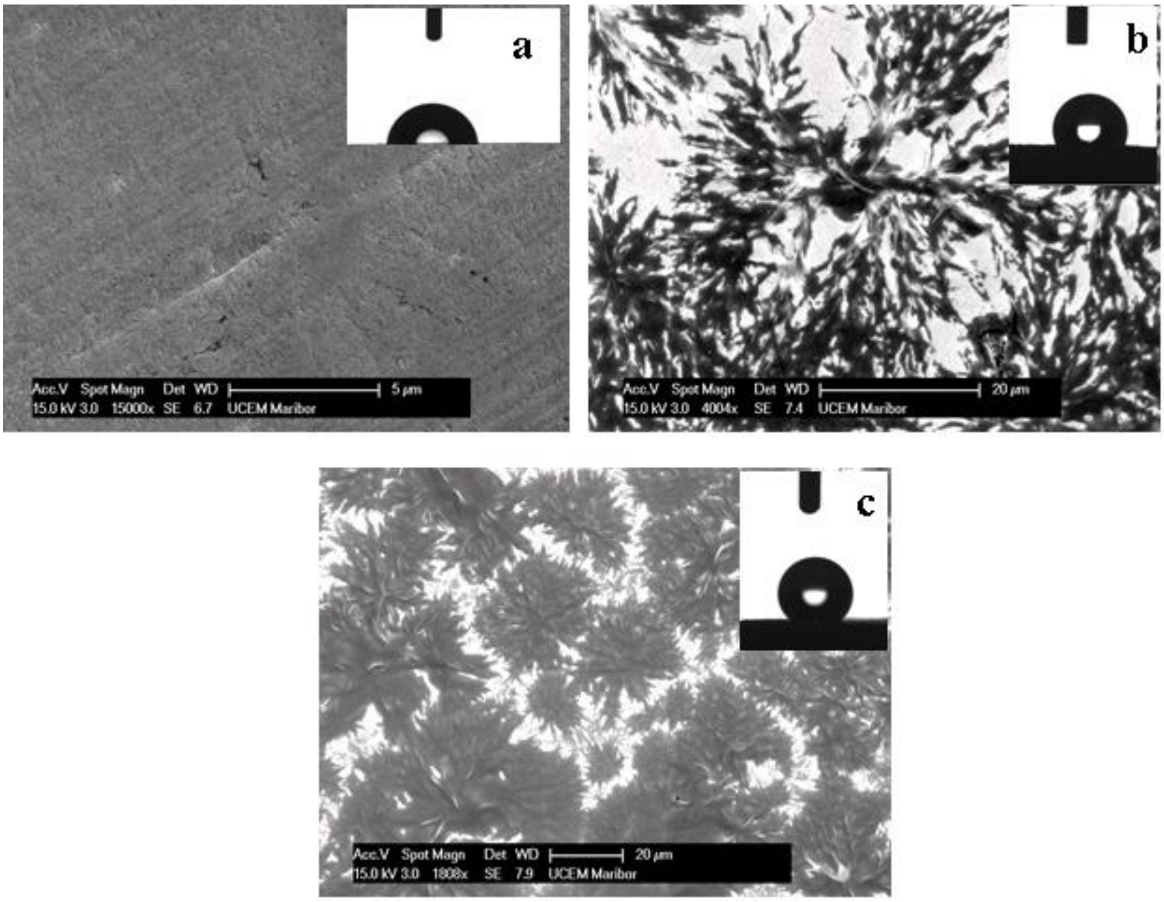


Figure 8: SEM of the untreated and modified surface of SS type X4Cr13 (a) untreated and etched surface (CA=71.5°±3), (b) modified surface in SA solution for one hour (CA=122.8°±2) and (c) modified surface in SA solution with the addition of 2% of Vitamin E for one hour (CA=138.7°±3).

3% NaCl

Further study aimed to demonstrate the stability and effectiveness of the as-prepared hydrophobic layer on the (SS) X4Cr13 within a 3% NaCl solution at 25 °C and also the long-term stability of those layers on the (SS) X4Cr13 under the same conditions.

Potentiodynamic curves in 3% NaCl solution for a bare stainless steel and surface modified by immersion in stearic acid with and without the addition of Vitamin E are shown in Figure 9. Compared to bare stainless steel, the modified SS surface showed a decrease of the current density in the cathodic and anodic direction. But when Vitamin E was added to the solution of 3% NaCl, the cathodic and anodic current densities decreased by up to three decades. After a 100 h duration test, the corrosion current density as well as the inhibition effectiveness *(IE)* of SS type X4Cr13 had minimally decreased by just 1% when the given concentrations of added Vitamin E were 0.5% or 1.0%. In contrast, *IE* values in the case of 2% added Vitamin E (within the 0.05 M ethanolic solution in the process of preparing the hydrophobic layer) had even slightly increased. These results unambiguously show the high inhibition capability of the as-prepared hydrophobic layer in a solution of 3% NaCl. This result suggests that the resulting film completely stops the corrosion, even after hundreds of hours of exposure to 3% NaCl.

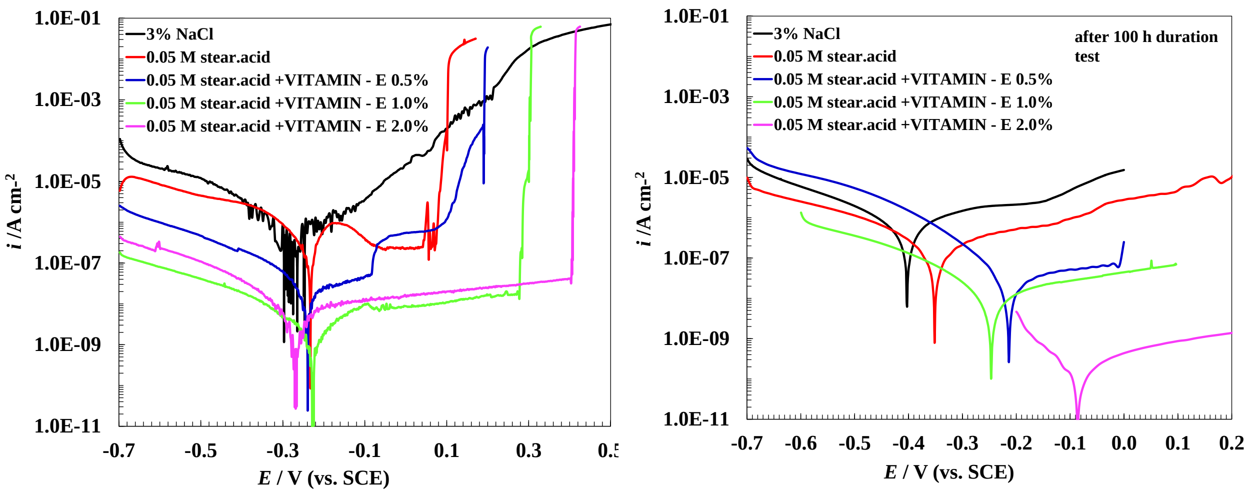


Figure 9: Potentiodynamic polarisation curves (1 mVs-1) for SS type X4Cr13 for bare and modified surfaces in 3% NaCl at 25ºC. The modified surfaces were prepared by immersion of SS type X4Cr13 in 0.05 M stearic acid in ethanol with and without the addition of Vitamin E. (after tests of 1 hour and 100 hours duration test).

The values of the total polarisation resistance (R_p) obtained from the Nyquist plots (Figs.10) are in good agreement with those obtained from potentiodynamic techniques, i.e. the film deposited from ethanolic solutions of 0.05M stearic acid containing Vitamin E exhibited much better protection properties, even after 100 hours of exposure to 3% NaCl.

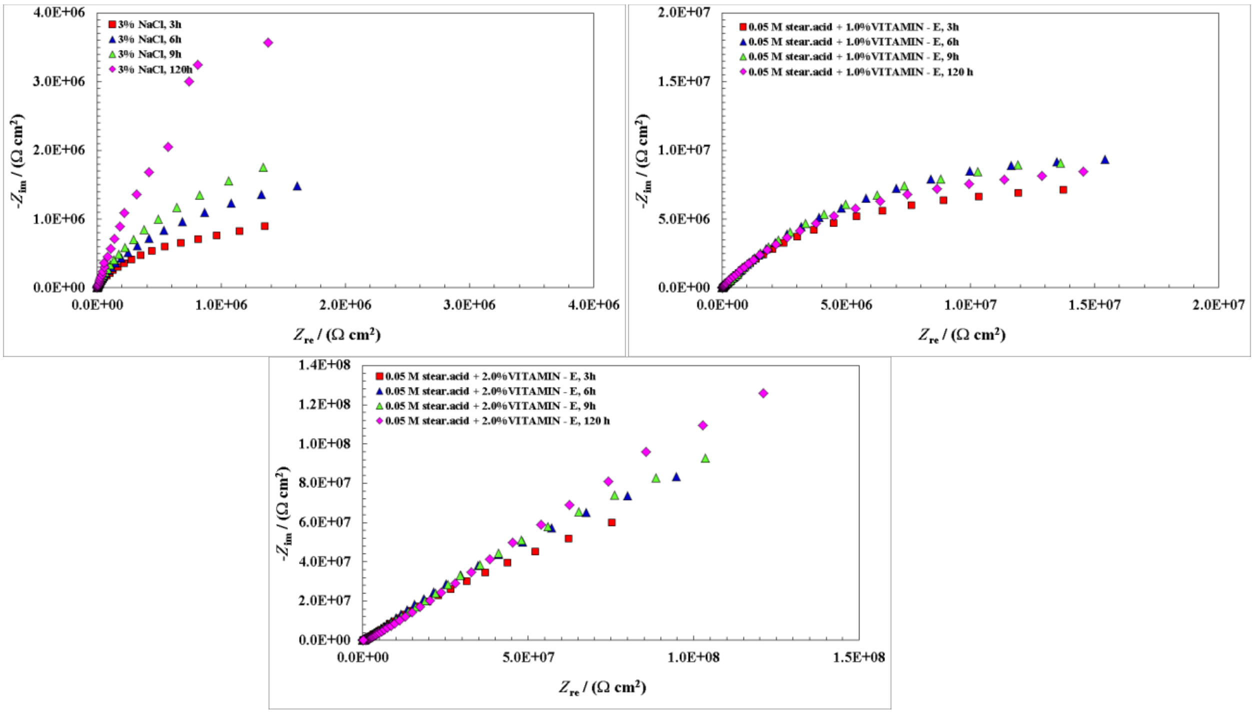


Figure 10: EIS Nyquist plots for SS type X4Cr13 for bare and modified surfaces.(prepared by immersion of SS type X4Cr13 in 0.05 M stearic acid in ethanol with and without the addition of Vitamin E) in 3% NaCl measured after 3, 6, 9 , and 100 h of immersion.

Stainless steel (X4Cr13)

Simulated urban rain (pH =3)

It was shown above that the modified layers formed in the presence of stearic acid alone and in combination with Vitamin E had an effect on the electrochemical properties of SS type X4Cr13 in a 3% NaCl solution. It was therefore natural to extend these studies. The main goal of this research is to demonstrate the long-term stability and effectiveness of the as-prepared hydrophobic layer on the (SS) X4Cr13 within simulated urban rain with a pH of 3.0 at 25 °C. The inhibitive efficiency increased noticeably with the addition of Vitamin E in an ethanolic solution of 0.05 M stearic acid, in effect, from 54% to more than 99.0 %, and after testing of 120 h in duration, from 80% to more than 99.0%. The inhibition efficiency *IE* was calculated via the kinetic parameters measured during corrosion processes, as well as the polarisation resistance R_p and the corrosion current density i_{corr}, cf. Equations 1 and 2). In the case of the polarisation resistance, *IE* was calculated via Equation (2), where X = R_p . Equation (1) was used in connection with the corrosion current density where Y = i_corr

$$\boldsymbol{IE}\,\% = \left[1 - \frac{\boldsymbol{X}'}{\boldsymbol{X}}\right]\cdot 100 \qquad (1)$$

$$\boldsymbol{IE}\,\% = \left[1 - \frac{\boldsymbol{Y}}{\boldsymbol{Y}'}\right]\cdot 100 \ \ , \qquad (2)$$

where the notations i_corr and R_p, were used for those measurements without inhibition action, whilst the primed quantities i_corr' and R_p', were applied when measurements were performed on the modified surfaces of SS type X4Cr13 in the artificial acid rain solution. Figures 11 and 12 show the electrochemical response of the potentiodynamic and EIS measurements.

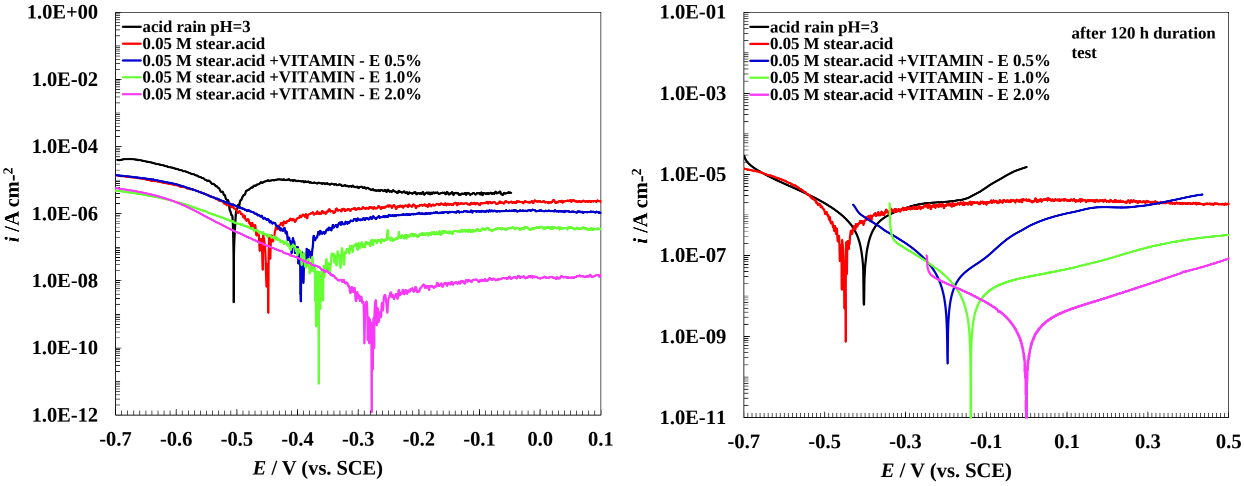


Figure 11: Potentiodynamic polarisation curves (1 mVs-1) for SS type X4Cr13 for bare and modified surfaces within artificial acid rain with a pH of 3.0 at 25ºC (after 1 h of immersion and after a test of 120 hours duration). The modified surfaces were prepared by immersion of SS type X4Cr13 in 0.05 M stearic acid in ethanol with and without the addition of Vitamin E

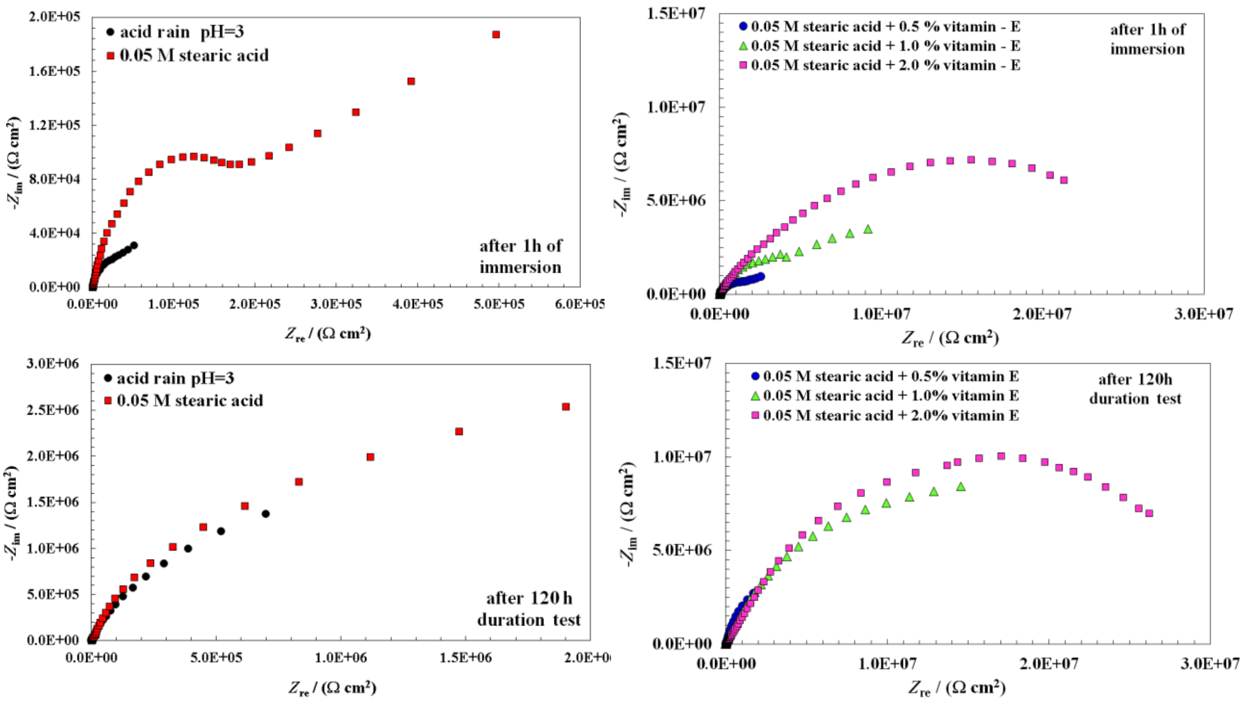


Figure 12: Nyquist plots of SS type X4Cr13 for bare and modified surfaces in artificial acid rain with a pH of 3.0 at 25°C (after 1 h of immersion and after a test of 120 hours duration). The modified surfaces were prepared by immersion of SS type X4Cr13 in 0.05 M stearic acid in ethanol with and without the addition of Vitamin E.

From the all used techniques, in the presence of Vitamin E in the ethanolic solution of 0.05 M stearic acid, the inhibition effectiveness of the modified surface of SS type X4Cr13 in a solution of simulated urban rain (pH=3) noticeably increased. Electrochemical measurements indicated that film deposited from ethanolic solutions of 0.05M stearic acid containing Vitamin E have shown excellent protection properties, even after 120 hours of exposure to a solution of simulated urban rain.

References:

1. Holmberg, K., Jönsson,B., Kronberg, B.,Lindman, B., *Surfactants and polymers in aqueous solution*, 2 edn., John Wiley Sons., 2002, pp. 389-402.
2. Bormashenko, E., Progress in understanding wetting transitions on rough surfaces, *Adv. Colloid Interface Sci*.**,** 2015, 222, 92-103.
3. Barthlott,W., Neinhuis,C., Purity of the sacred lotus, or escape from contamination in biological surfaces, *Planta*, 1997, 202, 1-8.
4. Boreyko,J.B., Baker, C.H., Poley, C.R., Chen, C.-H., Wetting and Dewetting Transitions on Hierarchical Superhydrophobic Surfaces, *Langmuir*, 2011, 27, 7502-7509.
5. Nosonovsky, M., Bhushan,B., Multiscale Dissipative Mechanisms and Hierarchical Surfaces, Springer, Berlin, Heidelberg, 2008, pp. 199-230.
6. Chen, S., Chen,Y., Lei, Y.,Yin,Y., Novel strategy in enhancing stability and corrosion resistance for hydrophobic functional films on copper surfaces, *Electrochem. commun*., 2009 11, 1675-1679.
7. Guo, Z., Liu,W., Su, B.-L., Superhydrophobic surfaces: from natural to biomimetic to functional, *J.Colloid. Interface. Sci*., 2010, 353, 335-355.

8. Chen, H., Yuan, Z., Zhang, J., Liu,Y., Li, K., Zhao, D., Li, S., Shi, P., Tang, J., Preparation, characterization and wettability of porous superhydrophobic poly (vinyl chloride) surface, *J. Porous. Mater*., 2009, 16, 447-451.
9. Li, X-M., Reinhoudt, D., Calama, M.C., What do we need for a superhydrophobic surface? A review on the recent progress in the preparation of superhydrophobic surfaces, *Chem. Soc. Rev.*, 2007, 36, 1350-1368.
10. Wang, S., Jiang, L., Definition of superhydrophobic states, *Adv. Mater.*, 2007, 19, 3423–3424.
11. Jafari, R., Farzaneh, M., Fabrication of superhydrophobic nanostructured surface on aluminum alloy, *Appl. Phys.*, 2011, 102, 195-199.
12. Xue, C.-H, Jia, S.-T. , Zhang,J., Ma, J.-Z., Large-area fabrication of superhydrophobic surfaces for practical applications: an overview, *Sci. Technol. Adv. Mater*., 2010, 11, 1-15.
13. Momen, G., Farzaneh, M., Jafari, R., Ice repellency behavior of superhydrophobic surfaces: effects of icing conditions and surface roughness", *Appl. Surf. Sci.*, 2015, 349, 211-218.
14. Ma, M., Hill, R. M., Superhydrophobic surfaces, *Curr. Opin. Colloid Interface* Sci., 2006, 1, 193-202.
15. Jafari, R., Menini, R., Farzaneh, M., Superhydrophobic and icephobic surfaces prepared by RF sputtered polytetrafluoroethylene coatings on anodized aluminium, *Appl. Surf. Sci.*, 2010, 257, 1540-1543.
16. Momen, G., Farzaneh, M., Jafari, R., Wettability behaviour of RTV silicone rubber coated on nano-structured aluminium surface, *Appl. Surf. Sci.*, 2011, 257, 9489- 6493.
17. Balu, B., Breedveld, V., Hess, D.W., Fabrication of "Roll-off" and "Sticky" Superhydrophobic Cellulose Surfaces via Plasma Processing, Langmuir, 2008, 24, 4785-4790.
18. Xu,W., Song, J., Sun, J., Lu, Y., Yu, Z., Rapid Fabrication of Large-Area, Corrosion-Resistant Superhydrophobic Mg Alloy Surfaces, *Appl. Mater. Interfaces*., 2011, 3, 4404–4414.
19. Chen, L.J., Chen, M., Zhou, H.D., Chen, J.M., Improving the hydrophilicity of metallic surfaces by nanosecond pulsed laser surface modification, *Appl. Surf. Sci.*, 2008, 255, 3459–3462.
20. Wang, J. , Li, D., Gao, R., Liu, Q., Jing, X., Wang, Y., et al., Construction of superhydrophobic hydromagnesite films on the Mg alloy, *Mater. Chem. Phys.*, 2011,12 ,154–160.
21. Liu,Q., Chen, D.,Kang, Z., Surf. One-Step Electrodeposition Process To Fabricate Corrosion Resistant Superhydrophobic Surface on Magnesium Alloy, *Appl. Mater. Interfaces*, 2015, 7, 1859−1867.
22. Wang, P., Zhang, D., Qiu, R., Wu, J., Super-hydrophobic metal-complex film fabricated electro-chemically on copper as a barrier to corrosive medium, *Corros. Sci.*, 2014, 83, 317–326.
23. Liu, L., Chen, R., Liu, W., Zhang, Y., Shi, X., Pan, Q., Fabrication of superhydrophobic copper sulfide film for corrosion protection of copper, *Surf. Coat.Technol.*, 2015, 272, 221–228.
24. Boinovich, L.B., Gnedenkov, S.V., Alpysbaeva, D.A., Egorkin, V.S., Emelyanenko, A.M., Sinebryukhov, S.L., et al., Corrosion resistance of composite coatings on low-carbon steel containing hydrophobic and superhydrophobic layers in combination with oxide sublayers , *Corros. Sci*,. 2012, 55, 238–245.
25. Wang, P., Zhang, D., Qiu, R., Liquid/solid contact mode of super-hydrophobic film in aqueous solution and its effect on corrosion resistance, *Corros. Sci.*, 2012, 54 , 77–84.
26. Fuchs-Godec, R., Zerjav, G., Corrosion resistance of high-level-hydrophobic layers in combination with Vitamin E – (a-tocopherol) as green inhibitor, *Corros. Sci.*, 2015, 97, 7-16.

PREDAVANJA PO POZIVU

INVITED LECTURES

Fabrication of Palladium/Platinum Core-Shell Nanoparticles by Electroless Metal Plating

Masataka Sakai[1], Shota Noda[1], Yoshio Kobayashi[1], Ken-ichi Watanabe[2], Hidekazu Koda[2], Hiroshi Kunigami[2], Hideki Kunigami[2]

[1]Ibaraki University, Department of Biomolecular Functional Engineering, College of Engineering, Hitachi, Ibaraki, Japan,

[2]K. K. Shinko Kagaku Kogyosho, Mashimori, Koshigaya, Saitama, Japan

Abstract

An electroless metal plating method was used to form metallic platinum (Pt) shells on metallic palladium (Pd) nanoparticles. The electroless metal plating method comprised two steps: (1) reduction of Pd ions to fabricate Pd nanoparticles and (2) deposition of Pt nuclei and the following formation of Pt shells by immersing the Pd nanoparticles in a Pt-plating solution. TEM observation revealed that the nanoparticles had a size of 5.7±1.9 nm, were composed of Pd nanoparticles as core and Pt shells. The Pd/Pt core-shell nanoparticles were immobilized electrostatically on carbon support surface-modified with poly(diallyldimethylammonium chloride) (Pd/Pt/C). Cyclic voltammetry revealed that the Pd/Pt/C exerted hydrogen adsorption/desorption, expecting the Pd/C to function as catalyst for fuel cell.

Keywords: *Pd; Pt; Core-shell; Particles; Electroless metal plating; Catalyst*

1. Introduction

Composites of plural materials are of special interest because they exhibit multiple functions derived from their individual components. Among the numerous structures that have been proposed for functional materials to date, core-shell structures, in which a metallic core particle is coated with a metallic shell, have attracted significant attention owing to their unique properties and potential applications in fields such as catalysis, optics and biotechnology [1-3]. Core-shell structures are also interesting economically because a small amount of expensive material can be used to cover a core of inexpensive material [4].

Pt is an interesting noble metal because Pt nanomaterials and nanomaterials containing Pt exhibit extraordinary chemical and physical properties that can be harnessed for sensors, magnetic materials and catalysts [5-10]. Pt is also used as a catalyst for fuel cells [11-13], and its oxygen reduction reaction (ORR) activity is desired to be improved. According to Zhang et al.'s work, the ORR activity of Pt is dependent on support species, and a metallic palladium support promotes the activity the most efficiently among various metals examined [14]. Their results indicate that composite particles composed of Pd as core and Pt as shell will function as the catalyst with high ORR activity. From this viewpoint, several researchers studied on Pd/Pt core-shell nanoparticles for fuel cell catalysts [15-17]. Many studies produced the Pd/Pt core-shell nanoparticles with reduction of Pt ions to form Pt with reductant in the presence of Pd nanoparticles, in which the formation of Pt may take place not only on Pd nanoparticle surface but also in the solution. This may result in production of not only Pd/Pt core-shell nanoparticles but also Pt nanoparticles that are not in contact with Pd nanoparticles. This unexpected production reduces efficiency of fabrication of Pd/Pt core-shell nanoparticles.

This study aimed to develop a method for fabricating Pd/Pt core-shell nanoparticles. Our previous work performed fabrication of TiO_2/Pt core-shell particles by electroless metal plating [18]. Because reduction of metal ions to metal takes place at surface of catalyst nuclei deposited on support in the electroless metal plating process, all the generated metal nuclei should be consumed to produce metal layer on the support. The electroless metal plating process was extended to the fabrication of Pd/Pt core-shell nanoparticles. The method is composed of two steps. The first step is fabrication of Pd nanoparticles with reduction of palladium ions in aqueous solution. The Pd nanoparticles were used as catalyst nuclei for the following Pt-plating. The second step is Pt-plating, *or* formation of Pt shells on the Pd nanoparticle surfaces with reduction of platinum ions in the presence of the Pd nanoparticles. The present work also demonstrated immobilization of the Pd/Pt nanoparticles on carbon support (Pd/Pt/C), and electro-chemical measurement using the Pd/Pt/C.

2. Experimental

2.1 Chemicals

The starting reagents for the Pd nanoparticles and the Pt shells were $PdCl_2$ (97.0%) and hydrogen hexachloroplatinate (IV) hexahydrate ($H_2PtCl_6·6H_2O$) (98.5%), respectively. Ethanol (99.5%) was used as both of a solvent and a reducing reagent for Pd ions in preparation of the Pd nanoparticle colloid solution. A reducing reagent for Pt ions was hydrazine monohydrate (98.0%). Polyvinylpyrrolidone (PVP) (K-30 (Mw=40000)) was used as a dispersing agent in preparation of nanoparticles. Hydrochloric acid (HCl) (35.0-37.0%) was used to dissolve the $H_2PtCl_6·6H_2O$ in water. Nafion™ dispersion solution (5%, DE520 CS type) and 2-propanol (super special grade) were used for preparing suspension of Pd/Pt/C for fabrication of Pd/Pt/C-immobilized electrode. Poly(diallyldimethylammonium chloride) solution (PDADMAC) (20 wt% in H_2O, Mw=1000,000-2000,000) was used for surface-modification of the carbon support. An electrolyte for measurement of electro-chemical property was perchloric acid (60.0-62.0%, Ultrapur). The Nafion™ dispersion solution and the 2-propanol were purchased from Wako Pure Chemical Industries, Ltd., and the PDADMAC from Sigma-Aldrich Co. LLC. All chemicals besides them were purchased from Kanto Chemicals Co., Inc. The PDADMAC was dialyzed using a cellulose tube (pore size: 5.0 nm, As-One Co., Osaka, Japan) prior to use. All the chemicals besides the PDADMAC were used as received. The water used for solution preparation was ion-exchanged and distilled using an Advantec RFD372VC. The support for the Pd/Pt nanoparticles in the electro-chemical measurement was carbon particles (Carbon Black Vulcan XC-72).

2.2 Preparation

To obtain catalyst nuclei in electroless metal plating, Pd nanoparticles were fabricated by the reduction of Pd ions with the following process. $PdCl_2$ and PVP were added to a co-solvent of 60/40 (v/v) H_2O/ethanol under sonication, and the mixture was refluxed at $80^{o}C$ for 3 h. The initial concentrations of Pd and PVP were 5.3 mM and 7.6 g/L, respectively, in the co-solvent.

The formation of Pd/Pt core-shell particles was achieved using an electroless metal plating method with the following process. Following previous studies on electroless Pt plating [18,19], a Pt plating solution was prepared by dissolving $H_2PtCl_6·6H_2O$ in a 4% HCl aqueous solution to give a Pt concentration of 19 mM. The Pt plating solution and water was added to the Pd nanoparticle colloid solution at 5°C. After 1 h, hydrazine was added to the mixture to initiate Pt deposition (Pd/Pt). The initial concentrations of Pd, PVP, Pt and hydrazine were 2.9 mM, 3.8 g/L, 0.80 mM and 20 mM, respectively. After 24 h, the solvent of the Pd/Pt nanoparticle colloid solution was removed with evaporation under low pressure, and ethanol was added to the residue to re-disperse the nanoparticles in ethanol. The nanoparticles re-dispersed in ethanol were washed with a process composed of centrifugation, removal of the solvent, addition of ethanol, and shaking on a vortex mixer. The washing process was repeated three times.

The Pd/Pt nanoparticles were immobilized on the carbon powder for the following electro-chemical measurement with the following process. The Pd/Pt nanoparticles were expected to be colloidally stable in water, because their surface was made ionic due to oxide layer produced with passivation. The carbon surface is hydrophobic. Accordingly, the carbon surface should be hydrophilic to increase affinity between the Pd/Pt particle surface and the carbon surface. Thus, prior to the immobilization, the carbon powder was surface-modified with ionic polymer to make the carbon surface hydrophilic with the following process. The carbon particles were added to a PDADMAC aqueous solution under sonication, and the suspension of carbon particles was aged at 35^{o}C for 24-48 h (PDADMAC-C). The initial concentrations of carbon and PDADMAC were 0.27 and 1 g/L, respectively. After the aging, the PDADMAC-C particles were washed with the same process as for the nanoparticles, in which water, however, was used for the re-dispersion. Subsequently, the colloid solution of washed Pd/Pt nanoparticles and water were added to the suspension of washed PDADMAC-C particles, and the mixture was aged at 35^{o}C for 6 h to produce Pd/Pt-immobilized carbon particles (Pd/Pt/C). The initial concentrations of Pd, Pt, and carbon were 0.665 mM, 0.2 mM, and 0.135 g/L, respectively. After the immobilization, the Pd/Pt/C particles were washed with the same process as for the nanoparticles, in which water, however, was used for the re-dispersion. In the final re-dispersion, the concentrations of Pd, Pt, and carbon were adjusted to 1.33 mM, 0.4 mM, and 0.27 g/L, respectively, by decreasing the amount of water used for the re-dispersion.

2.3 Characterization

Transmission electron microscopy (TEM) was used to investigate the morphology of the nanoparticles and performed with a JEOL JEM-2100 microscope operating at 200 kV. To prepare samples for TEM, the colloid solution was dropped on a collodion-coated copper grid, and the dispersion medium was evaporated in air, and then in a vacuum. The volume-average particle sizes were determined by measuring dozens of particle diameters in the TEM images. The particle powder was characterized by X-ray diffractometry (XRD). For preparing a powder sample for the XRD measurement, supernatant of the particle colloid was removed by decantation, and then the residue of the colloid was dried at room temperature for 24 h in a vacuum. The XRD measurements were performed with a Rigaku Ultima IV X-ray diffractometer at 40 kV and 30 mA using CuKα radiation. The study of the surface composition of particles was performed using X-ray photoelectron spectroscopy (XPS) measurements. The XPS samples were produced by the same prosed as that for the XRD samples. The XPS spectra were obtained using a JEOL JPS-9010 equipped with a monochromatic Mg Kα radiation source (200 W, 10 kV, 1253.6 eV). To study the composition below the surface, the particles were etched using 500 kV Ar^{+} sputtering for 1 min. The introduction of PDADMAC on the particle surfaces was qualitatively confirmed using ζ-potential measurements. To measure the ζ-potential of the particles, electrophoretic light scattering (ELS) was performed with a Brookhaven ZetaPlus zeta potential analyzer. Either aqueous HCl or aqueous NaOH was added to the colloid solution to vary the pH for the ELS measurement.

Electro-chemical property of the Pd/Pt/C was measured with a cyclic voltammetry. To fabricate a working electrode, the suspension of Pd/Pt/C nanoparticles, which was prepared by mixing the Pd/Pt/C powder, the 5% Nafion™ dispersion solution, and the 2-propanol, was put onto surface of a glassy carbon rotating electrode (Hokuto Denko, HR2-D1-GC5), and then was dried by applying a hot air. A reference electrode and a counter electrode were a reversible hydrogen electrode kit (ALS, 013373) and a platinum electrode (Hokuto Denko, HX-C5), respectively. The CV was performed with a Hokuto Denko HZ-5000 electrochemical measurement system operating at a scan speed of 50 mV/s in a range of 0.05-1.2 V in 0.1 M perchloric acid in nitrogen gas with no rotating.

3. Results and Discussion

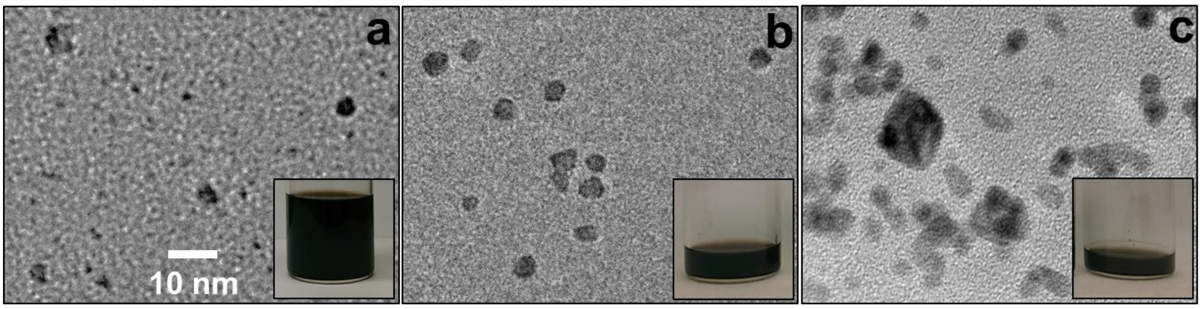


Fig. 1 TEM images of (a) Pd nanoparticles, (b) Pd/Pt nanoparticles prior to evaporation of solvent, and (c) Pd/Pt nanoparticles after the evaporation. Insets show photographs of colloid solutions of them.

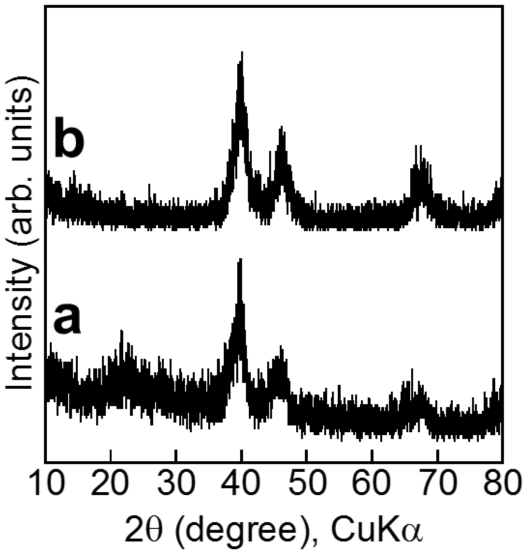


Fig. 2 XRD patterns of (a) Pd nanoparticles and (b) Pd/Pt nanoparticles after the evaporation.

3.1 Pd nanoparticles

An inset of **Fig. 1 (a)** shows a photograph of the as-prepared Pd nanoparticle colloid solution. The solution, which was a brownish suspension prior to the reflux, became a black solution during the reflux, implying the reduction of Pd^{2+} to produce metallic Pd nanoparticles. No particle sedimentation was observed in the solution, suggesting that the Pd nanoparticles were colloidally stable. **Fig. 1 (a)** shows a TEM image of the as-prepared Pd nanoparticles. The particles were quasi-spherical with an average size of 3.4±1.3 nm. **Fig. 2 (a)** shows the XRD pattern of the nanoparticles. Several diffractions were detected at ca. 40, 46 and 68 degrees. It was hard to determine detailed peak angles for the diffractions, since they were not strong. However, these diffractions could be attributed to the (111), (200) and (220) planes of cubic metallic Pd (ICSD No.: 01-071-3757), respectively, which indicated that the production of metallic Pd nanoparticles. This indication supported the implication for production of metallic Pd nanoparticles.

3.2 Pd/Pt nanoparticles

An inset of **Fig. 1 (b)** shows a photograph of the as-prepared Pd/Pt nanoparticle colloid solution prior to the evaporation of solvent. The solution had a color of black. Since Pt nanoparticle colloid solution is blackish as well as Pd nanoparticles, it was hard to confirm production of metallic Pt by naked eyes. The nanoparticles were also colloidally stable because of no observation of particle sedimentation in the solution. **Fig. 1 (b)** shows a TEM image of the nanoparticles. The particles were quasi-spherical with an average size of 3.6±1.3 nm. The particle size appeared to slightly increase with the electroless metal plating process, though there was no large increase. The increase in particle size implied formation of Pt shell on Pd nanoparticles.

An inset of **Fig. 1 (c)** shows a photograph of the as-prepared Pd/Pt nanoparticle colloid solution after the evaporation of solvent. The solution was still black. The nanoparticles were also colloidally stable because of no observation of particle sedimentation in the solution, so that the evaporation process did not influence the colloidal stability of the particles. **Fig. 1 (c)** shows a TEM image of the nanoparticles. Nanoparticles appeared to contain a core or multiple cores, and the particles had an average size of 5.7±1.9 nm. Pt shells became thick with the evaporation of solvent, which increased the particle size. The evaporation of solvent decreased the volume of solution, which increased various concentrations of species such as Pd particles, generated Pt nuclei and unreacted chemicals. The increase in the concentrations of unreacted chemicals increased ionic strength of the solution. Increased ionic strength has been reported to compress the double layer of colloidal particles [20-22]. The evaporation of solvent therefore decreased the double-layer repulsion between the Pd nanoparticles and the Pt nuclei. The increased ionic strength was thus primarily responsible for the adsorption of the Pt nuclei on the Pd nanoparticles in the present system. The adsorption was then followed by formation of the Pt shells, or formation of core-shell structure. It should be noted that several nanoparticles appeared to contain multiple cores. The evaporation of solvent also decreased the double-layer repulsion between the Pd nanoparticles. The increased ionic strength was also responsible for the aggregation of Pd nanoparticles in the present system. The aggregates were then coated with Pt shells, which resulted in the production of nanoparticles containing the multiple Pd nanoparticles as the core. **Fig. 2 (b)** shows the XRD pattern of the nanoparticles. Several diffractions were detected at ca. 40, 46 and 68 degrees as well as the Pd nanoparticles. There were two possibilities in attribution of these diffractions. One was the (111), (200) and (220) planes of cubic metallic Pd, and the other was the (111), (200) and (220) planes of cubic metallic Pt (ICSD No.: 01-071-3756). It was hard to conclude which attribution was reasonable, because there is no large difference in *d*-spacing between cubic metallic Pd (*d*-spacing: 0.389 nm) and cubic metallic Pt (*d*-spacing: 0.392 nm), and the diffractions for the Pd/Pt nanoparticles were also not strong. According to our previous work on TiO_2/Pt core-shell particles fabricated with the electroless metal plating method, the crystalline Pt shells formed on the TiO_2 particles [18]. Since the electroless metal plating process in the present system was quite similar to that in our previous work, the crystalline Pt shells were considered to be also obtained in the present system, though the XRD did not remarkably provide conclusion on formation of crystalline Pt shells. The XPS measurement revealed existence of elements of Pd and Pt. Atomic ratios of Pd + Pt for the surfaces of the Pd/Pt nanoparticles were estimated from the XPS peak area intensity. Prior to the Ar etching, the atomic ratios of Pd and Pt were 73.2 and 26.8 atom%, respectively. These ratios increased to 74.3 atom% and decreased to 25.7 atom%, respectively, after the Ar^+ etching. This result indicated that the etching of the particle surface revealed the surface of the Pd particles, which further supported the formation of Pt shells on the Pd nanoparticles.

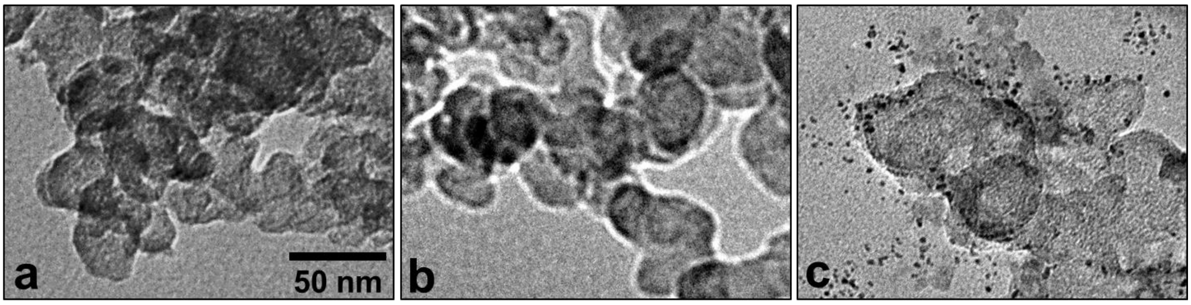


Fig. 3 TEM images of (a) as-received carbon particles, (b) surface-modified carbon particles fabricated with a surface-modification time of 24 h, and (c) Pd/Pt/C particles produced using surface-modified carbon particles fabricated with a surface-modification time of 48 h.

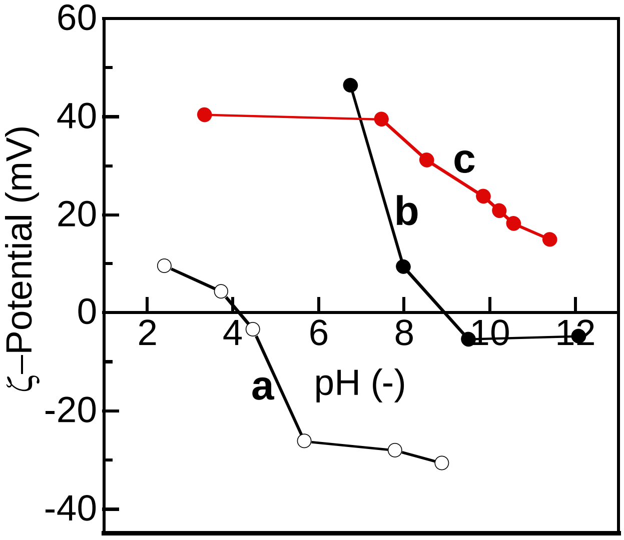


Fig. 4 ζ-Potentials of (a) as-received carbon particles, (b) surface-modified carbon particles fabricated with a surface-modification time of 24 h, and (c) surface-modified carbon particles fabricated with a surface-modification time of 48 h.

3.3 Surface-modified carbon particles

Figs. 3 (a) and (b) show TEM images of the as-received and the surface-modified carbon particles, respectively. The as-received carbon particles were spherical particles with a size of 44.9±13.9 nm. The surface-modified carbon particles were also spherical particles, and had a size of 41.6±11.0 nm that was almost the same as that of the as-received carbon particles. Accordingly, it was hard to confirm existence of PDADMAC on the carbon particles. Fig. 4 shows the ζ-potentials of various carbon powders as a function of the pH. In the as-received carbon and the surface-modified carbon fabricated for a surface-modification time of 24 h, the ζ-potentials decreased and passed through isoelectric points (IEP) as the pH increased. The IEPs of the as-received carbon and the surface-modified carbon were 4.0 and 9.0, respectively. The IEP for the surface-modified carbon was higher than that for the as-received carbon. Because the PDADMAC is a cationic polymer, this shift to higher pH indicated that the PDADMAC molecules were present on the carbon powder surface, *or* the carbon powder surface was successfully modified with the PDADMAC. The surface-modified carbon fabricated for a surface-modification time of 48 h did not have an IEP, and had positive ζ-potentials in the range of pH examined. This indicated that an increase in surface-modification time increased the amount of PDADMAC on particles. As a result, the carbon surface became cationic.

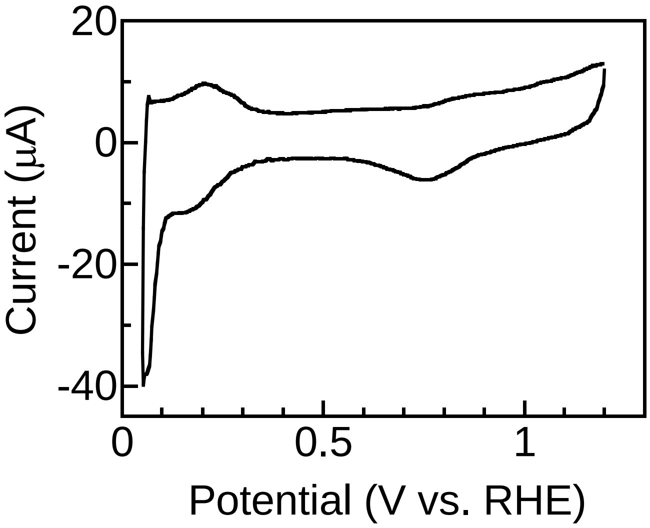


Fig. 5 Cyclic voltammogram of Pd/Pt/C particles. The Pd/Pt/C particles used for the measurement was the sample (c) in Fig. 3.

3.4 Pd/Pt/C powder

Fig. 3 (c) shows a TEM image of Pd/Pt/C powder. Darker and lighter parts of particles were determined to be Pd/Pt particles and carbon powder, respectively, due to the electron density differences between them. The Pd/Pt nanoparticles were immobilized on the carbon, though several Pd/Pt nanoparticles were not. The ELS measurement revealed that the surface-modified carbon was cationic in the range of pH ca. 3-12, as shown in **Fig. 4 (c)**. According to studies on zeta-potentials of Pt nanoparticles [23,24], the Pt nanoparticles have an isoelectric point of ca. 3; The Pt nanoparticle surface should be anionic at neutral pH. Since the Pd/Pt-immobilization was performed at neutral pH, the Pt surface of Pd/Pt nanoparticles and the surface of surface-modified carbon powder were probably anionic and cationic, respectively. This indicated that electrostatic attractive power acted on them. Consequently, the Pd/Pt nanoparticles were immobilized on the surface-modified carbon powder.

Fig. 5 shows a cyclic voltammetry curve for Pd/Pt/C. A negative peak detected at ca. 0.7 V was ascribed to reduction of Pt oxide. Peaks based on hydrogen adsorption/desorption were detected in a voltage range as low as ca. 0-0.3 V. The result on the detection expected the Pd/Pt/C to function as a catalyst for fuel cell. Further electrochemical characterizations are required to be performed in a future work for evaluating catalytic properties of the Pd/Pt/C.

4. Conclusions

The Pd nanoparticles with the size of 3.4 ±1.3 nm were produced by the reduction of Pd ions, and then the Pt shells were fabricated on the surfaces of the Pd nanoparticles by using the electroless metal plating technique. The size of Pd/Pt core-shell nanoparticles after the evaporation treatment was 5.7 ±1.9 nm. The surfaces of carbon support powder were modified with the PDADMAC with the cationic group, and then the Pd/Pt core-shell nanoparticles with anionic surfaces were immobilized electrostatically on the surface-modified carbon support. The hydrogen adsorption/desorption took place for the Pd/Pt/C powder. A study on application of the Pd/Pt/C particles to catalyst for fuel cells is being prepared for their practical use.

Acknowledgements

This work was partially supported by K. K. Shinko Kagaku Kogyosho. We express our thanks to Prof. T. Noguchi at the College of Science of Ibaraki University, Japan (current affiliation: Faculty of Arts and Science of Kyushu University, Japan) for his help with the TEM observation.

References

1. Saha, S., Basu, A., Das, D., Ganguly, A., Banerjee, D., Kargupta, K., Novel graphene supported Co rich connected core (Pt)-shell (Co) nano-alloy catalyst for improved hydrogen generation and electro-oxidation, *Int. J. Hydrogen Energy* 2016, 41, 18451-18464.
2. Liu, Y., Dai, J., Xu L., Liu, X., Liu, J., Li, G., Red to brown to green colorimetric detection of Ag^+ based on the formation of Au-Ag core-shell NPs stabilized by a multi-sulfhydryl functionalized hyperbranched polymer, *Sens. Actuat. B* 2016, 237, 216-223.
3. Song, L., Mao, K., Zhou, X., Hu, J., A novel biosensor based on Au@Ag core-shell nanoparticles for SERS detection of arsenic (III), *Talanta* 2016, 146, 285-290.
4. Jankiewicz, B.J., Jamiola, D. J., Jaroniec, C. M., Silica-metal core-shell nanostructures, *Adv. Colloid Int. Sci.* 2012, 170, 28-47.
5. Choi, S. W., Kim, J., Byun, Y. T., Highly sensitive and selective NO_2 detection by Pt nanoparticles-decorated single-walled carbon nanotubes and the underlying sensing mechanism, *Sens. Actuat. B* 2017, 238, 1032-1042.
6. Yu, C., Wu, Y., Liu, X., Fu, F., Gong, Y., Rao, Y. J., Chen, Y., Miniature fiber-optic NH_3 gas sensor based on Pt nanoparticle-incorporated graphene oxide, *Sens. Actuat. B* 2017, 244, 107-113.
7. Dalavi, S. B., Panda, R. N., Observation of high coercive fields in chemically synthesized coated Fe-Pt nanostructures, *J. Magn. Magn. Mater.* 2017, 428, 306-312.
8. Shokrollahi, H., Khorramdin, A., Isapour, G., Magnetic resonance imaging by using nano-magnetic particles, *J. Magn. Magn. Mater.* 2014, 369, 176-183.
9. Li, Y., Fan, Y., Jian, J., Yu, L., Cheng, G., Zhou, J., Sun, M., Pt-based structured catalysts on metallic supports synthesized by electroless plating deposition for toluene complete oxidation, *Catal. Today* 2017, 281, 542-548.
10. Sondomoyee, K., Moromi, S. M. A., Siddiki, H., Kon, K., Toyao, T., Shimizu, K., Acceptorless dehydrogenation of N-heterocycles by supported Pt catalysts, *Catal. Today* 2017, 281, 507-511.
11. Antoniassi, R. M., Otubo, L., Vaz, J. M., Neto, A. O., Spinacé, E. V., Synthesis of Pt nanoparticles with preferential (100) orientation directly on the carbon support for direct ethanol fuel cell, *J. Catal.* 2016, 342, 67-74.
12. Zhang, J., Yi, X., Liu, S., Fan, H. L., Ju, W., Wang, Q. C., Ma, J., Vertically aligned carbon nanotubes/carbon fiber paper composite to support Pt nanoparticles for direct methanol fuel cell application, *J. Phys. Chem. Solids* 2017, 102, 99-104.
13. Hussain, S., Erikson, H., Kongi, N., Merisalu, M., Ritslaid, P., Sammelselg, V., Tammeveski, K., Heat-treatment effects on the ORR activity of Pt nanoparticles deposited on multi-walled carbon nanotubes using magnetron sputtering technique, *Int. J. Hydrogen Energy* in press.
14. Zhang, J., Vukmirovic, M. B., Xu, Y., Mavrikakis, M., Adzic, R. R., Controlling the catalytic activity of platinum-monolayer electrocatalysts for oxygen reduction with different substrates, *Angw. Chem. Int. Edit.* 2015, 44, 2132-2135.
15. Sánchez-Padilla, N. M., Morales-Acosta, D., Morales-Acosta, M. D., Montemayor, S. M., Rodríguez-Varela, F. J., Catalytic activity and selectivity for the ORR of rapidly synthesized M@Pt (M=Pd, Fe_3O_4, Ru) core-shell nanostructures, *Int. J. Hydrogen Energy* 2014, 39, 16706-16714.
16. Lee, Y. W., Lee, J. Y., Kwak, D. H., Hwang, E. T., Sohn, J. I., Park, K. W., Pd@Pt core-shell nanostructures for improved electrocatalytic activity in methanol oxidation reaction, *Appl. Catal. B Environ.* 2015, 179, 178-184.
17. Park, J., Vara, M., Xia, Y., A systematic study of the catalytic durability of Pd@Pt2−3L nano-sizedoctahedra toward oxygen reduction, *Catal. Today* 2017, 280, 266-273.
18. Kobayashi, Y., Ishii, Y., Yamane, H., Watanabe, K., Koda, H., Kunigami, H., Kunigami, H., Fabrication of TiO_2/Pt core-shell particles by electroless metal plating, *Colloids Surf. A* 2014, 448, 88-92.

19. Chen, C. M., Chen, C. H., Cherng, S. J., Wei, T. C., Electroless deposition of platinum on indium tin oxide glass as the counter electrode for dye-sensitized solar cells, *Mater. Chem. Phys.* 2010, 124, 173-178.
20. Dickson, D., Liu, G., Li, C., Tachiev, G., Cai, Y., Dispersion and stability of bare hematite nanoparticles: effect of dispersion tools nanoparticle concentration humic acid and ionic strength, *Sci. Total Environ.* 2012, 419, 170-177.
21. Li, Z., Li, J., Xu, R., Hong, Z., Liu, Z., Streaming potential method for characterizing the overlapping of diffuse layers of the electrical double layers between oppositely charged particles, *Colloids Surf. A* 2015, 478, 22-29.
22. Dimic-Misic, K., Hummel, M., Paltakari, J., Sixta, H., Maloney, T., Gane, P., From colloidal spheres to nanofibrils: extensional flow properties of mineral pigment and mixtures with micro and nanofibrils under progressive double layer suppression, *J. Colloid Int. Sci.* 2015, 446, 31-43.
23. McCafferty, E., Relationship between the isoelectric point (pH_{pzc}) and the potential of zero charge (E_{pzc}) for passive metals, *Electrochim. Acta* 2010, 55, 1630-1637.
24. Marzun, G., Streich, C., Jendrzej, S., Barcikowski, S., Wagener, P., Adsorption of colloidal platinum nanoparticles to supports: charge transfer and effects of electrostatic and steric interactions, *Langmuir* 2014, 30, 11928-11936.

Electrochemical biosensors based on Electroconducting Polymers

Elektrohemijski biosenzori na bazi elektroprovodnih polimera

Milica Gvozdenović

University of Belgrade, Faculty of Technology and Metallurgy, Belgrade, Serbia

Univerzitet u Beogradu, Tehnološko-metalurški fakultet Beograd

Izvod

Zahvaljujući jedinstvenim svojstvima: električnoj provodljivosti, hemijskoj postojanosti, elektrohemijskoj i optičkoj aktivnosti, korozionoj otpornosti, lakoći sinteze, i sl., elektroprovodni polimeri (EPP) ne gube na značaju u istraživanjima u različitim oblstima prktične primene. Pored pobrojanih svojstava, EPP su se pokazali kao materijali pogodni za imobilizaciju biološki receptora, enzima, antitela, nukleinskih kiselina, tkiva, delova tkiva, mikroorganizama i sl., pa ne čudi porast interesovanja za njihovu primenu u izradi elektroda elektrohemijskih biosenzora. Elektrohemijski biosenzori su analitički uređaji čiji je ubrzan razvoj motivisan potrebom za praktičnom primenom u medicini, farmaciji, industriji hrane, praćenju zagađenja životne sredine i sl. Elektrohemijski biosenzori (EHBS) u sebi kombinuju visoku selektivnosti biološkog receptora i tačnost, preciznost i reproduktibilnost elektrohemijskih tehnika detekcije, a sam princip rada se svodi na jednostavni način analize uzorka sa biološki aktivnom substancom direktnim pretvaranjem biološkog događaja u električni signal. U ovom radu biće dat pregled primene EPP u izradi elektroda elektrohemijskih biosenzora, sa posebnim osvrtom na enzimske biosenzore, kao najrasprostranjeniji tip EHBS.

Abstract

Owing to unique properties: electrical conductivity, chemical stability, electrochemical and optical activity, corrosion resistivity etc. electroconducting polymers (ECP) are still important topic of many research. Among listed properties, ECP were considered as good matrix for immobilization of biochemical receptors such are enzymes, antibodies, nucleic acids, microorganisms, tissues etc. therefore lately got the importance as electrode materials in electrochemical biosensors. Electrochemical biosensors are analytical devices whose rapid development is a result of practical importance in many fields, at the first place medicine, pharmaceutics, food industry and environmental monitoring. Electrochemical biosensors combine two important practical aspects, selectivity of a biochemical receptor and accuracy and reproducibility of electrochemical techniques. The principle of an electrochemical biosensor is based on easy means of analysis of a simple containing biochemically active compound by the direct conversion of a biochemical event to an electrochemical signal. The aim of this paper is to provide a short overview application of ECP as electrode materials for electrochemical biosensors with special focus on enzymatic biosensors as the most studied type of electrochemical biosensors.

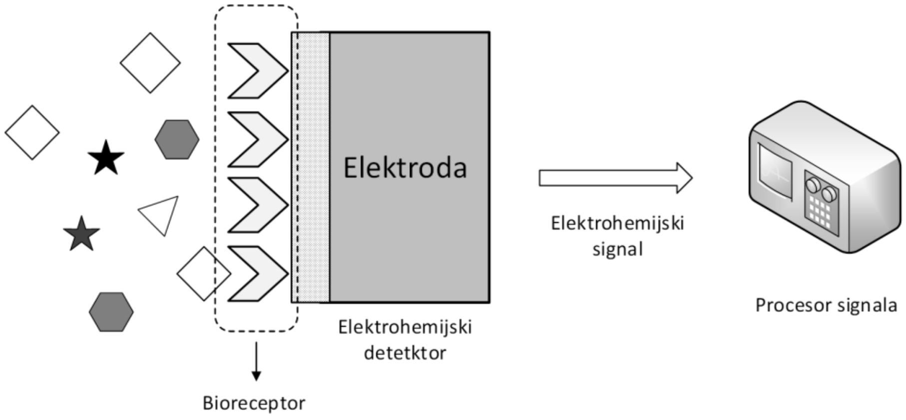
1. Uvod

Poznato je da je praktična primena organskih polimernih materijala, pored dobre postojanosti i obradivnosti, bazirana na izolatorskim svojstvima. Ovo tradicionalno shvatanje o organskim polimerima kao dobrim izolatorima izmenjeno je otkrićem provodljivosti poliacetilena 70-tih godina prošlog veka. Tada počinje razvoj u oblasti elektroporovodnih polimera, u daljem tekstu EPP, koji i danas traje. Poliacetilen, iako prvi otkriveni EPP nije našao praktičnu primenu, ali su do

sada sintetizovani mnogobrojni elektroprovodni polimeri koji se razmatraju u praktičnoj primeni u raznim oblstima od kojih elektrohemijski biosenzori zauzimaju značajno mesto[1,2].
Osnovni uslov za postojanje električne provodljivosti EPP je konjugovan sistem dvostrukuh veza u lancu polimera, ali je neophodan uslov dopovanje. Dopovanje EPP, iako kao termin preuzet iz terminologije neorganskih poluprovodnika, predstavlja uvođenje stehiometrijske količine jona a postiže se oksidacijom (veoma retko redukcijom). Kako su dopanti anjoni (retko katjoni) njihovo prisustvo, pored provodljivosti, unosi promene u strukturu polimernog lanca EPP uslovljavajući niz novih svojstava značajnih za praktičnu primenu [3]. Elektroprovodni polimeri se mogu dobiti hemijskom i elektrohemijskom sintezom, oksidativnom polimerizacijom odgovarajućeg monomera koje sledi mehanizam radikalne polimerizacije [4].
Imajući u vidu da je uslovima sinteze, bilo hemijske bilo elektrohemijske, otvorena mogućnost podešavanja niza svojstava uključujući morfologiju, provodljivost, elektrohemijsku aktivnost i sl. EPP su se pokazali kao materijali pogodni za imobilizaciju bioloških receptora i formiranje elektroda u elektrohemijskim biosenzorima, u daljem tekstu EHBS, [5,6,7]. Ono što EHBS svrstava u najznačajniji tip biosenzora je svakako činjenica da se biološki događaj detektuje elektrohemijskim tehnikama, koje pored svoje jednostavnosti u eksperimentalnom smislu, pružaju mogućnost brzog, reproduktibilnnog, tačnog, preciznog i visoko osetljivog određivanja biološki aktivne komponente uzoraka [2,8].

2. Pojam elektrohemijskog biosenzora

Senzor je analitički uređaj koji registruje neku fizičku ili hemijsku veličinu i pretvara je u odgovarajući signal. Pa tako hemijski senzor, hemijske informacije tj koncentraciju uzorka prevodi u merljiv signal. Hemijski senzor se sastoji od dva dela: receptora ili tzv. hemijskog sistema rekognicije i fizičko-hemijskog pretvarača, tzv. detektora. Receptor ili hemijski sitem rekognicije ima zadatak da obezbedi selektivni odgovor vezan za konkretnu substancu (ili više njih)[9]. Biosenzor ili biohemijski senzor je poseban tip hemijskog senzora koji poseduje biološke receptore: enzime, proteine, antitela, mikroorganizme, nukleisnke kiseline, ćelije, tkiva itd.
EHBS je poseban tip hemijskog biosenzora, koji kao pretvarač, odnosno detektor ima modifikovanu elektrodu. Na slici 1 prikazan je shematski elektrohemijski biosenzor [10].



Slika 1. Shematski prikaz elektrohemijskog biosenzora.

2.1. Klasifikacija elektrohemijskih biosenzora prema prirodi bioereceptora

Opšta klasifikacija biosenzora podrazumeva klasifikaciju prema prirodi bioreceptora. Pa tako postoje katalitički elektrohemijski biosenzori i nekatalitički odnosno senzori afiniteta (od eng. affinity biosensors). Biokatalitički EHBS kao receptore ukjučuju imobilisane biološke katalizatoreenzime, a njihova konstrukcija podrazumeva formiranje tzv. enzimskih elektroda, dok nekatalitički EHBS prncip rada baziraju na selektivnim interakcijalma između bioloških komponenata, kao što su antitela i nukleinske kiseline [11]. Najznačajni EHBS iz ove grupe su imunosenzori i senzori DNK.

2.2. Definicija elektrohemijskog biosenzora i klasifikacija prema prirodi tehnike detekcije

Međunarodna unija za čistu i primenjenu hemiju (IUPAC), konkretno njene komisije za Fizičku hemiju i Analitičku hemiju, izdale su preporuke vezane za definiciju i klasifikaciju EHBS [10]. Prema ovim preporukama, EHBS smatra se samostalni integrisani uređaj koji može da pruži specifične kvantitative analitičke informacije uz pomoć biološkog elementa rekognicije, odnosno uz pomoć biohemijskog receptora, prostorno vezanog za elektrohemijski pretvarač, tj. detektor [12]

Preporučeno je da se EHBS, osim već uobičajene klasifikacije biohemijskih senzora na katalitičke i nekatalitičke, klasifikuju na osnovu tehnike elektrohemijske detekcije na: potenciometrijske, voltametrijske, amperometrijske, konduktometrijske i impedimetrijske [7,10].

Potenciometrijski biosenzori koriste potenciometrijsku tehniku za detekciju. Potenciometrijska tehnika je tzv. tehnika nulte struje (od eng. zero-current). Informacija o analitu se dobija merenjem razlike potencijala koja zavisi od koncentacije analita, a slobodno se uspostavlja na granici faza, najčešće na membrani. Kako je potenciometrijska tehnika vrlo jednostavna, sama konstrukcija ovog tipa EHBS je jednostavna. Kao elektrode koriste se jon-selektrivne elektrode, modifikovane elektrode i jon-osetljivi tranzistori sa efektom polja (od eng. field effect transistors) [13,14].

Voltametrijski EHBS koriste različite voltametrijske tehnika za detekciju, a imaju ulazni signal u vidu kontrolisanog potencijala, koji se sistemu nameće iz spoljašnjeg izvora. Kao rezultat nametanja kontrolisanog potencijala uređaj detektuje i meri struju koja je funkcija nametnog potencijala a proporcionalna je i zavisi od vrste i količine analita. Kako se kontrolisani potencijal nameće iz spoljnog izvora, ove tehnike spadaju u dinamičke tehnike [14].

Amperometrijski biosenzori koriste amperometrijsku tehniku čiji je ulazni signal potencijal. Izlazni signal amperometrijskog biosenzora je u obliku struje. Za funkcionisanje i izučavanje amperometrijskih biosenzora od ključnog značaja je izbor potencijala kojim bi se omogućilo da se elektrohemijska reakcija odvija u uslovima difuzione kontrole [10]. U ovom slučaju struja koja se postiže u stacionarnom stanju direktno je proporcinalana količini analita. Karakteristike amperometrijski biosenzora u velikoj meri zavise od materijala radne elektrode [8,13,14].

Princip analitičkog konduktormetrijskog određivanja se zasniva promeni jonske jačine rastvora usled odigravanja reakcija katalizovanih enzimima [10]. U literaturi se ovi snezori često razmatraju kao poseban slučaj impedimetrisjkih senzora. Mada do sada konduktometrijski senzori nisu u velikoj meri izučavani ni komercijalizovani sa razvojom nanostruktuiranih materijala raste interseovanje za ovaj tip senzora [10].

Impedimetrijski biosenzori zasnivaju se na primeni tehnike spektroskopije elektrohemijske impedancije (od eng. electrochemical impedance spectroscopy). Ova tehnika podrazumeva nametanje radnoj elektrodi signala u vidu sinusoidnog potencijla male amplitude, koji kao rezultat ima izlazni signal struje takođe male amplitude. Impedancija predstavlja sinusnu prenosnu funkciju koja je definisana kap generalizovana otpornost u kojoj se kriju informacije vezane za promene otpornosti i kapacitivnosti izazvane biohemijskim reakcijama [13].

3. Sinteza i svojstva elektroprovodnih polimera

Na početku interesovanja za EPP, za njihovo dobijanje primenjivana je hemijska sinteza, ali razvojem ove oblasti i detaljnim uvidom u mehanizam polimerizacije, postaje jasno da je EPP moguće dobiti i elektrohemijskim postupkom. Nezavisno od toga da li se polimer dobija hemijskim ili elektrohemisjkim postupcima, sinteza se odvija seldeći mehanizam oksidativne radikalne polimerizacije. Ovaj mehnizam podrazumeva formiranje radikal katjona koji se dobija oksidacijom monomera, a rast polimeranog lanca se ostvaruje kupolovanjem radikala i daljom oksidacijom monomera. Pored hemijske i elektrohemijske sinteze u literaturi se mogu naći podaci vezani za tzv. alternativne postupke sinteze EPP koji su u domenu teorijskih razmatranja.

3.1. Hemijska i elektrohemijska sinteza

Hemijska sinteza EPP pogodna je za dobijanje veće količine željenog polimera, ali imajući u vidu mehanizam polimerizacije zahteva primenu oksidacionog sredstva što osim dužeg vremena za izvođenje, zahteva ispiranje zaostalog oksidacionog sredstva i rastvarača [15]. Prema načinu izvođenja, hemijska sinteza EPP se može svrstati u polimerizaciju u heterogenoj sredini, a u literaturi je najzastupljeniji tzv. taložni tip polimerizacije, mada se EPP mogu dobiti i suspenzionim, disperzionim i emulzionim postupcima [16].

Sa druge strane, elektrohemijska sinteza omogućava direktno odvijanje reakcije na anodi, čime je izbegnuto korišćenje oksidacionog sredstva. Na ovaj način film EPP dobija se direktno na anodi, što osim jednostavnosti izvođenja samog postupka, omogućava dalju karakterizaciju i procesiranje, što je od posebnog značaja za primenu u formiranju elektroda elektrohemijskih biosenzora [6].

3.2. Najvažnija svojstva elektroprovodnih polimera za primenu u elektrohemijskim biosenzorima

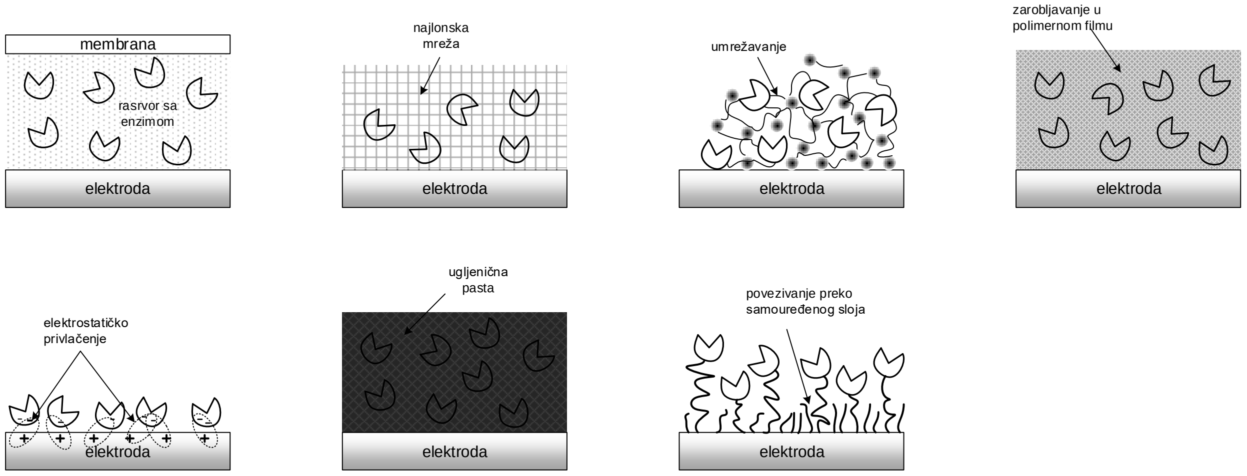
Svakako najvažnije svojstvo EPP je postojanje makroskopske električne provodljivosti. Već je bilo reči o tome da je za ostvarivanje provodljivosti EPP neophodno dopovanje. Dopanti su joni, a služe da bi se polimernom lancu oduzeli (oksidativno dopovanje) ili dodali (reduktivno dopovanje) elektroni [17] Oksidativno dopovanje (reduktivno je retko i u domenu teorije) odgovara *p* dopovanju. U fizikom smislu provodljivost EPP se objašnjava polaronskim i bipolaronskim mehanizmom. Imajući u vidu zonski model električne porovodljivosti, dopovanje vodi formiranju lokalizovaih stanja u zabranjenoj zoni (energetski rascep između valentne i provodne zone) u kojoj elektroni mogu da se nađu.

Proces dopovanja i dedopovanja je praktično reverzibilan i predstavljau osnov elektrohemijske aktivnosti EPP i važno svojstvo za praktičnu primenu. Tokom dedopovanja, tj. u elektrohemijskom smislu redukcije, anjoni dopanata „napuštaju“ polimerni lanac, dok se u procesu dopovanja, tj. oksidacije „vraćaju“ u lanac polimera. Na ovaj način omogućena je uloga EPP kao redoks medijatora i praktična primena u izradi elektroda tzv. druge generacije elektrohemijskih biosenzora [11,12].

3.3. Imobilizacija bioloških receptora u elektroprovodnim polimerima

Izborom uslova sinteze EPP moguće je ostvariti morfologiju polimera koja je pogodna za imobilizaciju bioloških receptora [20]. Kako su enzimski EHBS komercijalno dostupni imobilizacija bioloških receptora u EPP biće razmatrana na primeru imobilizacije enzima. Imobilizacijom enzima formira se tzv. enzimska elektroda, koja je ključni deo za funkcionisanje EHBS.

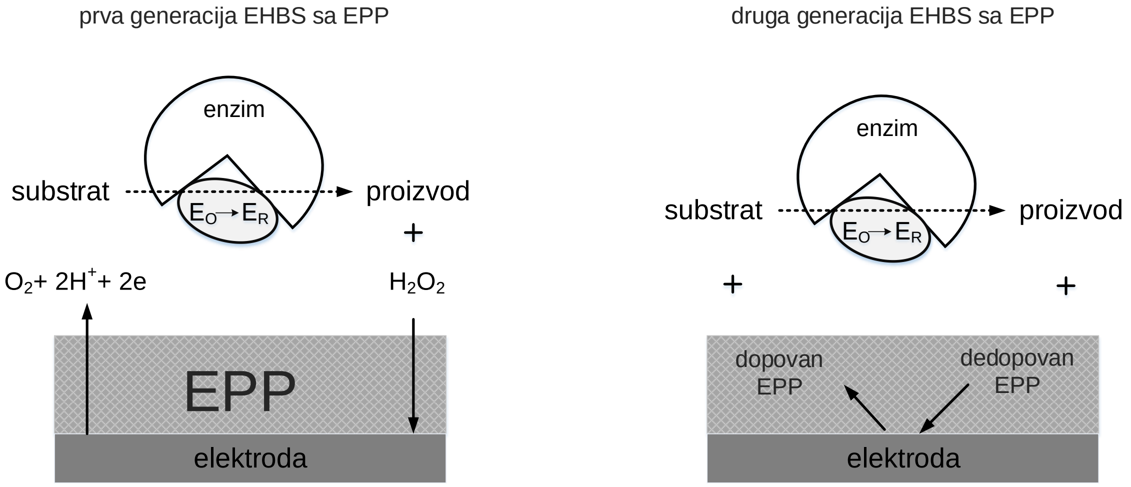
Za imobilizaciju u EPP se koriste uobičajene tehnike imoblizacije: zarobljavanje, fizička adsorpcija, umrežavanje, kovalentno vezivanje i zarobljavanje tokom polimerizacije EPP, koje su shematski date na slici 2 [10, 20]. Najjednostavni način je tzv. zarobljavanje enzima (od eng. entrapment) u rastvoru u konstaktu sa elektrodom preko membrane, ovo je ujedno i najstariji način formiranja enzimske elektrode predložen od strane Klarka (Clark) korišćen za formiranje enzimske elektrode za određivanje glukoze u krvi [22]. Kontakt enzima i elektrodne površine se uspostavlja premo najlonske mreže u kojoj je enzim hemijski vezan kovalentnim vezama. Vrlo rasporostranjen način veza preko filma koji je povezan umrežavanjem (od eng. cross linking) za elektrodnu površinu korišćenjem glutaraldehida [6]. Umreženi film u kome se nalazi enzim kvasi se elektrolitom u kome je prisutan analizirani substrat. Enzim je moguće „zarobiti“ unutar polimerizovanog filma koji se dobija polimerizacijom monomera na elektrodnoj površini, u ovom slučaju pažnju treba posvetiti uslovima polimerizacije da bi se u najvećoj meri izbegla gubitka aktivnosti enzima. Postoje primeri i imobilizacije enzima tokom elektrohemijske siteze EPP, u zom smislu nakviše je izučavana imobilizacija enzima glukozooksidaze tokom elektrohemijske polimerizacije pirola i anilina i formiranja enzimske elektrode [7].



Slika 2. Shematski prikaz najčešće koriščenih tehnika imobilizacije u EPP [10].

3.4. Funkcionisanje enzimskih elektroda na bazi elektroprovodnih polimera

Imobilizacijom odgovarajućeg enzima u elektrodnom materijalu dolazi do formiranja tzv. enzimske elektrode. Pojam enzimske elektrode uveo je prvi Klark, kada je imobilisao glukozooksidazu u kiseoničnoj elektrodi preko membrane [23]. Princip rada svodio se na merenje potrošnje kiseonika koji potiče iz enzimski katalizovane reakcije. Kasnije, daljim razvojem ove oblasti, princip određivanje glukoze svodio se na anodnu oksidaciju vodonik-peroksida koji nastaje u enzimski katalizovanoj reakciji glukoze i kiseonika. Na posrednom određivanju zasniva se rad prve generacije enzimskih EHBS. Pored prve generacije, EPP mogu imati i ulogu tzv. redoks medijatora što je osnov funkcionisanja druge generacije EHBS [1,10,22,24]. Na slici 3 prikazan je princip funkcionisanja EHBS na bazi EPP, prve i druge generacije [10].



Slika 3. Funkcionisanje EHBS na bazi EPP [10].

Ako posmatramo prvu generaciju EHBS, tokom enzimske reakcije, u prvom stupnju doći će do transformacije oksidovanog, EO, oblika enzima u redukovan oblik, E_R:

$$E_O + \text{substrat} \rightarrow E_R + \text{proizvod} \qquad (1)$$

redukovani oblik enzima, $E_{R,}$ će se regenerisati u reakciji sa kiseonikom u skladu sa:

$$E_R + O_2 \rightarrow E_O + H_2O_2 \qquad (2)$$

Izlazni signal EHBS biti rezultat oksidacije nastalog vodonik-peroskida iz reakcije (2) na anodi u skladu sa:

$$H_2O_2 \rightarrow O_2 + 2H^+ + 2e \qquad (3)$$

Kada se razmatra funkcionisanje druge generacije EHBS, redoks medijator, u ovom slučaju EPP, preuzima ulogu elektrohemijski aktivne vrste koja podleže reakciji oksidacije na elektrodi. Kada enzim reaguje sa substratom dajući proizvod, dolazi do njegove trenformacije u redukovani oblik. Redukovani oblik enzima će reagvati sa oksidovanim, tj. dopovanim oblikom EPP, i regenerisaće se, dok će EPP preći u svoj redukovani oblik, u skladu sa:

$$E_R + \text{dopovani EPP} \rightarrow E_O + \text{dedopovani EPP} \qquad (4)$$

U sledećoj reakciji, redukovani EPP se oksidovati, tj dopovati na elektrodi i formirati izlazni signal, proporcionaln količini analiziranog substrata [10].

4. Zaključak

Elektrohemijski biosenzori su uređaji kojima se stiču analitičke informacije pomoću biohemijskog receptora koji je u prostornoj vezi sa elektrohemijskim pretvaračem. Na ovaj način elekrohemijski biosenzor kombinuje selektivnost biološkog receptora sa jednostavnošću, tačnošću, preciznošću elektrohemijskih tehnika. Sobzirom na svojstva elektroprovodnih polimera, koji osim provodljivosti, poseduju praktično reverzibilnu elektrohemijsku aktivnost ostvarenu dopovanjem/dedopovanjem i morfologiju pogodnu za uspešnu imoblilizaciju bioloških receptora, ne čudi povećano interseovanje za njihovu praktičnu primenu u izradi modifikovanih elektroda elektrohemijskih biosenzora. U tom smislu najviše pažnje u literaturi posvećeno je izradi enzimskih elektroda imoblizacijom enzima u elektropovodnim polimerima.

5. Zahvalnica

Ovaj rad ostvaren je u okviru projekata Ministarstva prosvete nauke i tehnološkog razvoja republike Srbije, pod brojem 172046.

6. Literatura

1. J. Lai *et al.*, “Polyaniline-based glucose biosensor: A review,” *J. Electroanal. Chem.*, vol. 782, pp. 138–153, 2016.
2. F. W. Scheller, U. Wollenberger, a Warsinke, and F. Lisdat, “Research and development in biosensors.,” *Curr. Opin. Biotechnol.*, vol. 12, no. 1, pp. 35–40, Feb. 2001.
3. R. J. R. Skotheim A., Ed., *Conducting Polymers-Theory, Sinthesis, Properties and Characterization*. New York: CRC-Press, Teyor& Francis Group, 2007.

4. S. Jovanović, G. Nestorović, and K. Jeremić, “Elektroporovodni polimerni materijali,” *Hem. Ind.*, vol. 57, no. 11, pp. 511–525, 2003.
5. D. Bezbradica, B. Jugović, M. Gvozdenović, S. Jakovetić, and Z. Knežević-Jugović, “Electrochemically synthesized polyaniline as support for lipase immobilization,” *J. Mol. Catal. B Enzym.*, vol. 70, no. 1–2, pp. 55–60, Jun. 2011.
6. M. M. Gvozdenović, B. Z. Jugović, D. I. Bezbradica, M. G. Antov, Z. D. Knežević-Jugović, and B. N. Grgur, “Electrochemical determination of glucose using polyaniline electrode modified by glucose oxidase,” *Food Chem.*, vol. 124, no. 1, pp. 396–400, Jan. 2011.
7. W. Putzbach and N. J. Ronkainen, “Immobilization techniques in the fabrication of nanomaterial-based electrochemical biosensors: a review,” *Sensors (Basel).*, vol. 13, no. 4, pp. 4811–4840, 2013.
8. R. Paper, “Electrochemical Biosensors - Sensor Principles and Architectures,” no. January, pp. 1400–1458, 2008.
9. N. J. Ronkainen, H. B. Halsall, and W. R. Heineman, “Electrochemical biosensors,” *Chem.Soc.Rev.*, vol. 39, no. 5, pp. 1747–1763, 2010.
10. M. Gvozdenović, *Elektrohemijski biosenzori, materijal za pripremu ispita*. .
11. B. Byrne, E. Stack, N. Gilmartin, and R. O. Kennedy, “Antibody-Based Sensors: Principles, Problems and Potential for Detection of Pathogens and Associated Toxins,” no. Table 1, pp. 4407–4445, 2009.
12. D. R. The, “ELECTROCHEMICAL BIOSENSORS : RECOMMENDED Electrochemical biosensors : Recommended de ® nitions and classi ® cation (Technical Report),” *IUPAC*, vol. 71, no. 12, pp. 2333–2348, 1999.
13. M. Pohanka and C. Republic, “Electrochemical biosensors – principles and applications,” pp. 57–64, 2008.
14. T. Emir, *Uvod u hemijske senzore i biosenzore*. Sarajevo: Prirodno matematički fakultet, Univerzitet u Sarajevu, 2012.
15. S. Jovanović and J. Đonlagić, *Hemija makromolekula*. Beograd: Tehnološko-metalurški fakultet Beograd, 2004.
16. G. Odian, *Principles of Polymerization*, 4th ed. New Jersy: John Wiley & Sons, 2004.
17. M. Gvozdenović, *Elektroporovodni polimeri*. Beograd: Akademska misao, 2013.
18. H. Zhong, R. Yuan, Y. Chai, W. Li, X. Zhong, and Y. Zhang, “In situ chemo-synthesized multi-wall carbon nanotube-conductive polyaniline nanocomposites: Characterization and application for a glucose amperometric biosensor,” *Talanta*, vol. 85, no. 1, pp. 104–111, 2011.
19. C. Dhand, G. Sumana, M. Datta, and B. D. Malhotra, “Electrophoretically deposited nano-structured polyaniline film for glucose sensing,” *Thin Solid Films*, vol. 519, no. 3, pp. 1145–1150, 2010.
20. M. Gerard, M. Gerard, A. Chaubey, and B. D. Malhotra, “Application of conducting polymers to biosensors . Biosens Bioelectron Application of conducting polymers to biosensors,” *J. Biosens. Bioelectron.*, vol. 17, no. 5, pp. 345–359, 2002.
21. J. Rusling, B. Wang, and S. Yun, “Electrochemistry of Redox Enzimes,” in *Bioelectrochemistry, Fundamentals, Experimental Techniques and Applications*, P. N. Bartlett, Ed. Chichester: John Wiley & Sons Ltd., 2008.
22. J. Wang, “Electrochemical Glucose Biosensors,” pp. 814–825, 2008.
23. J. Wang, “Glucose Biosensors : 40 Years of Advances and Challenges,” pp. 983–988, 2001.
24. J. D. Newman and S. J. Setford, “Enzymatic Biosensors,” vol. 32, 2006.

Microstructural characterization and mechanical properties of ceramic

Mikrostrukturna karakterizacija i mehanička svojstva keramičkih materijala

Bojan M. Jokić

Faculty of Applied Arts, University of Arts in Belgrade

Faculty of Technology and Metallurgy, University of Belgrade

Fakultet primenjenih umetnosti, Univerzitet umetnosti u Beogradu

Tehnološko-metalurški fakultet, Univerzitet u Beogradu

Izvod

Razvoj nauke o keramičkom materijalima u prethodnih nekoliko decenija omogućio je primenu savremenih keramičkih materijala u različitim oblastima poput avio industije, automobilske i telekomunikacione industrije, industrije obnovljivih izvora energije, biomedicine i dr. Keramičke materijale odlikuju izuzetna svojstva kao što su: velika tvrdoća, krutost, modul elestičnosti, otpornost na habanje i koroziju, hemijska inertnost na povišenim temperaturama. Uprkos pomenutim dobrim svojstvima u poređenju sa metalnim i polimernim materijalima keramičke materijale karakteriše velika krtost što ograničava njenu primenu kao strukturnog i nestrukturnog materijala. U poslednje vreme postignut je značajan napredak na razvoju keramičkih materijala koji se odlikuju velikom žilavošću kao i bolja kontrola svih mikrostrukturnih parametara i faznog sastava koji utiču na druga fizička svojstva materijala. U ovom radu biće prikazan uticaj mikrostrukture na mehanička svojstva kermičkih materijala. Takođe, u radu će biti razmotrene prednosti i nedostaci metoda koje se koriste za određivanje mehaničkih parametara.

Abstract

Advancement of ceramic science in the last few decades has enabled the use of ceramic materials to develop from more traditional application to advance material indispensible in aerospace, automotive, telecommunication, renewable energy industry, biomedical application etc. Ceramics have many useful properties such as high hardness, stiffness, elastic modulus, wear and corrosion resistance associated with chemical inertness at elevated temperatures. Despite many attractive properties compared to metallic and polymeric materials, poor fracture toughness of ceramic materials is the major limitations for structural and nonstructural applications. Thus, much research has been done to minimize this limitation by improving ceramic brittleness with appreciable success provided better control over aspects of microstructure and phase composition that govern other physical properties. In this paper the influence of microstructure on the mechanical behavior of ceramics will be presented. Also, advantage and short-coming of methods for calculation of mechanical parameters will be discussed.

Uvod

Razumevanje strukture i hemijskog sastava materijala je od izuzetne važnosti za potencijalnu primenu materijala u industriji. Ispitivanje fizičkih svojstava materijala, pored određivanja strukturnih parametara i hemijskog sastava je od posebnog značaja za razvoj materijala za specijalne namene. Sve brži razvoj savremenih instrumentalnih metoda omogućava dobijanje sa velikom pouzdanošću informacija o svojstvima materijala na nano i makro nivou.

Keramički materijali nalaze sve veću primenu u svakodnevnom životu od upotrebne, tradicionalne keramike do savremenih keramičkih materijala koji se koriste u automobilskoj i avio industriji, telekomunikacionoj industriji, industrij obnovljivih izvora energije, medicini i dr. Danas bi bilo nezamislivo funkcionisanje bilo kog savremenog uređaja bez karamičkih materijala.

Razvoj savremenih keramičkih materijala poslednjih decenija je sve više usmeren na dobijanje biokeramičkih materijala koji se koriste u medicini, pre svega za izradu ortopedskih i stomatoloških implanata. Ovi biokeramički materijali se u zavisnosti od svojstava i primene mogu podeliti u tri velike grupe: bioinertna keramika (keramika na bazi aluminijum- i cirkonijum-oksida), bioaktivna stakla i staklo-keramika, i bioaktivna keramika koja po svojstvima i sastavu odgovara prirodnom koštanom tkivu a bazira se na kalcijum-fosfatu kao osnovnoj neorganskog komponenti koštanog tkiva. [**1**] [**2**]

Iako je danas u svetu postignut značajan napredak na razvoju sintetičkih biokeramičkih materijala koji po svojim fizičkim i hemijskim svojstvima u kombinaciji sa odgovarajućim organskim materijalima skoro u potpunosti odgovaraju tkivu u koje se aplikuju, često se u praksi javljaju neželjne fiziološke reakcije. Tako se pored biokompatibilnosti od biokeramičkih materijala, koji se koriste kao implanti, zahtevaju i odgovarajuća mehanička svojstva. [**3**] [**2**]

Keramika predstavlja heterogen materijal, koji karakteriše određena mikrostruktura. Mikrostruktura kristalnih materijala se definiše tipom, strukturom, brojem, oblikom i topološkim uređenjem faza. Keramički materijali obično imaju polikristalnu strukturu koju karakterišu tačkasti defekti, dislokacije, način slaganja, granice zrna i međufazne granice, raspodela, veličina i orijentacija zrna, prisustvo, raspodela i orijentacija pora, specifična površina.

Efektivna svojstva (efektivni emodul elestičnosti, efektivna termička provodljivost, električna provodljivost, dielektrična konstanta, magnetska propustljivost i koeficijent termičkog širenja) predstavljaju makroskopska svojstva heterogenih materijala kao što su polikristalni keramički materijali, kompoziti i porozna keramika i najčešće su zavisna od mikrostrukturnih karakteristika.

Određivanje navedenih mikrostrukturnih parametara je od izuzetnog značaja za predviđanje mehaničkih karakteristika keramičkih materijala koji opredeljuju njegovu dalju primenu.

U nastavku će biti prikazane neke od metoda koje se najčešće koriste za određivanje mehaničkih svojstava keramičkih materijala sa posebnim osvrtom na prednosti i nedostatke pojedinih metoda, kao i greškama koje se najčešće javljaju prilikom tumaćenja rezultata, pre svega tvrdoće i žilavosti.

Mehaničke karakteristike biokeramičkih materijala

Biokeramika na bazi hidroksiapatita (HAp) predstavlja najzastupljeniju keramiku koja se koristi u medicini i stomatologiji za zamenu oštećenih delova kosti uzrokovanim različitim patološkim stanjima ili mehaničkim oštećenjima. **[**2**]** **[**4**]** Nažalost, dobro je poznato da je mehanička pouzdanost biokeramike na bazi HAp veoma slaba, naročito u vlažnom okruženju kakvo vlada na mestima na kojima se aplikuje biokeramika. **[**1**]**

Izmerena žilavost (K_{Ic}) HAp keramike ne prelazi vrednost od 1 MPam$^{-1/2}$ što je daleko manje od vrednosti žilavosti ljudske kosti koja se kreće od 2-12 MPam$^{-1/2}$ **[**2**]** **[**3**]** **[**5**]**

U literature navedene vrednosti Weibull modula za gustu HAp keramiku se kreću u opsegu od 5 do 18, što ukazuje na izuzetno veliku krtost kojom se odlikuje HAp keramika. **[**6**]** **[**7**]**

Značajan nedostatak biokeramike na bazi HAp predstavlja smanjenje vrednosti koeficijenta sporog napredovanja pukotine koji se kreće od 26-80 u suvim uslovima i 12-49 u vlažniim uslovima, što ukazuje na težnju napredovanja već nastalih pukotina u vlažnom okruženju i nakon prestanka delovanja sile. **[**6**]**

Posebno treba istači značaj kontrole Ca/P odnosa čije smanjenje može značajno uticati na pojavu naprezanja na granici zrna kod gusto sinterovane keramike a koje se javlja kao posledica visokotemperaturnih faznih transformacija nestehiometrijskog HAp. **[**2**]** **[**8**]** **[**9**]** **[**10**]**

Sve napred navedeno ukazuje da HAp keramika može biti korišćena za izradu implanta samo u uslovima kontrolisanog opterećenja, u obliku praha za ispune, poroznih implanata koji nisu izloženi velikom naprezanju, gde biokeramički material ima ulogu promotora formiranja koštanog tkiva. [3]
Navedene loše mehaničke karakteristike HAp keramike mogu biti donekle prevaziđene korišćenjem HAp u obliku tankih prevlaka na metalnim supstratima gde Hap kao biaktivni materijal ima ulogu da obezbedi bolju vezi između inertnog implanta i okolnog tkiva. [11]
Jedan od načina za poboljšanje pouzdanosti biokeramičkih materijala predstavlja pre svega poboljšanje mehaničkih svojstava keramičkih materijala povećanjem vrednosti tvrdoće i žilavosti.

Poboljšanje mehaničkih svojstava keramičkih materijala

Pored brojnih, već pomenutih svojstava, koja daju značajnu prednost keramičkim materijalima u odnosu na metale i metalne legure u specifičnim uslovima u kojima se od materijala zahteva da poseduju veliku tvrdoću, otpornost na habanje, veliki modul elestičnosti, stabilnost na visokim temperaturama, krtost, odnosno nedostatak duktilnosti na nižim temperaturama, predstavlja jedan og glavnih nedostataka keramičkih materijala. Poslednjih decenija učinjeni su značajni pomaci kako bi se povećala žilavost keramičkih materijala. Veoma je viliki broj faktora koji utiču na svojstva keramičkih materijala. Uopšteno, svi faktori mogu biti svrstani u jednu od dve grupe: unutrašnji i spoljašnji faktori. U Tabela 1 su navedeni neki od faktora koji imaju značajan uticaj ponašanje keramičkih materijala:

Tabela 1. Faktori koji utiču na svojstva keramičkih materijala

Unutrašnji faktori	Spoljašnji faktori
- veličina zrna, - pore, - mikropukotine	- sastav, - veličina uzorka, - oblik uzorka itd.

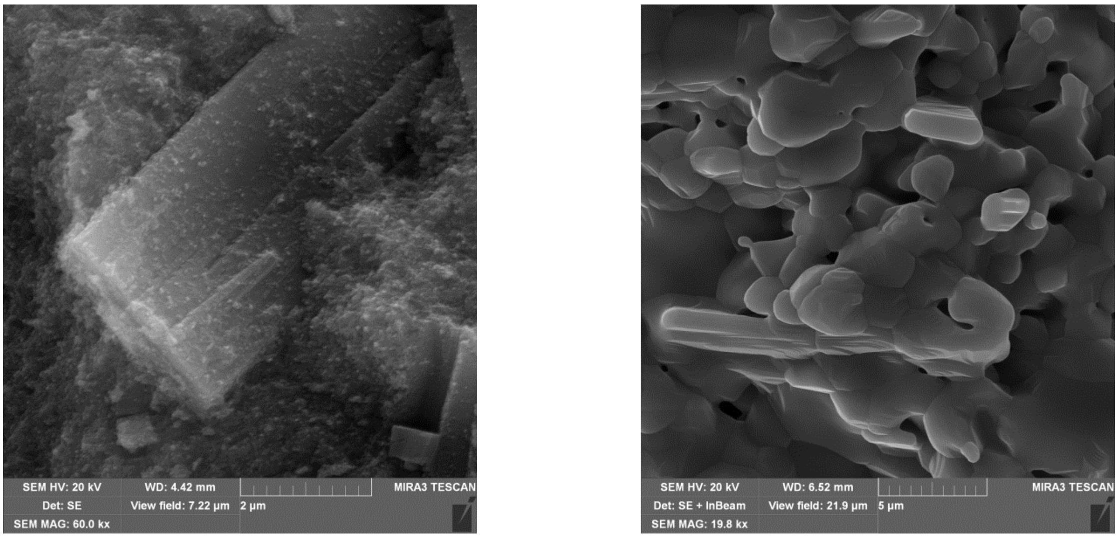
Jedan od osnovnih načina za poboljšanje pouzdansoti keramičkih materijala tokom procesa eksploatacije predstavlja povećanje žilavosti. Postoji više načina ili mehanizama ojačavanja koji mogu doprineti povećanju žilavosti keramičkih materijala. Ukoliko se na vratu pukotine odvija mehanizam premošćavanja pukotine, izvlačenja, transformacionog ojačavanja ili nastanak mikropukotina dolazi do povećanja žilavosti materijala. Sve ovo ima za posledicu povećanje otpornosti keramičkog materijala na pojavu i širenje pukotina. Poslednjih nekoliko decenija je učinjen veliki pomak na razvoju keramičkih kompozita povećane žilavosti korišćenjem jednog ili više mehanizama ojačavanja. Stvaranje mikropukotina koje nastaju u slučaju izloženosti većem spoljašnjem naprezanju se postiže ubacivanjem vlakana ili čestica u keramičku matricu, a deüava se kao posledica razlike u koeficijentima termičkog širenja ubacenih keramičkih vlakana i keramičke matrice. [12]
Prisustvo mikropukotina može uzrokovati skretanje i grananje pukotine što doprinosi smanjenju intenziteta naprezanja na vrhu pukotine jer ravan pukotine nije više upravna na pravac istezanja. Teorijsko proučavanje i eksperimentalna istraživanja su potvrdila da čestice štapičastog oblika najviše utiču na povećanje žilavosti.
Pomeniti mehanizamo povećanja žilavosti značajno zavisi od mikrostrukturnih parametara kao što su: zapreminski udeo čestica, oblik, veličina, orijentacija i raspodela čestica u keramičkoj matrici.
Povećanje žilavosti usled izvlačenja vlakana iz matrice je posledica dodatnog rada koji je potrebno utrošiti na izvlačenje vlakana koji ostvaruju određenu vezu sa matricom. Kritična vrednost dužine vlakana data je jed. (1). [13] [14]

$$l_{\mathrm{c}} = \frac{\sigma_{\mathrm{f}} d_{\mathrm{f}}}{2\tau_{\mathrm{i}}} \tag{1}$$

gde je: l_c – dužina vlakna, σ_f - napon pucanja vlakna, d_f – prečnik vlakna, τ_i – napon smicanja na međuspoju čestica-matrica.

Iz jednačine (1) se vidi da slabija međuveza vlakna i matrice povećava vrednost kritične dužine vlakna, što omogučava da veći broj vlakana doprinosi povećanju žilavosti. Međutim, neophodno je da i jačina međuveze bude dovoljno velika kako bi se povećala energija koja je potrebna za izvlačenje vlakana.

Ostvarena veza može biti posledica hemijskih reakcija ili mehaničke frikcije, ili kombinovana. Tako, npr. ojačavanje biokeramičkih materijala se po pravilu vrši dodavanjem biokeramičkih vlakana u biokoeramičku matricu. Ovo se radi pre svega jer je neophodno da i ojačavajuća vlakna budu biokompatibila i biokativno što ne bi bilo moguće u slučaju kada se kao ojačavajuća vlakna koriste metalna vlakna. Iako biokeramička vlakna pokazuju slična mehanička svojstva kao i matrica, ovde se veza između vlakana i matrice ostvaruje formiranjem hemijskih veza (Slika 1.)



a) *b)*

Slika 1. SEM ispresovanog a) i sinterovang b) uzorka HAp kompozita na kome se vide vlakna HAp u HAp matrici

Određivanje tvrdoće i žilavosti keramičkih materijala

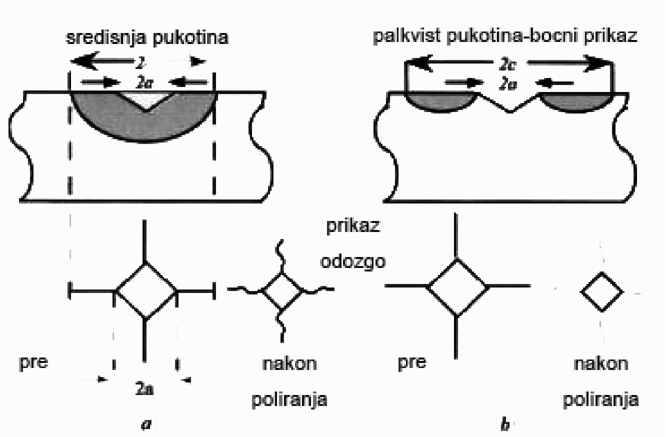
Tvrdoća i žilavost keramičkih materijala predstavljaju najvažnije parametre koji u najvećoj meri određuju dalju primenu keramičkih materijala, stoga, od izuzetne važnosti predstavlja izbor odgovarajuće metode za određivanje pomenutih parametara kao i pravilna priprema uzoraka i tumaćenje dobijenih rezultata. Za određivanje žilavosti krtih materijala razvijene su brojne metode kao što su: Ševronov zarez (Chevron notch bar-CNB), **[**15**]**, jednostrukog V-zareza (single-edge V-notched beam - SEVNB) **[**16**]** , jednostrukok prenapuklog reza (single-edge pre-cracked beam - SEPB) **[**17**]** i dr.

Neke od navedenih metoda imaju ograničenu primenu jer podrazumevaju zahtevnu pripremu uzoraka kao i velike troškove vezane za samo merenje. U cilju rešavanja pomenutih nedostataka poslednjih nekoliko decenija se radi na unapređenju metoda koje se zasnivaju na merenju i tumačenju otiska koji identer ostavlja u materijalu. Korišćenjem različitih identera i primenom različite sile utiskivanja i vremena zadržavanja identera moguće je proizvesti seriju pukotina kontrolisane veličine i oblika. Analizom morfologije nastalih pukotina moguće je odrediti žilavost materijala. Prednosti pomenute metode se ogledaju u relativno jednostavnoj pripremi uzoraka za anlizu, brzom merenju i relativno jeftinoj aparaturi.

Za merenje žilavosti materijala obično se koriste tri modela koje se zasnivaju na Vikersovoj metodi. Metod se zasniva na merenju dijagonala otiska koji ostavlja identer uz poznavanje nekoliko parametara kao što su modul elestičnosti i Poisonov odnos. **[**18**]**

Prva dva modela se zasnivaju na merenju mikronaprslina koje nastaju nakon utiskivanja identera a razlikuju se po tipu mikropukotina na koje se primenjuju. Prvi model ili Palmkvistov model se bazira na pukotinama koje imaju polueliptičnu substrukturu, dok se drugi središnji model zasniva na pukotinama koje imaju substrukturu polovine novčića (half-penny ili median cracks) **(**Slika 2**)**. Treći model se zasniva na tehnici fitovanja krive.

Na osnovu procene naprsline i vrednosti odnosa *c/a* može se odrediti o kom tipu modela se radi. Vrednost odnosa *c/a* koja je manja od 2 ukazuje da se radi o Palmkvistovom modelu iako postoje različite diskusije u pogledu vrednosti odnosa koji određuje o kom modelu se radi.



*Slika 2. Shematski prikaz dva modela nastanka mikropukotina: a) središnji i b) Pamkvistov[**19**]*

Postoji neka opšta pretpostavka na osnovu koje je moguće svrstati nastale pukotine u prvi ili drugi model. Tako se pukotine nastale ispitivanjem relativno žilavih materijala koje se izvode pri relativno umerenim opterećenjem svrtstavaju u Palmkvistov model, a pukotine koje se formiraju na materijalu male žilavosti pri relativno velikim opterećenjima u tip substruktuke koja ima izgled polu-novčića.

Tokom poslednih nekoliko decenija predložen je veliki broj jednačina za izračunavanje žilavosti materijala na osnovu Vikersovog otiska u obliku četvorostrane dijamatske piramide, a sve jednačine su razvijene poluempirijski tako što su koeficijenti u jednačinama dobijani metodom probe i greške (Tabela 2).

Tabela 2. Jednačine za izračunavanje žilavosti

Broj	Jednačina	Ref.
	Palmkvist	
1	$K_c = 0{,}0515\dfrac{P}{c^{3/2}}$	**[20]**
2	$K_c = 0{,}079\dfrac{P}{a^{3/2}}log\left(4.5\dfrac{a}{c}\right)$	**[21]**
3	$K_c = 0{,}035\left(\dfrac{l}{a}\right)^{-1/2}\left(\dfrac{H_v}{E\Phi}\right)^{-2/5}\left(\dfrac{H_v a^{1/2}}{\Phi}\right)$	**[22]**

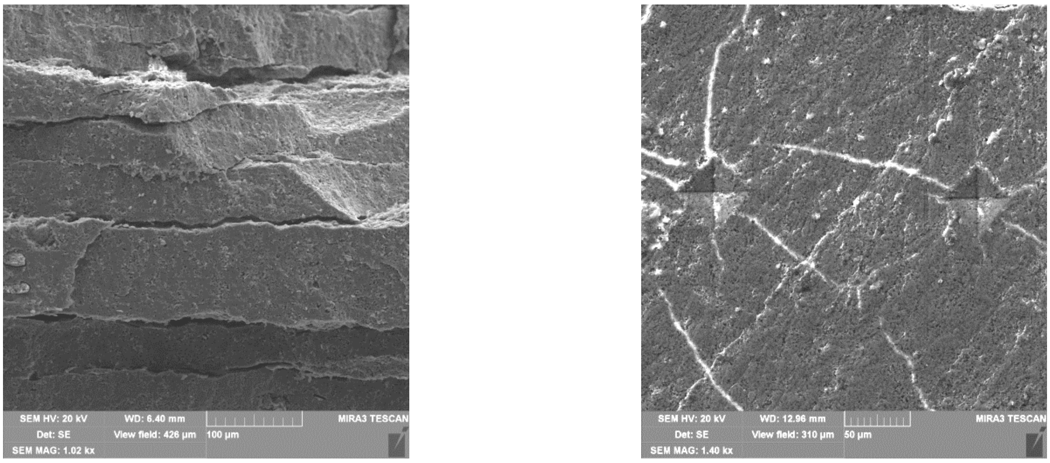
4	$K_c = 0{,}048\left(\frac{l}{a}\right)^{-1/2}\left(\frac{H_v}{E\Phi}\right)^{-2/5}\left(\frac{H_v a^{1/2}}{\Phi}\right)$	[**23**]
	Median	
5	$K_c = 0{,}0726\frac{P}{c^{3/2}}$	[**20**]
6	$K_c = 0{,}0752\frac{P}{c^{3/2}}$	[**24**]
7	$K_c = 0{,}129\left(\frac{c}{a}\right)^{-3/2}\left(\frac{H_v}{E\Phi}\right)^{-2/5}\left(\frac{H_v a^{1/2}}{\Phi}\right)$	[**22**]
8	$K_c = 0{,}014\left(\frac{E}{H_v}\right)^{1/2}\left(\frac{P}{c^{3/2}}\right)$	[**25**]
9	$K_c = 0{,}016\left(\frac{E}{H_v}\right)^{1/2}\left(\frac{P}{c^{3/2}}\right)$	[**26**]
10	$K_c = 0{,}0725\left(\frac{P}{c^{3/2}}\right)$	[**27**]
	Površina	
11	$K_c = 0{,}00366\left(\frac{E}{H_v}\right)^{1/2} t^{3/2}\left(\frac{P}{A^{3/2}}\right)$	[**28**]

U Tabeli 1. K_C je žilavost materijala (MPa·m$^{1/2}$); P je sila identacije (N); c je dužina poukotine (mm); E je Jungov modul (GPa); HV je Vikersova tvrdoća (GPa); Φ je konstanta, $\Phi \cong 3$; a je poludužina otiska identera (mm); t i A predstavljaju srednju debljinu svih mikropukotina formiranih oko otiska identera na merenom uzorku (mm) i ukupnu površinu mikropukorina oko zone identera (mm^2)

Poredeći jednačine date u Tabeli 1. za određivanje žilavosti materijala korišćenjem Vikersovog testa uočava se da su vrednosti žilavosti u svim jednačinama manje ili više zavisne od strukture materijala, krtosti, Jungovog modula, Vikersove tvrdoće kao i drugih mehaničkih svojstava pri čemu u jednačini 11, koju su predložili Moradkhani i saradnici, umesto dužine figuriše površina mikropukotine. Na taj način se izbegava veliki broj merenja koji je neophodan za preciznije izračunavanje žilavosti a koji zahteva merenje samo onih mikropukotina koje imaju pravilan oblik. Nedostatak predloženog postupka se ogleda u potrebi korišćenja softvera za određivanje srednje vrednosti širine mikropukotine na osnovu koje se izračunava srednja vrednost površine mikropukotine.

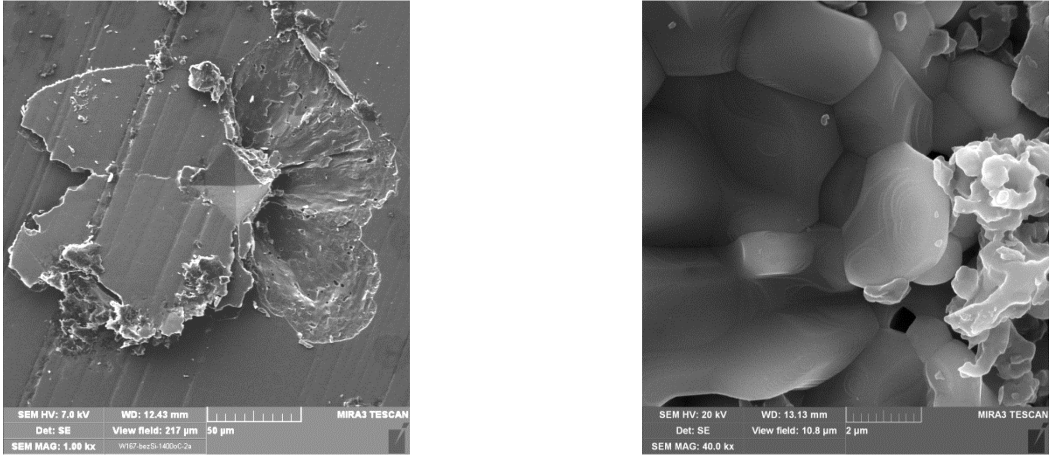
Pored pomenutih teškoća prilikom određivanja dužine i površine mikropukotina problemi koji se javljaju prilikom identacije mogu biti uzrokovani i drugim faktorima, kao što su: prisustvo nečistoća, odljuspavanje, mikropukotine, delaminacija, neuniformnost materijala po zapremini, nedovoljno polirana površina, neadekvatan izbor sile, oštečenje identera i dr.

Napred pomenuti faktori koji značajno utiču na formiranje mikropukotina se teško uočavaju jer karakterizacija pod optičkim mikroskopom i skenirajućim elektronskim mikroskopom ne pruža informaciju o strukturi i nepravilnostima po zapremini uzorka.



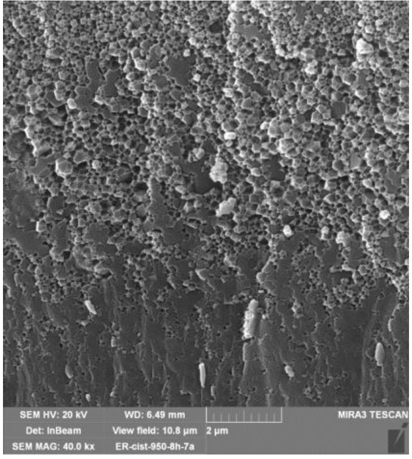
Delaminacija uzorka-poprečni presek

Mikronaprsline koje su posledica naprezanja u keramičkom materijalu tokm procesiranja



Odljuspavanje nastalo kao posledica delovanja velike sile

Prisustvo nečistoća u strukturi koje nije vidljivo na poliranom uzorku



Neuniformost gustine uzorka uzrokovana ivičnim efektom tokom presovanja praha

Slika 3. Prikaz mikrostrukturnih nepravilnosti koje se javljaju u sinterovanim uzorcima a koje mogu znatno uticati na određivanje tvrdoće i žilavosti Vikersovom metodom

Neki od napred navedenih faktora prikazani su na slici 3. Na slici se jasno uočavaju neki od mikrostrukturnih defekata koji najčešće nisu vidljivi pod optičkim mikroskopom koji je spregnut sa instrumentom za određivanje tvrdoće i žilavosti. Greške koje mogu značajno uticati na srednju vrenost izmerenih vrednosti su vezane za mikropukotine i lamelarno razdvajanje kod nanostrukturnih materijala koje moze nastati tokom procesiranja keramičkih materijala ali i prilokom poliranja uzoraka za ispitivanje. Treba imati na umu da se većina ispitivanja keramičkih materijala odnosi na uzorke koji su dobijeni u laboratorijskim uslovima i da ispitivanje mehaničkih svojstava uzoraka za industrijsku primenu pored određivanja tvrdoće i žilavosti podrazumeva i određivanje zatezne čvrstoće, čvrstoće na savijanje, otpornost na zamor i dr., što opet zahteva pripremu znatno većih uzoraka, kako je definisano važećim standardima.

Zaključak i diskusija

Proteklih nekoliko decenija učinjen je značajan napredak na razvoju postupaka dobijanja keramičkih materijala poboljšanih svojstava boljom kontrolom gustine, veličine, oblika i raspodele zrna, faznog sastava, vrstom, količinom i raspodela defekata. Cilj je bio da se razvije keramika koja se odlikuje većom otpornošću na lom, tj. žilavošću, bez veče uticaja na vrednost tvrdoće. Takođe, pored poboljšanja mehaničkih svojstava kao što su tvrdoća i žilavost, poslednjih godina se sve veća pažnja posvećuje pouzdanosti keramičkih materijala, što podrazumeva praćenje promene svojstava i smanjenje procesa degradacije keramičkih materijala tokom procesa eksploatacije.

U radu je prikazana korelacija između tvrdoće i žilavosti keramike sa osnovnim mikrostrukturnim parametrima. Diskusija je ograničena na osnovna mehanička svojstva i metode koje se koriste za izračunavanje mahaničkih svojstava biokeramičkih materijala u cilju otklanjanja nedostataka tokom procesiranja i grešaka koje se mogu javiti tokom izračunavanja.

Iako je razumevanje mehaničkih i fizičkih svojstava keramičkih materijala od izuzetnog značaja za eksploataciju u različitim okruženjima za sveobuhvatno razumevanje ponašanja keramičkih materijala neophodna je detaljna analiza sastava materijala po površini i zapremini u zavisnosti od vrste i namene keramike.

Svako dizajniranje poostoje'ih i novih keramičkih materijala zahteva optimizaciju mikrostrukture matrice kontrolom veličine i oblika zrna u cilju postizanja veće otpornosti na lom. Uključivanje nove faze istog ili različitog sastava u obliku iglica ili vlakana, u zavisnosti od namene, može značajno povečati žilavost. Kombinovanje različitim procesa ojačavanja, kao što je npr. ojačavanje premošćavanjem i transformaciom stvara mogućnost za razvoj veoma žilavih keramičkih kompozita koje dostižu vrednosti žilavosti od 20 MPa $m^{1/2}$. Da bi se proces dobijanja keramičkih materijala mogao bolje pratiti neophodno je jednostavno, brzo, pouzdano i jeftino ispitivanje osnovnih mehaničkih svojstva koje bi bilo uporedivo sa istim merenjim obavljenim u drugim laboratorijama. Istaknute predosti pojedinih metoda kao i greške koje se mogu javiti tokom merenja a koje su prikazane u radu su od presudnog značaja za tačnost dobijenih rezultat, od čega zavisi i dalji pravci istraživanja.

Literatura

1. S. Dorozhkin, M. Epple, "Biomineralization of calcium phosphates.," Agnew Chem Int Ed, vol. 41, pp. 3130-46, 2002.
2. L.L. Hench, J. Wilson, "An Introduction to Bioceramics," World Scientific Publishing, 1998.
3. L.L. Hench, J.M. Polak , "Third generation biomaterials. Science 2002;295(5557):1014.," Science, vol. 295, no. 5557, p. 1014, 2002.
4. E. I. Dorozhkin, M. Epple, S.V. Dorozhkin, "Biomimetic crystallization of calcium phosphates under constant conditions from the revised SBF," Bioceramics 15, Key Eng Mater, vol. 240-242, pp. 85-8, 2003.
5. A. Ravaglioli, A. Krajewsk, Bioceramics: Materials Properties Applicationsi.: Springer Science & Business Media, 2012.

6. Van Dijk, H. J. A., N. Hattu, K. Prijs, "Preparation, microstructure and mechanical properties of dense polycrystalline hydroxy apatite," Journal of materials science, vol. 16, no. 6, pp. 1592-1598., 1981.
7. A.J. Ruys, M. Wei, C.C. Sorrell, M.R. Dickson, A. Brandwood, B.K. Milthorpe, "Sintering effects on the strength of hydroxyapatite," Biomaterials, vol. 16, no. 5, pp. 409-415, 1995.
8. B. Jokić, I. Janković-Častvan, Dj. Veljović, R. Petrović, S. Drmanić, Dj. Janaćković, "Preparation of α-TCP Cements from Calcium Deficient Hydroxyapatite obtained by Hydrothermal Method," Key Engin. Mater., pp. 309-311, 2006.
9. B. Jokic, M. Mitric, M. Popovic, L. Sima S. M. Petrescu, R. Petrovic, Dj. Janackovic, "The influence of silicon substitution on the properties of spherical- whisker-like biphasic α-calcium-phosphate/hydroxyapatite particles," J Mater Sci: Mater Med, vol. 22, 2011.
10. B. Jokić, M. Mitrić, V. Radmilović, S. Drmanić, R. Petrović, Dj. Janaćković, "Synthesis characterization of monetite hydroxyapatite whiskers obtained by a hydrothermal method," Ceram. Int., vol. 37, no. 1, pp. 167-173 , 2011.
11. M.N. Rahaman, D.E. Day, B.S. Bal, Q. Fu, S.B. Jung, L.F. Bonewald, A.P. Tomsia, "Bioactive glass in tissue engineering," Acta biomaterialia, vol. 7, no. 6, pp. 2355-2373, 2011.
12. R. W. Davidge, "Cracking at grain boundaries in polycrystalline brittle materials. Acta Metallurgica," vol. 29, no. 10, pp. 1695-1702, 1981.
13. M.F. Ashby, "Mechanisms of deformation and fracture. Advances in applied mechanics," vol. 23, pp. 117-177, 1983.
14. A. Kelly, Strong solids.: Clarendon Press, Oxford, 1966.
15. Munz, Dietrich G., John L. Shannon, Raymond T. Bubsey, "Fracture toughness calculation from maximum load in four point bend tests of chevron notch specimens," International Journal of Fracture, vol. 16, no. 3, pp. R137-R141, 1980.
16. J. Kübler, "Fracture toughness of ceramics using the SEVNB method: preliminary results," Proceedings of the 21st Annual Conference on Composites, Advanced Ceramics, Materials, and Structures-B: Ceramic Engineering and Science Proceedings, vol. 18, no. 4, 1997.
17. S. Yasuhide, "Single-edge precracked beam test and electric fracture mechanics analysis for piezoelectric ceramics," Smart Materials and MEMS. International Society for Optics and Photonics, 2001.
18. F. Sergejev, M. Antonov, "Comparative study on indentation fracture toughness measurements of cemented carbides," Proc. Estonian Acad. Sci. Eng., vol. 12, no. 4, pp. 388-398, 2006.
19. M. Barsoum, M.W Barsoum, Fundamentals of Ceramics.: CRC Press, 2012.
20. H. R. Lawn, E.R. Fuller , "Equilibrium penny-like cracks in indentation fracture. J. Mater. Sci.," vol. 10, pp. 2016–2024, 1975.
21. A. G. Evans,T. R. Wilshaw, "Quasi-static solid particle damage in brittle solids – I. Observations, analysis and implications," Acta Metall., vol. 24, pp. 939–956, 1976.
22. K. Niihara, R.Morena, D.P.H Hasselman, "Evaluation of KIc of brittle solids by the indentation method with low crack-to-indent ratios," J. Mater. Sci. Lett., vol. 1, pp. 13–16, 1982.
23. A. Niihara, "A fracture mechanics analysis of indentation-induced Palmqvist crack in ceramics," J. Mater. Sci. Lett., vol. 2, pp. 221–223, 1983.
24. A. G. Evans, E. A. Charles, "Fracture toughness determinations by indentation," J. Am. Ceram. Soc., vol. 59, pp. 371–372, 1976.
25. B. R. Lawn, A. G. Evans, D. B. Marshall, "Elastic/plastic indentation damage in ceramics: the median/radial crack system," J. Am. Ceram. Soc., vol. 63, pp. 574–581, 1980.
26. G. R. Anstis, P. Chantikul, B. R. Lawn, B. R. D. B. Marshall, "A critical evaluation of indentation techniques for measuring fracture toughness – I. Direct crack measurements," J. Am. Ceram. Soc., vol. 64, pp. 533–538, 1981.
27. K. Tanaka, "Elastic/plastic indentation hardness and indentation fracture toughness: the inclusion core model," J. Mater. Sci., vol. 22, pp. 1501–1508, 1987.
28. A. Moradkhani, H. Baharvandi, M Tajdari, Hamidre, "Determination of fracture toughness using the area of micro-crack tracks left in brittle materials by Vickers indentation test," Journal of Advanced Ceramics, vol. 2, no. 1, pp. 87–102, 2013.

USMENA SAOPŠTENJA

ORAL PRESENTATIONS

Chemical fractionation and mobility of potentially toxic metals in urban soils from four cities in Serbia

Marija Pavlović, Dragana Pavlović, Milica Marković, Dragan Čakmak, Olga Kostić, Snežana Jarić, Miroslava Mitrović, Pavle Pavlović

Department of Ecology, Institute for Biological Research "Siniša Stanković", University of Belgrade, Bulevar despota Stefana 142, 11000 Belgrade, Serbia

Abstract

Urban environments are strongly influenced by anthropogenic activities, which are often reflected by high degree of contamination in relation to the natural environment. Knowledge of the total concentration of heavy metals is not enough to fully assess the environmental impact of urban soils. That is why determination of metal speciation is important to evaluate their environment and mobilization capacity. The optimized four step BCR sequential extraction procedure has been applied to fractionate chromium (Cr), copper (Cu), lithium (Li), nickel (Ni) and strontium (Si) concentrations in urban soil samples from four cities in Serbia (Pančevo, Smederevo, Obrenovac and Belgrade). The sampling locations were chosen based on their proximity to industrial complexes and heavy traffic. Mobility factor was also evaluated in order to assess their availability and potential hazard to the environment. Sequential extraction results showed that concentrations of Cr, Cu and Li were predominantly bound to residual fraction. However, Ni from Pančevo and Smederevo was also found in large quantities bound to the reducible fraction. The biggest threat represents presence of Sr that was predominantly related to the acid/soluble/exchangeable phase at all sampling sites, and as such is highly mobile and bioavailable and can easily enter biota. This was also confirmed by mobility factor.

Key words: *urban soils, sequential extraction, potentially toxic metals, mobility factor*

Introduction

Urban soils are an important component of the urban ecosystem [1]. They are often highly variable in composition because of human impact, and generally have higher contamination due to high density of anthropogenic activity in urbanised areas [2]. This represents serious environmental problem, especially in areas close to industrial facilities, as emissions reach soil by different routes making them a major sink, particularly heavy metals [3]. Heavy metals represent group of inorganic chemical hazards that can lead to deterioration of the environment, decrease in ecological function of the soil, as well as decrease in growth of urban plants [1]. Furthermore, metals affect both water and air quality, since they are pollutant source, thus have indirect influence on people. Unlike organic contaminants, metals in soil do not undergo microbial or chemical degradation, and therefore can persist for long time [4].

Although total concentrations of metals have been widely used to assess soil contamination and status as a quantitative measure of pollution [5], generally this is not sufficient criteria for estimating environmental effects [1]. Sequential extraction techniques do not provide a direct characterization of metal speciation, but rather an indication of chemical reactivity [6] and may provide comparative information on how metals behave in changing environmental conditions (pH, redox potential) [7]. Sequential extraction is one of the most widely applied protocols under the auspices of the European Commission, Community Bureau of Reference (BCR). It has the advantages of simplicity (only four steps involved) and availability of certified reference materials (BCR 701) for method validation [2].

The objectives of this study were to: (a) determine pseudo-total concentrations of chromium (Cr), copper (Cu), lithium (Li), nickel (Ni) and strontium (Sr) in urban soils from four Serbian cities, and (b) determine their mobility and availability by fractionation of these metals using the optimized BCR sequential extraction protocol.

Materials and methods

Study area

The research sites were municipal parks in four cities in Serbia, within 50 km of each other, exposed to different sources of pollution Pančevo, Smederevo, Obrenovac and Belgrade (two sampling sites, one exposed to heavy traffic, second without direct source of pollution). Detailed information on sampling sites and their sources of pollution are presented in Table 1. The research was carried out in October 2012.

Table 1. Description of sampling sites and sources of pollution

Sampling site	GPS coordinates	Sources of pollution
Pančevo - National Garden (Narodna Bašta)	44°51'54" N, 20°39'23" E	NIS-RNP Oil Refinery, the Nitrogen Fertilizer Plant (HIP-Azotara d.o.o.), and the Petrochemical Complex (HIP-Petrohemija)
Smederevo - National Heroes Park (Park Narodnih heroja)	44°40'22" N, 20°55'67" E	Smederevo Steelworks (Železara Smederevo)
Obrenovac - City Park (Gradski park)	44°39'17" N, 20°12'30" E	'Nikola Tesla A' and 'Nikola Tesla B' thermoelectric power plants, two ash disposal sites
Belgrade 1 - Pioneer Park (Pionirski park)	44°48'53" N, 20°29'70" E	Heavy traffic
Belgrade 2 - Arboretum of the Faculty of Forestry (Arboretum Šumarskog fakulteta)	44°46'59" N, 20°25' 31" E	Without direct source of pollution

Sampling

Composite topsoil samples at 0-20 cm depth were obtained from each site by mixing five subsamples with a stainless steel shovel. Stones and foreign objects were removed by hand, and soil samples were stored in clean plastic bags. Samples were first air dried, then by dryer Binder (Tuttlingen, Germany) at the temperature of 105 °C. Dried samples were ground with a stainless steel mill and sieved through sieve with a mash diameter of 1.5 mm.

The physical properties of soils entailed determination of particle size distribution by combined pipette and sieving techniques with 0.4 N solution of sodium pyrophosphate. Fractionation was carried out according to Atteberg. Soil pH in an aqueous solution was measured using a glass electrode (1:2.5 soil-water ratio), as well as in 1 M KCl (1:2.5 soil-KCl ratio) after agitating samples for approximately 30 min [8]. Organic and total carbon in soil samples were determined by CNS analyzer, Vario model EL III (Elemental Analysis systems GmbH, Hanau, Germany).

Sequential extraction

Sequential extraction was performed using the optimised BCR procedure [9, 10]. Concentrations of Cr, Cu, Li, Ni and Sr were analysed using inductively coupled plasma optic emission spectrometry

(ICP-OES, Spectro Genesis, Spectro-Analytical Instruments GmbH, Kleve, Germany). The optimized BCR sequential extraction scheme is presented in Table 2.

Table 2: The optimized BCR sequential extraction scheme

Extraction steps	Procedure	Operationally defined phases
Step 1	0.11 mol dm^{-3} CH_3COOH, shaken for 16h (overnight), room temperature	Water soluble, exchangeable and bound to carbonate
Step 2	0.5 mol dm^{-3}, $NH_2OH·HCl$, adjusted to pH 1.5, shaken for 16h (overnight), room temperature	Reducible (bound to Fe and Mn oxides)
Step 3	8.8 mol dm^{-3}H_2O_2; 1 h (water bath), 85 °C (two times); 1 mol dm^{-3}, CH_3COONH_4 adjusted to pH 2, shaken for 16 h (overnight), room temperature	Oxidizable (bound to organic matter and sulfides)
Step 4	Aqua regia, ($HCl:HNO_3$=3:1); 1 h (water bath), 85 °C (two times)	Residual (bound to silicate minerals)

Quality control for soil was performed using the sediment certified reference material (BCR 701) for optimised sequential extraction. The recovery values found were within 84.1-107.2 % while the detection limits for the analysed elements in the soil samples were as follows (mg kg^{-1}): Cr-0.000315, Cu-0.00069, Li-0.164, Ni-0.011 and Sr-0.00348.

Results and discussion

Selected chemical and physical soil properties

Active and potential acidity, particle size distribution, organic carbon (OC), as well as the total carbon (TOC) are given in Table 3.

Table 3: Chemical and physical properties of selected urban soils

Property	Sampling sites				
	Pančevo	Smederevo	Obrenovac	Belgrade 1	Belgrade 2
pH (H_2O)	8.44	8.56	8.69	8.78	8.69
pH (KCl)	6.86	7.10	7.14	7.20	6.96
Total sand % (2.0-0.02 mm)	43.72	52.88	45.87	43.4	39.89
Silt % (0.02-0.002 mm)	28.98	24.91	27.76	31.32	33.22
Clay % (<0.002 mm)	27.3	22.21	26.37	25.28	26.89
Organic C (%)	2.58	2.53	2	2.55	2.68
Total C (%)	2.83	3.33	3.05	4.07	2.88

Given values are mean, taken at depth 0-20 cm

The chemical reaction of the soil (pH H_2O) varied in a narrow range from 8.44 in Pančevo to 8.78 at Belgrade 1 site, classifying these soils as moderately alkaline [11] (Table 3). However, the pH values in KCl solution remained around neutral, with the lowest measured in Pančevo 6.86 and the highest also at Belgrade 1 site. High alkalinity is quite common in urban areas due to the process of deposition of alkaline dust of anthropogenic origin [4], and is one of the most negative features of soils [12]. Transport, absorption, as well as solubility of essential nutrients directly depend on soil pH reaction [12]. Still, high alkalinity can also have positive effect since labile, potentially toxic forms in such conditions can be immobilized by creation of durable complexes [13]. Soils in Pančevo, Smederevo, Obrenovac and Belgrade 1 were dominated by total sand fraction. At the same sampling sites, percentage of silt and clay remained relatively uniformly distributed. Only at Belgrade 2 sampling site total sand, silt and clay fraction were approximately equally represented (Table 3). Soil texture is a very important factor given the fact that whole range of physical and chemical properties depend on it. Unlike soils which contain uniform percentage of sand, clay and silt (Belgrade 2) that generally have better characteristics, better drainage, and more nutrients and moisture, soils that contain high percentage of sand are commonly very poor in nutrients, although well aerated and with large water permeability [12]. Organic C varied from 2.00 % in Obrenovac to 2.68 % at Belgrade 2 site, while the total carbon ranged from 2.83 % in Pančevo, up to 4.07 % at Belgrade 1 site. Organic carbon in soil can be the result of either natural (product of plant and animal debris) or anthropogenic origin. It contributes to soil fertility and is included in many biogeochemical processes [14]. Generally, it was found that content of both organic and total carbon was rather low at all sampling sites, which indicates low fertility and unfavourable conditions for soil biota and plant development.

Pseudo-total concentrations and partitioning of elements in sampled urban soils

In order to obtain information on the distribution, mobility, as well as availability of chemical elements in the tested soil samples, modified BCR procedure was used. Furthermore, mean values for worldwide soils proposed by Kabata-Pendias and Pendias [15] and values established for toxic elements set by Regulation of the Government of the Republic of Serbia (OGRS, [16]) were used to determine current environmental status of investigated soil samples. The results of the partitioning of elements are shown in Figure 1, and pseudo-total concentrations of metals in soil samples are presented in Table 4.

Pseudo-total concentrations of Cr varied from 22.14 mg kg^{-1} measured at Belgrade 1 site up to 75.78 mg kg^{-1} in Smederevo. Soil samples from Pančevo (52.19 mg kg^{-1}) and Smederevo were slightly above mean values for Cr described for worldwide soils (Table 4), but below limit standard values set by OGRS [16]. Chromium is naturally present in soil as a part of parental material (rock), and its content is calculated to be 54 mg kg^{-1} for worldwide surface soils [15]. Nevertheless, the presence of chromate in soils is closely related to various types of industry, such as plaiting and alloying, but also in the manufacture of steel and other alloys [17, 18]. Fractionation profile, however showed that practically none of the sampling sites contained Cr in the acid soluble/exchangeable fraction, meaning that it poses no threat to environment, what so ever. The largest proportion was associated with residual fraction (70-80 %), while the rest was bound to organic matter and sulphides (15-23 %) and the smallest amount was bound to reducible fraction (3-14 %). Strong association of Cr with residual fraction indicates that this metal is stable under anthropogenic pressure and is quite likely of geological origin [19].

Copper content in soil varied greatly from 20.31 mg kg^{-1} measured in Obrenovac up to 167.08 mg kg^{-1} at Belgrade 1 site. Pseudo-total content of Cu at Belgrade 1 sampling site exceeded the limit standard values set by OGRS [16] and was significantly above normal values for worldwide soils proposed by Kabata-Pendias and Pendias [15]. Nevertheless fractionation profile of Cu showed that, as in the case of Cr, the major proportion was strongly associated with residual fraction (50-70 %). Both reducible (6-22 %) and oxidizable (17-20 %) fraction were equally represented in profile. The smallest proportion of Cu was bound to acid soluble/exchangeable fraction (1-5 %). Although research by Kabata-Pendias and Pendias [15] showed that Cu has a tendency to accumulate in the top horizons of soil profiles and only small amount of Cu is actually present in the first phase of fractionation profile, extremely high Cu content at Belgrade 1 site probably originates from anthropogenic sources, i.e. traffic and abrasion of brakes [20].

The lowest pseudo-total content of Li was recorded in Obrenovac (98.76 mg kg^{-1}) and the highest in Smederevo (178.14 mg kg^{-1}). Obtained results from all sampling sites, besides Obrenovac exceed both mean and normal values for worldwide soils [15]. Unfortunately, national regulation does not propose limit or remediation values in soil for Li. Although Li is widely distributed throughout Earth's crust, its content in soil is controlled more by conditions of soil formation then its content in parent rock. Furthermore, Li is known to be very mobile in geochemical processes and is also readily absorbed by clay minerals [15]. Nevertheless, fractionation profile of Li showed that it is mostly of geological origin since the biggest proportion was bound to residual fraction (80-91 %). Less than 2 % was associated with acid soluble/exchangeable fraction, while both Fe-Mn oxide fraction (reducible) and oxidizable fraction were equally presented.

Nickel content in soil varied widely between sampling sites from 38.29 mg kg^{-1} measured in Obrenovac to 105.65 mg kg^{-1} in Smederevo. All recorded values were in normal range for worldwide soils [15], but above upper limit standard values of 35 mg kg^{-1} established by OGRS [16]. Although soils of central Serbia are known to have high Ni content due to geological origin [21], its concentration can also be the result of emissions from metal processing operations and combustion of coal and oil [15]. This is also evident in fractionation profile which quite differs from Cr, Cu and Li. The smallest proportion of Ni was bound to acid soluble/exchangeable fraction (4-5 %). The biggest difference, however, in relation to above mentioned metals is reducible fraction. It ranged from 18.97 % at Belgrade 1 site up to 52.13 % in Pančevo, where it represented the main share of extraction procedure. The rest was associated with organic (oxidizable) (12-18 %) and residual fraction (30-59 %). These results coincides with findings of Kabata-Pendias and Pendias [15] that Ni is mainly tide with Fe-Mn oxides (reducible) fraction and is easily mobilized during weathering. Baring in mind that metals that originate from anthropogenic sources are most often released in first three fractions of BCR procedure [19], special attention should be paid because under suitable conditions (pH and redox potential) Ni bound to reducible fraction can be released which could represent serious threat to environment [22].

Strontium is a metal found in the environment subsequent to both degradation of minerals naturally containing Sr^{2+} such as celestite and strontianite [23] and to anthropogenic activities such as nuclear weapon tests, or nuclear accidents [24]. All obtained results from fractionation profile fell within mean values (87-210 mg kg^{-1}) for worldwide soils [15]. As is the case with above mentioned Li, national regulation does not propose limit or remediation values in soil for Sr. The lowest Sr content was measured in Pančevo (25.01 mg kg^{-1}), while the highest in Obrenovac (139.96 mg kg^{-1}). Interestingly enough, the greatest proportion of Sr was bound to acid/soluble/exchangeable phase (37-85.99 %) indicating its high mobility, as well as its anthropogenic origin. Significant part of this element is also associated with reducible fraction (10.44-31.19 %). Furthermore, the smallest part of Sr fractionation profile was bound to the silicate lattice and crystallized oxide minerals (0.53-3.09 %). Only small portion (3.02-28.18 %) of Sr points to its lithogenous origin i.e. belongs to residual fraction. High proportion of Sr that is found in the acid/soluble/exchangeable phase of modified BCR extraction procedure is quite likely airborne and consequence of aerial deposition.

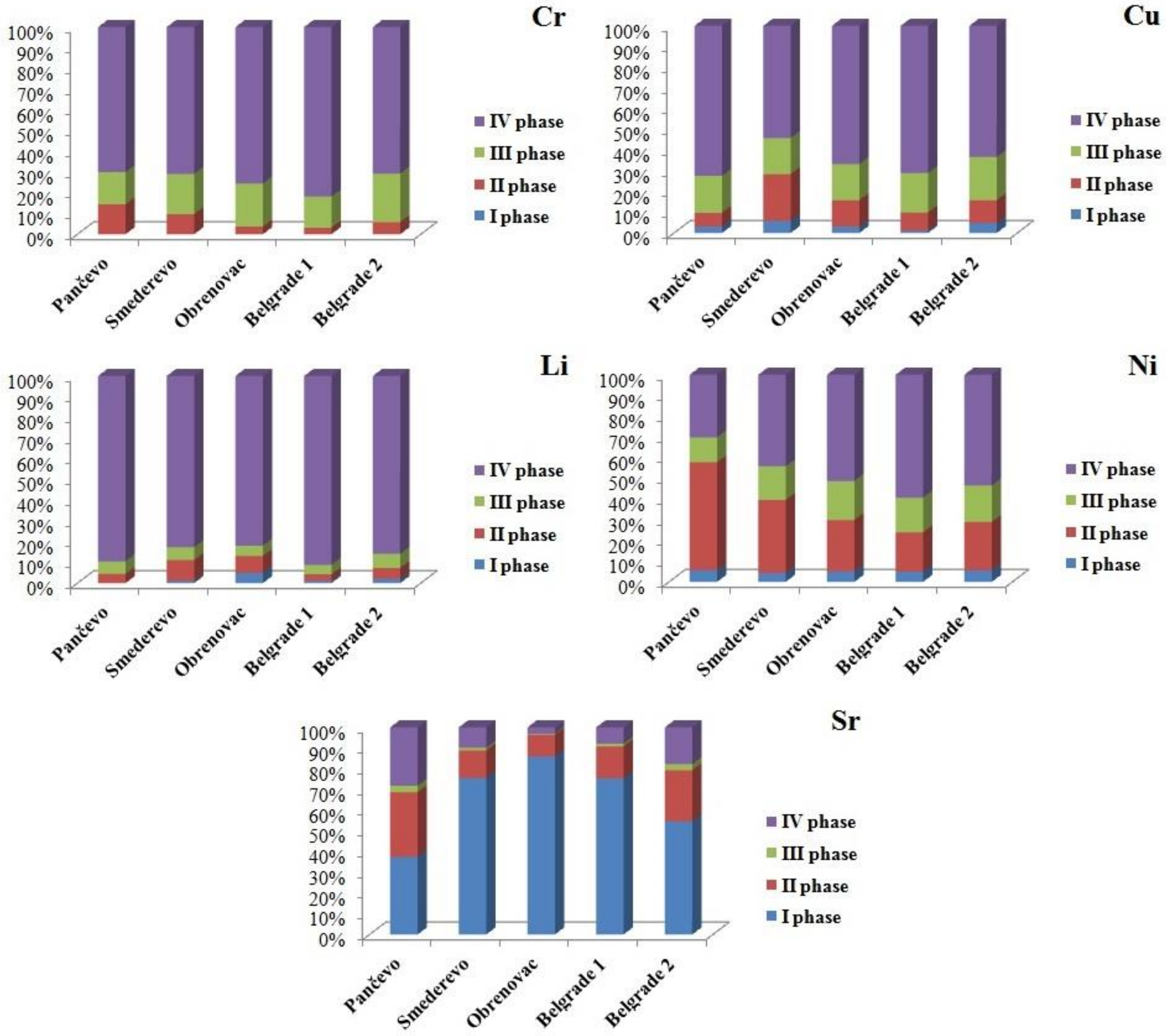


Figure 1. Partitioning of Cr, Cu, Li, Ni and Sr in selected urban soils from Pančevo, Smederevo, Obrenovac and two sampling sites from Belgrade

Table 4: Pseudo-total heavy metal concentrations (mg kg-1 d.w.) in selected urban soils

Site	Cr mg kg^{-1}	Cu mg kg^{-1}	Li mg kg^{-1}	Ni mg kg^{-1}	Sr mg kg^{-1}
Pančevo	52.19	28.83	147.44	72.21	25.01
Smederevo	75.78	37.79	178.14	105.65	81.13
Obrenovac	25.48	20.31	98.76	48.06	139.96
Belgrade 1	22.14	167.08	133.78	38.29	76.17
Belgrade 2	32.45	30.20	131.00	50.64	37.90
[a]Normal	1.4-530	1-100	1.4-130	1-110	5-1000
[a]Mean	47-51	13-23	22-56	13-26	87-210
[b]Upper limit RS	100	36	/	35	/
[b]Remediation value RS	380	190	/	210	/

[a]Mean values for selected metals (Kabata-Pendias and Pendias, 2001);[b]values set by Official Gazette of Republic of Serbia (2010)

Mobility factor (MF)

Mobility factor is a relative index which is used to assess metals mobility [1]. It is represented as the fraction (percentage) of metal in exchangeable fraction that is weakly bonded and can easily become available, and is the consequence of anthropogenic activities [25] (Liu et al., 2008). It is calculated as:

$$MF = \frac{F1}{\sum F} \times 100$$

where F1 represents water soluble, exchangeable and carbonate-bound fractions, and ∑F represents the sum of all fractions [7]. High MF values have been interpreted as symptoms of relatively high mobility and bioavailability [25], while the low shows stability of tested metals in soil. Values that are below 10 % in surface layers indicate their high stability. In present study, MF index was low (<10 %) for all investigated elements, except for Sr. Mobility factor for Sr varied from 37 % measured in Pančevo up to 85 % in Obrenovac, which is shown in Table 5. Significantly high MF for Sr pose potential hazard to environment.

Table 5: The mobility factor for Cr, Cu, Li, Ni and Sr for selected sampling sites

Site	Cr %	Cu %	Li %	Ni %	Sr %
Pančevo	0	3.17	0	5.62	37.52
Smederevo	0	5.83	1.18	4.36	75.55
Obrenovac	0	3.15	4.97	5.07	85.99
Belgrade 1	0	1.22	1.17	4.96	75.35
Belgrade 2	0	4.83	2.06	5.54	54.67

Conclusion

The present research assessed pseudo-total, as well as fractional concentrations of Cr, Cu, Li, Ni and Sr in soils taken from five urban parks in Serbian cities exposed to different sources of pollution. The modified BCR sequential extraction procedure showed that Cr, Cu and Li were primarily bound to residual fraction. However Ni content from Pančevo and Smederevo was evenly distributed both in reducible and residual phase. Presence of Sr that was dominantly bound to acid/soluble/exchangeable phase is of concern because Sr in this form is highly mobile and available. Baring in mind that any change in the environmental conditions (redox potential, pH) can cause new state of metal, which can make it available and mobile, special attention should be paid to possible threats to environment. Mobility factor for Sr was closely related to its pseudo-total content indicating it has anthropogenic origin.

The environmental consequences of the results need to be further investigated.

Acknowledgment

This work was supported by the Ministry of Education, Science and Technological Development of the Republic of Serbia, grant No 173018

References

1. Lu, Y., Zhu, F., Chen, J., Gan, H., Guo, Y. Chemical fractionation of heavy metals in urban soils of Guangzhou, China, *Environ. Monit. Assess.* 2007, 134, 429-439

2. Davidson, C.M., Urquhart, G.J., Ajmone-Marsan, F., Biasioli, M., da Costa Duarte, A., Dıaz-Barrientos, E., Grcman, H., Hossack, I., Hursthouse, A.S., Madrid, L., Rodrigues, S., Zupan, M. Fractionation of potentially toxic elements in urban soils from five European cities by means of a harmonised sequential extraction procedure, *Anal. Chim. Acta.* 2006, 565, 63-72
3. Wuana, R.A., Okieimen, F.E. Heavy metals in contaminated soils: a review of sources, chemistry, risks and best available strategies for remediation, *ISRN Ecology*. 2011, article ID 402647, doi:10.5402/2011/402647
4. Adriano, D.C., *Trace elements in terrestrial environments*, Springer-Verlag, New York, 2001, pp. 61-89
5. Tokalioğlu, Ş., Yilmaz, V., Kartal, Ş. An Assessment on Metal Sources by Multivariate Analysis and Speciation of Metals in Soil Samples Using the BCR Sequential Extraction Procedure, *Clean - Soil, Air, Water.* 2010, 38(8), 713-718
6. Olajire, A.A., Ayodele, E.T., Oyediran, G.O., Oluyemi, E.A. Levels and speciation of heavy metals in soils of industrial southern Nigeria, Environ. Monit. Assess. 2002, 85, 135-155
7. Kabala, C., Singh, B.R. Fractionation and mobility of copper, lead, and zinc in soil profiles in the vicinity of a copper smelter, *J. Environ. Qual*. 2001, 30, 485-492
8. Dick, W.A., Cheng, L., Wang, P. Soil acid and alkaline phosphatase activity as pH adjustment indicators, *Soil. Biol. Biochem.* 2000, 32, 1915-1919
9. De Andrade Passos, E., Alves, J.C., dos Santos, I.S., Alves, J.P.H., Garcia, C.A.B., Costa, C.S. Assessment of trace metals contamination in estuarine sediments using a sequential extraction technique and principal component analysis, *Microchem.* 2010, 96, 50-57
10. Sutherland, R.A. BCR-701: A review of 10-years of sequential extraction analyses, *Anal. Chim. Acta.* 2010, 680, 10-20
11. *Soil Survey Division Staff. Chapter 3, selected chemical properties. Soil survey manual. Soil Conservation Service, 1993, U.S. Department of Agriculture Handbook 18*
12. *Antić, M., Jović, N., Avdalović, V., Pedology, Naučna knjiga, Beograd, 1980, p. 462 (In Serbian)*
13. Parzych, A., Jonczak, J. Pine needles (*Pinus sylvestris* L.) as bioindicators in the assessment of urban environmental contamination with heavy metals, *J. Ecol. Eng.* 2014, 15(3), 29-38
14. Saint-Laurent, D., Beaulac-Gervais, V., Berthelot, J.S. Comparison of soil organic carbon and total nitrogen contents in inundated and non-inundated zones in southern Québec, Canada, *Catena*, 2014, 113, 1-8
15. Kabata-Pendias, A., Pendias, H, *Trace elements in soils and plants*, CRC Press, London, DC, 2001, p. 432
16. OGRS, Regulations on a systematic soil quality monitoring programme, indicators for assessing the risk of soil degradation, and methodology for the preparation of remediation programmes, *Official Gazette of the Republic of Serbia (Sluzbeni glasnik RS)*, 2010, 88 (In Serbian)
17. Kimbrough, D.E., Cohen, Y., Winer, A.M., Creelman, L., Mabuni, C. A critical assessment of chromium in the environment, *Crit. Rev. Environ. Sci. Technol.* 1999, 29(1), 1-46
18. Avudainayagam, S., Megharaj, M., Owens, G., Kookana, R.S., Chittleborough, D., Naidu, R. Chemistry of chromium in soils with emphasis on tannery waste sites, *Rev. Environ. Contam. Toxicol.* 2003, 178, 53–91
19. Ghrefat, H.A., Yusuf, N., Jamarh, A., Nazzal, J. Fractionation and risk assessment of heavy metals in soil samples collected along Zerqa River, Jordan, *Environ. Earth. Sci.* 2012, 66, 199-208
20. Van Bohemen, H.D., Van de Laak, W.H.J. The influence of roads infrastructure and traffic on soil, water, and air quality, *Environ. Manage.* 2003, 31(1), 50-68
21. Kuzmanoski, M.M., Todorović, M.N., Aničić-Urošević, M.P., Rajšić, S.F. Heavy metal content of soil in urban parks of Belgrade, *Hem. Ind.* 2014, 68, 643-651
22. Jain, C.K., Malik, D.S., Yadav, R. Metal fractionation study on bed sediments of Lake Nainital, Uttaranchal, India, *Environ. Monit. Assess.* 2007, 130, 129-139
23. West, H.K., Davies, M.S., Morgan, A.J., Herbert, R.J. The relationship between Sr and Ca accumulation in the major constituents of a terrestrial community resident on a celestitic (SrSO4) soil in S.W. England, *Eur. J. Soil. Biol.* 2001, 37, 333-336
24. Stamoulis, K.C., Assimakopoulos, P.A., Ioannides, K.G., Johnson, E., Soucacos, P.N. Strontium-90 concentration measurement in human bones and teeth in Greece, *Sci Total Environ.* 1999, 229, 165-182

25. Liu, J., Zhang, X-H., Tran, H., Wang, D-Q., Zhu, Y-N. Heavy metal contamination and risk assessment in water, paddy soil and rice around an electroplating plant, *Environ. Sci. Pollut. Res.* 2011, 18, 1623-1632

Electrochemical deposition of niobium oxides from acidic solution on glassy carbon

Elektrohemijsko taloženje niobijum oksida iz kiselih rastvora na staklastom ugljeniku

Nataša M. Vukićević[1], Vesna S. Cvetković[1], Ljiljana S. Jovanović[2], Jovan N. Jovićević[1]

[1]Institute of Chemistry, Technology and Metallurgy, University of Belgrade, Njegoševa 12, Serbia

[2] Faculty of Science, University of Novi Sad, Trg Dositeja Obradovića 3, Serbia

[1]Institut za hemiju, tehnologiju i metalurgiju, Univerzitet u Beogradu, Njegoševa 12, Srbija

[2]Prirodno matematički fakultet, Univerzitet u Novom Sadu, Trg Dositeja Obradovića 3, Srbija

Abstract

Electrochemical synthesis of niobium oxides from four different strongly acidic solutions onto vitreous carbon electrodes was studied. Linear sweep voltammetry and potential step techniques were used for electrochemical experiments and scanning electron microscopy and energy dispersive spectroscopy for analysis of the working electrode surface and deposits formed. Change of the working electrode potential to negative values, negative to 0.5 V vs. SCE, leads to simultaneous reduction of niobium, hydrogen, nitrate and sulphated ions, which induces alkaline media in the immediate vicinity of the electrode surface and formation of several niobium oxides and oxyhidoxides. Despite reduction of niobium ions there are no firm evidence of the permanent metal niobium clusters. Change of the electrode potential into positive direction, positive to – 1.000 vs. SCE, leads to simultaneous oxidation of niobium ions from lower oxidation state and additional formation of niobium oxides. Morphology and crystallographic forms of the deposits obtained by SEM and EDS analysis confirmed above assumptions.

Izvod

Elektrohemijskim putem sintetizovani su oksidi niobijuma iz četiri različita veoma kisela rastvora na elektrodi od staklastog ugljenika. U elektrohemijskim eksperimentima upotrebljavane su metode linearne cikličke voltametrije i potenciostatskog pulsa, a metode skenirajuće elektronske mikroskopije i energetsko disperzivne spektroskopije poslužile su za analizu elektrodne površine i taloga formiranog na njoj. Pri promeni radnog potencijala u negativnu stranu (a negativnije od 500 mV vs. ZKE) dolazi do simultanog odvijanja procesa redukcije niobijumovih, vodonikovih, hidroksidnih, nitratnih i sulfatnih jona, što u formiranoj baznoj sredini u neposrednoj blizini radne elektrode dovodi do nastanka nekoliko niobijumovih oksida i oksihidroksida na njenoj površini. Mada dolazi do redukcije niobijumovih jona nema čvrstih dokaza da se njihova redukcija odvija do formiranja održivih nakupina metalnog niobijuma. Pri promeni radnog potencijala u pozitivnom smeru (pri potencijalima pozitivnijim od – 1.000 vs. ZKE) dolazi do zajedničkog odvijanja oksidacije niobijumovih jona nižeg oksidacionog stanja i dodatno se formiraju niobijumovi oksidi. Morfologija dobijenih taloga i uočene kristalografske forme analizirane SEM i EDS tehnikama potvrđuju gore navedene pretpostavke.

Uvod

U poslednjih nekoliko decenija nanostrukturni materijali zasnovani na oksidima prelaznih metala, iridijuma, volframa, niobijuma zbog svojih specificnih osobina imaju komercijalnu upotrebu i zauzimaju značajno mesto na tržištu materijala [1]. Specifična svojstva niobijuma, otpornost prema koroziji, superprovodnost, termostabilnost i biokompatibilnost, čine ga veoma interesantnim, bilo da se koristi za dobijanje tanke i porozne prevlake njegovog oksida bilo kao osnove za legure. Zbog relativno niske cene oksidi niobijuma (jeftiniji od oksida tantala, ili titana) imaju primenu u elektronskoj i hemijskoj industriji, a posebno su cenjeni katalizatori na bazi tih oksida koji se mogu upotrebljavati i u bio-sistemima [2-4].

Danas se tradicionalne metode sinteze oksida kao što su sol-gel procesi, hemijska precipitacija, sinteza na visokim temperaturama, zamenjuju novim i usavršenim postupcima zbog mogućnosti sinteze materijala visoke čistoće, poboljšanih karakteristika i kontrole morfologije. Metoda elektrohemijskog taloženja je od interesa pre svega zbog mogućnosti formiranja kristalnih umesto amorfnih oksidnih filmova na podlozi. Činjenica je da elektrohemijsko taloženje niobijuma iz vodenih rastvora termodinamički nije moguće, zato što je katodni potencijal taloženja ovog metala daleko negativniji od potencijala stabilnosti vode [5]. Ne postoji jednostavna niobijumska so koja ne hidrolizuje u vodi, a da se može upotrebiti kao elektrolit. Međutim, u literaturi postoje neke informacije o vodenim elektrolitima koji se ipak mogu koristiti za elektroredukciju niobijuma [6,7]. U predloženim elektrolitima niobijum jon je obezbeđivan direktnim elektrohemijskim rastvaranjem metala naizmeničnom strujom velikih amplituda, a tako pripremljeni elektroliti su stabilizovani dodavanjem nekog kompleksirajućeg agensa [8]. Određeni broj sporednih reakcija kao što su redukcija vodonika, hidroliza niobijumskih jedinjenja, utiču na stepen iskorišćenja struje i formiranje elektrohemijski neaktivnih vrsta u vodenim elektrolitima, ali i onemogućavaju taloženje metalnog niobijuma.

Cilj ovog rada bio je da se ispita mogućnost elektrohemijskog taloženja niobijumovih oksida iz mešovitih kiselih fluoridnih, nitratnih i sulfatnih rastvora na staklastom ugljeniku. Ispitivan je uticaj koncentracije elektrolita i primenjenog potencijala na morfologiju i dimenzije čestica.

Eksperimentalni deo

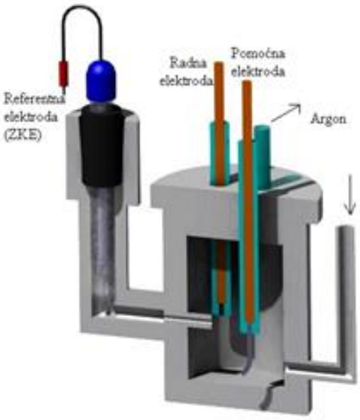
Elektrohemijski eksperimenti u izabranim rastvorima urađeni su u posebno projektovanoj elektrohemijskoj ćeliji napravljenoj od teflona (PTFE, „Aldrich“, SAD), otpornoj na dejstvo kiselina, uključujući i HF, Sl. 1. Na ćeliji, zapremine 50 cm^3, sa leve strane smeštena je Luggin-ova kapilara i nosač zasićene kalomelove referentne elektrode. Kroz središnji otvor poklopca prolazi teflonski nosač radne elektrode od staklastog ugljenika (GC) („Sigma Aldrich“ SAD), radne površine od 0,13 cm^2. Kroz otvor na desnoj strani ćelije prolazi teflonski nosač anode od niobijuma (99,99%, „LTS Chemical Inc.“, SAD) aktivne površine 1,2 cm^2. U ćeliju se uvodi argon (99,99%, „Messer“, Srbija) kojim se obezbeđuje inertna atmosfera u radnom prostoru. Na poklopcu ćelije obezbeđena je i cev za izvod argona i eventualnih gasova koji se razvijaju tokom rada. Sva elektrohemijska ispitivanja su vršena na sobnoj temperaturi (25 °C± 1°).

Kao elektroliti u radu korišćeni su rastvori:

I. 0,01M Nb + 2M H_2SO_4 + 1,4M HF + 0,8M HNO_3;
II. 0,02M Nb + 1M H_2SO_4 + 0,7M HF + 0,4M HNO_3;
III. 0,05M Nb + 1M H_2SO_4 + 0,7M HF + 0,4M HNO_3;
IV. 0,05M Nb + 0,7M HF + 0,4M HNO_3.

Za sva elektrohemijska ispitivanja korišćen je potenciostat/galvanostat EG&G PAR (Potentiostat/Galvanostat Model 273A) koji je računarski kontrolisan softverom (Power Suite software-Princeton Applied Research).

Radna elektroda od staklastog ugljenika je nakon mehaničkog poliranja brusnim papirom i na filcu impregnisanim sa Al_2O_3 prahom („Banner Scientific Ltd.“, SAD) oprana u razblaženoj HCl (p.a. „Merck“, Nemačka), a zatim ispirana destilovanom i dejonizovanom vodom. Anoda od niobijuma je nakon mehaničkog poliranja hemijski nagrižena u smeši kiselina konc. HF : konc. HNO_3 = 1 : 1 (p.a. „Acros organics“ SAD i „Merck“, Nemačka, respektivno) u tri intervala od po 10 s prekidanih ispiranjem dejonizovanom vodom, zatim detaljno isprana dejonizovanom vodom, pa apsolutnim etil-alkoholom.



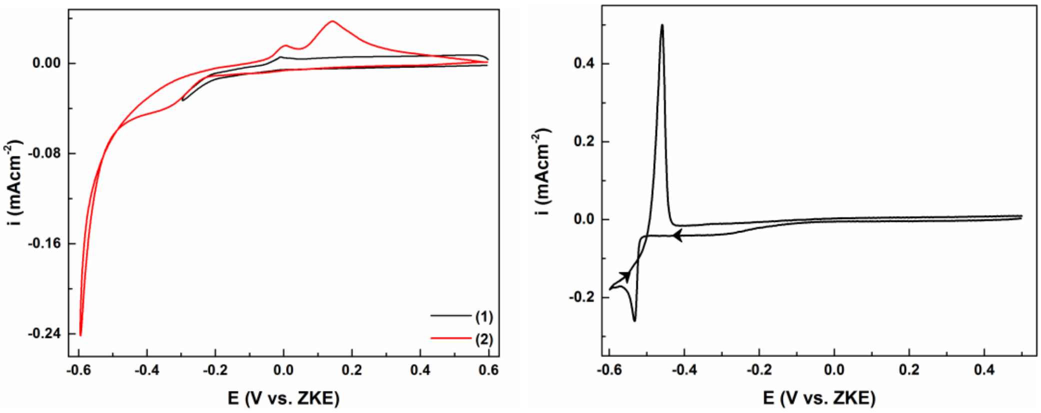
Slika 1. Presek teflonske elektrohemijske ćelije za rad u fluoridnim rastvorima

Elektrohemijski eksperimenti izvođeni tehnikom linearne cikličke voltametrije podrazumevali su promenu potencijala radne elektrode (meren u odnosu na ZKE) izabranom brzinom (od 5 mVs^{-1} do 500 mVs^{-1}) od početnog potencijala E_i (najčešće 50 mV negativniji od reverzibilnog potencijala staklastog ugljenika u datom rastvoru) do izabranog krajnjeg negativnog potencijala E_f i nazad. Zatim je, za isti raspon potencijala radne elektrode izabrani krajnji negativni potencijal, E_f, bio zadržavan određeno vreme, nakon čega se potencijal vraćao na početnu vrednost izabranom brzinom.

Površina radne elektrode nakon primene potenciostatskog pulsa analizirana je skenirajućim elektronskim mikroskop (SEM "JEOL", model JSM-5800, Japan) i energetsko disperzivnom spektroskopijom (EDS „Oxford INCA 3.2", V. Britanija).

Rezultati i Diskusija

U ispitivanim vrlo kiselim elektrolitima različitih koncentracija izabranih komponenata zapaženo je da se ravnotežni potencijal radne elektrode od staklastog ugljenika pomera ka negativnijim vrednostima sa povećanjem koncentracije niobijuma i smanjenjem koncentracije sumporne kiseline. Tipični rezultati linearne cikličke voltametrije u nekim od upotrebljenih rastvora prikazani su na Sl. 2 a i b), a rezultati dobijeni zadržavanjem potencijala na vrednostima E_f na Sl. 3.a) i b).



a) *b)*

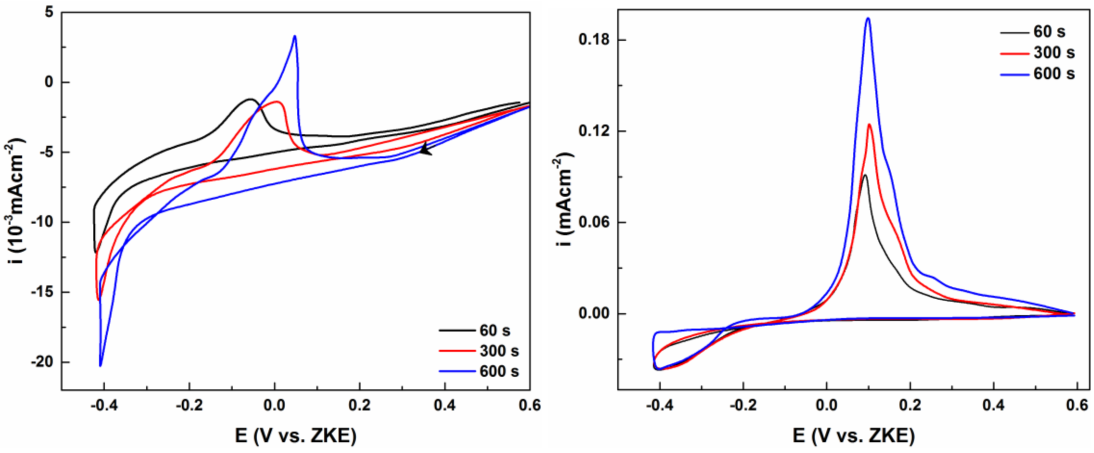
Slika 2. Voltamogrami dobijeni na GC radnoj elektrodi, v = 10 mV/s; a) 0,05M Nb + 1M H2SO4 + 0,7M HF + 0,4M HNO3, redosled promene potencijala: 1) Ei = 600 mV → Ef = – 300 mV; 2) Ei = 600 mV → Ef = – 600 mV; b) 0,05M Nb + 0,7M HF + 0,4M HNO3; redosled promene potencijala: Ei = 500 mV → Ef = − 600 mV.

Rezultati dobijeni cikličkom voltametrijom u sva četiri ispitivana fluoridna elektrolita, pokazuju dva redukciona strujna talasa, a na potencijalima negativnijim od – 700 mV i dodatni nagli porast gustine struje. U anodnom delu voltamograma, kao odgovori, javljaju se jedan veći i razvučeniji talas sa više maksimuma ili dva oksidaciona strujna talasa. U slučaju 0,05M Nb + 0,7M HF + 0,4M HNO$_3$ pri većim katodnim prenapetostima od – 900 mV dolazi do značajnog povećanja gustine struje krajnjeg katodnog strujnog talasa, što bi se moglo pripisati izdvajanju vodonika, ali ne izostaje anodni strujni talas.

Kada je potencijal radne elektrode zadržavan duže na graničnom negativnom potencijalu E_f, u sva četiri ispitivana elektrolita (I - IV) uočeno je da su:

a) vrednosti gustine struje i redukcionih i oksidacionih vrhova strujnih talasa rasli sa povećanjem vremena zadržavanja na graničnom negativnom potencijalu E_f,

b) i da su količine naelektrisanja ograničene oksidacionim strujnim talasom rasle sa povećanjem vremena zadržavanja na graničnom negativnom potencijalu E_f.

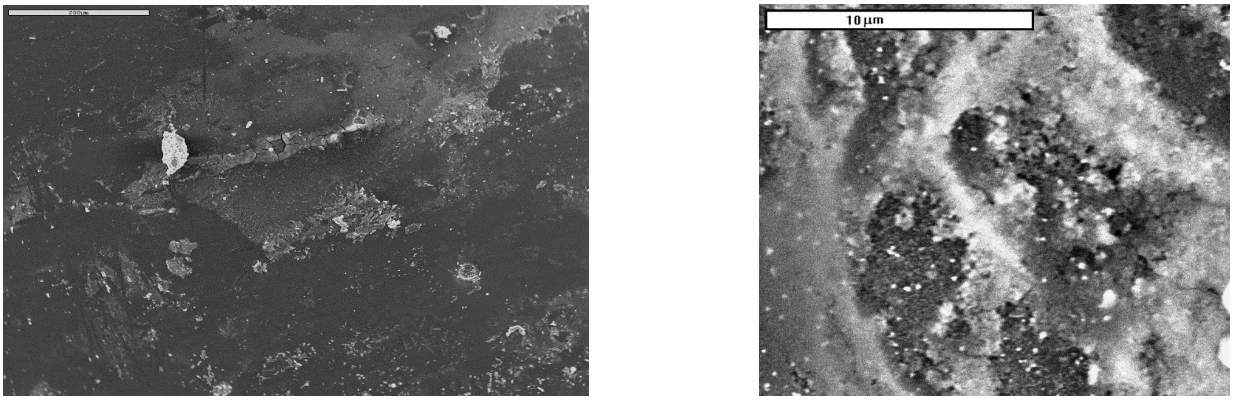


a) *b)*

Slika 3. Voltamogrami dobijeni na staklastom ugljeniku, v= 10 mV/s; raspon potencijala Ei = 600 mV → Ef = – 450 mV; sa zadržavanjem na Ef potencijalu; a) 0,01M Nb + 2M H2SO4 + 1,4M HF + 0,8M HNO3; b) 0,05M Nb + 1M H2SO4 + 0,7M HF + 0,4M HNO3.

Izgledi površine radne elektrode snimljene skenirajućim elektronskim mikroskopom nakon primene jediničnog potenciostatskog pulsa na izabranom potencijalu E_f određeno vreme prikazani su na Sl. 4. a) i b), a numerički izraz kvazi-kvantitativne analize energetskom disperzivnom spektroskopijom (EDS) jedne od elektroda u Tabeli 1.

Naelektrisanje potrošeno na odvijanje redukcija u dva katodna strujna talasa kada je krajnji negativni potencijal zadržavan neko vreme na vrednostima pozitivnijim od – 500 mV i naelektrisanje ograničeno oksidacionim strujnim talasima u anodnom delu voltamograma se međusobno neznatno razlikuju. To nije slučaj u eksperimentima u kojima je krajnji negativni potencijal radne elektrode bio negativniji od – 500 mV ili zadržavan neko vreme na tim vrednostima. U takvim primerima razmenjeno naelektrisanje ograničeno samo trećim katodnim talasom (onim koji se javlja pri najnegativnijim primenjenim potencijalima ciklusa linearne promene potencijala) bilo je 4, 5 i više puta veće od ukupnog naelektrisanja ograničenog anodnim strujnim talasima.



a) b)

Slika 4. SEM fotografije površine radne elektrode snimljene nakon delovanja katodne prenapetosti od – 350 mV ostvarene jediničnim potenciostatskim pulsom u 0,02M Nb + 1M H2SO4 + 0,7M HF + 0,4M HNO3 u trajanju od: a) 6 minuta, uvećanje 1500x; b) 60 minuta

Tabela 1. EDS analiza taloga sa površine staklastog ugljenika snimljene nakon 180 minuta delovanja katodne prenapetosti od – 420 mV ostvarene jediničnim potenciostatskim pulsom u 0,05M Nb + 0,7M HF + 0,4M HNO$_3$ elektrolitu.

Element	Tip spektra	Element (%)	**Atomski (%)**
C K	ED	45,55	23,23
O K	ED	49,36	75,45
Nb L	ED	5,09	1,34
Ukupno		100,00	100,00

U nama dostupnoj literaturi [6,7,9-12] nema dovoljno podataka o procesima koji se javljaju pri elektrohemijskom taloženju i rastvaranju niobijuma iz vodenih rastvora uopšte, a posebno ne iz fluoridnih rastvora koji bi mogli direktno da objasne ove rezultate. U ovom radu su upotrebljeni jako kiseli fluoridni, nitratni i sulfatni elektroliti koji se razlikuju od onih koji se mogu naći u literaturi (kiseli ili bazni, hloridni, sulfatni, sa organskim dodacima). Istovremeno, u ovom radu radna elektroda bila je staklasti ugljenik za razliku od Hg, Nb, Pt, SnO_2 koje se sreću u navedenoj literaturi.

Dobijeni rezultati ukazuju na formiranje različitih faza na površini radne elektrode tokom primene potencijala negativnijih od – 300 mV i njihovog delimičnog rastvaranja pri potencijalima pozitivnijim od – 300 mV. Dva redukciona strujna talasa koji se javljaju pri potencijalima pozitivnijim od – 500 mV najverovatnije pripadaju redukciji niobijumovih jona iz viših u niže oksidaciono stanje. Treći redukcioni nagli porast struje koji se javlja na potencijalima negativnijim od – 500 mV mora se pripisati izdvajanju vodonika, jer se primećuju i gasni mehurovi. Vrlo negativan potencijal pri kome dolazi do početka izdvajanja vodonika i pored veoma niske pH vrednosti može se pripisati velikoj prenapetosti izdvajanja vodonika na staklastom ugljeniku.

Pourbaix -ov dijagram za sistem Nb/H_2O [5] ukazuje na formiranje nekoliko oksida i hidroksida niobijuma (NbO, NbO_2, Nb_2O_5, $Nb(OH)_4^-$) u veoma kiselim sredinama (pH < 1) i u korišćenom rasponu potencijala od 500 mV do – 1000 mV. U prilog ovoj pretpostavci idu i rezultati nekih autora [6,7] dobijeni u hloridnim rastvorima koji tvrde da se redukcija niobijuma odvija u najmanje dva koraka i to od Nb (V) do Nb (IV) na – 495 mV i od Nb (IV) do Nb (II) na - 750 mV, koji je nestabilan i brzo prelazi u Nb (III), pri čemu put redukcije zavisi od koncentracije niobijuma u elektrolitu.

Proces izdvajanja vodonika u neposrednoj blizini elektrode formira atmosferu OH^- jona koji sa prisutnim niobijumovim jonima mogu da daju niobijum hidrokside, koji daljom redukcijom mogu formirati okside. Istovremeno, može doći do redukcije nitrata u nitrite i sulfata u sulfite uz formiranje O^{2-} jona koji sa prisutnim niobijumovim jonima mogu formirati okside, a sa niobijumovim hidroksidima oksihidrokside [5,10-12,13].

Zaključak

Na osnovu dobijenih rezultata može se zaključiti da dolazi do formiranja niobijum oksida i oksihidroksida na površini radne elektrode od staklastog ugljenika iz ispitivanih kiselih elektrolita.
Mada dolazi do redukcije niobijumovih jona nema čvrstih dokaza da se njihova redukcija odvija do formiranja održivih nakupina metalnog niobijuma.
Rezultati dobijeni SEM i EDS analizama potvrđuju gore navedene pretpostavke, a morfologija dobijenih taloga i uočene kristalografske forme slične su onima prikazanim u literaturi.

Reference

1. Özer, N., Barreto, T., Büyüklimanli, T., Lampert, C.M., Characterization of sol-gel deposited niobium pentoxide films for electrochromic devices, *Sol. Energy Mater. Sol. Cells*, 1995, 36, 433-443.
2. Santos, A. de S., Gorton, L., Kubota, L.T., Nile blue adsorbed onto silica gel modified with niobium oxide for electrocatalytic oxidation of NADH, *Electrochim. Acta*, 2002, 27, 3351-3360.
3. Eisenbarth, E., Velten, D., Breme, J., Biomimetic implant coatings, *Biomol. Eng.* 2007, 24, 27-32.
4. Bonakdarpour, A., Tucker, R.T., Fleischauer, M.D., Beckers, N.A. Brett, M.J., Wilkinson, D.P., Nanopillar niobium oxides as support structures for oxygen reduction electrocatalysts, *Electrochim. Acta*, 2012, 85, 492-500.
5. Asselin, E., Ahmed, M. T., Alfantazi, A., Corrosion of niobium in sulphuric and hydrochloric acid solutions at 75 and 95°C, *Corros. Sci*. 2007, 49, 694–710.
6. McCullough, J. G., Meites, L., The electroreduction of niobium (V) in hydrochloric acid solutions at mercury electrodes. I Polarography and chronopotentiometry, *J. Electroanal. Chem*. 1968, 18, 123-135.
7. McCullough, J. G., Meites, L., The electroreduction of niobium (V) in hydrochloric acid solutions at mercury electrodes. II Controlled-potential coulometry and stirred-pool chronoamperometry, *J. Electroanal. Chem*. 1968, 19, 111-123.
8. Chirkov, D. Vasiliovych, D., Attempts for the electrodeposition of niobium from ionic liquids, Master thesis, Padova, (2009-10).
9. D’Alkaine, C. V., de Souza, L. M. M., Nart, F. C., The anodic behavior of niobium-I. The state of the art, *Corros. Sci*. 1993, 34, 109-115.
10. Lee, G. R., Crayston, J. A., Studies on the electrochemical deposition of niobium oxide, *J. Mater. Chem.* 1996, 6, 187-192.
11. Zhitomirsky, I., Electrolytic deposition of niobium oxide films, *Mater. Letters*, 1998, 35, 188-193.
12. Fomanyuk, S. S., Krasnov, Y. S., Kolbasov, G. Y., Zaichenko, V. N., Electrochemical deposition of electrochromic niobium oxide films from an acidic solutions of niobium peroxo complexes, *Russ. J. Appld. Chem*. 2013, 86, 644-647.
13. Sugimoto, K., Belanger, G., Piron, D. L., Changes in the niobium electrode surface induced by strong cathodic polarization, *J. Electrochem. Soc*., 1979, 126, 535-541.

Relative importance of operating parameters in the membrane external loop airlift reactor

Predrag S. Kojić, Nataša Lj. Lukić, Milica Ž. Karadžić, Svetlana S. Popović

University of Novi Sad, Faculty of Technology, Bulevar cara Lazara 1, 21000 Novi Sad, Serbia

Abstract

Paper reports relative importance of the operating parameters such as superficial gas velocity, surface tension gradient, orifice diameter of gas distributor and the membrane inserted into the downcomer on the gas holdup and downcomer liquid velocity. Superficial gas velocity has the strongest influence on the gas holdup and liquid velocity. The second most influential parameter is a membrane resistance. Then follows the orifice diameter that has the stronger influence in the bubbly and transition regime than surface tension gradient, while the opposite situation is in the heterogenous regime.

Introduction

During the past decades airlift reactors have been widely used in chemical and biochemical processes, fermentation systems and wastewater treatment. The main advantage of airlift reactors is their simple construction and minimal room requirements, good mixing and the low cost. There are many variations of these reactors, but the two major groups are: internal loop airlift reactors (ILAR) and external loop airlift reactors (ELAR).

Rapidly progress in the industry requires reactors with continuous product removal. Therefore, airlift reactors were combined with membrane separation process, so in this integrated process, both the biomass formation and liquid separation with soluble products take place in one membrane bioreactor. This process has many advantages, such as an excellent and stable effluent quality, compact equipment, high volumetric load and less surplus sludge production [1]. One of the newest type of membrane reactors is the external loop airlift membrane reactor (ELAMR) that proves to be very energy efficient, because it does not require pump to circulate the liquid [2].

The hydrodynamics in an ELAMR has significance in the control of membrane fouling and maintenance of the steady operation [1]. The gas holdup and the downcomer liquid velocity are the most important hydrodynamic parameters [3]. It is well known that the gas holdup and downcomer liquid velocity in the ELAR depend on parameters such as superficial gas velocity, ratio of the downcomer to riser cross-sectional area, horizontal connector geometries, hydrodynamic resistance to the liquid flow, liquid height in the gas separator, type of gas distributor and physical properties of the liquid phase [4-6]. Also, a membrane module inserted in the downcomer represents hydrodynamic resistance to the liquid flow and has a strong influence on the gas holdup and liquid velocity.

Because of the complex effects previously mentioned the goal of this work was to systematically investigate influences and determined their relative influence on the gas holdup and liquid velocity. Artificial neural network (ANN) was chosen to predict the output parameters. Our previous publication [7] showed that ANN has better predictability than traditional empirical power low correlations. Yoon's model was chosen as the best model to sort operating parameters by their importance.

Experimental setup

Experimental setup was the cylindrical external loop airlift reactor made of Plexiglas consisted of a riser (54 mm i.d. and 2000 mm in height), downcomer (25 mm i.d. and 1950 mm in height) and rectangular gas separator. The air, sparged into the riser, was used as the gas phase. Three different gas distributors were tested: single orifice (4 mm i.d.), perforated plate (7 holes of 1 mm i.d., triangular pitch) and sinter plate (average pore size 115 µm). Tap water and dilute alcohol solutions (0.046 wt% ethanol, 0.011 wt% n-butanol and 0.0051 wt% n-hexanol) were used as the liquid phase. The superficial gas velocity, based on the riser cross-sectional area, was varied in the range 0.02 to 0.22 m/s. Two eDAQ (Australia) conductivity isoPods with miniature dip-in conductivity electrodes were used to determine downcomer liquid velocity. The gas holdup values in the riser (ε_{GR}) were obtained by measuring the pressures at the bottom and the top of the riser using piezometric tubes. The tubular ceramic membrane (ZrO2/TiO2, Novasep, France) 20 cm in length and 2.3 cm in diameter, with 7 channels (6 mm i.d.), was installed in the downcomer. To quantify the hydrodynamic resistance of the membrane itself, it was necessary to calculate the overall friction coefficient (K_f) in both reactors. The K_f was derived according to Verlaan [8] by plotting the square of the measured superficial liquid velocity as a function of the gas holdup:

$$W_{ld}{}^2 = \frac{2gH}{K_f}\varepsilon_G$$

Results and discussion

Hydrodynamic regimes

Hydrodynamics of an ELAR is characterized by different flow patterns depending on the gas flow rate: homogenous (bubble flow), transition, heterogeneous (churn turbulent flow) regimes and slug flow. In this study, we investigated relative influences of operating parameters in two regimes that are the most different between themselves: bubble flow and heterogenous regimes.
The transitions between regimes were identified by the change of the slope of the gas holdup vs. the superficial gas velocity curves. A more detailed analysis of the hydrodynamic regimes and their transitions at specified superficial gas velocities can be found in our earlier study [7].

Artificial neural network and Yoon's model

In this paper, we used one ANN for each hydrodynamic regime: bubble flow and churn turbulent flow, in order to predict the gas holdup (ε_G) and downcomer liquid velocity (W_{ld}). Neural network inputs were the same for both ANN: $0.022 < U_G < 0.218$ m/s, $0.027 < (d\sigma/dC_A) < 1.985$ mNm^2/mol, $0.115 < d_o < 4$ mm, $11.9 < K_f < 22.3$. Where $d\sigma/dC_A$ is the surface tension gradient and d_o is the orifice diameter of the gas distributor. The networks were trained with the Bayesian regulation back propagations training algorithm. The transfer functions were the linear transfer function (purelin) at output layers and the tangent sigmoid transfer functions (tansig) at hidden layers.
Successful creation of the ANNs and obtained weight matrices provide the determination of the relative importance (RI) of input values and its effect on the ε_G and W_{ld}. In this study, the following equation developed by Yoon et. al was used:

$$RI_{ij}\,[\%] = \frac{\sum_{k=0}^{n}(w_{ik}\,w_{kj})}{\sum_{i=0}^{m} abs\ \sum_{k=0}^{n}(w_{ik}\,w_{kj})}\ 100\ \%$$

where RI_{ij} is the relative importance of the ith input variable on the jth output, w_{ik} is the weight between the ith input and the kth hidden neuron, and w_{kj} is the weight between the kth hidden neuron and the jth output.

Relative importance of working parameters in the bubbly regime

The ANN topology was 4-8-2 for bubbly regime, R^2 was 0.996. From Figure 1 it can be seen that the greatest influence has U_G with approx. 55% of relative importance, the second most influential parameter is the membrane resistance (about 15%), and it is followed by orifice diameter (about 10%) and the surface tension gradient that has minimal effect. For all the gas liquid systems and both reactors (ELAR and ELAMR), the ε_G and W_{ld} increased with an increase in the superficial gas velocity, so the strongest influence of the U_G was expected, this is in agreement with experimental study. The insertion of the membrane in the downcomer of the ELAR increased the overall friction coefficient. Higher resistance in the ELAR leads to a decrease in the liquid velocity and an increase in the gas holdup. So, from Figure 1, we can concluded that the membrane resistance has a greater negative influence on the W_{ld} than positive effect on ε_G. Initial size and distributions of the bubbles are determined by the flow through the sparger, because of that the orifice diameter of gas sparger has noticeably effect on ε_G and W_{ld}. It is important to note that at small U_G in the bubbly regime coalescence does not appear so the alcohols have marginal influence, that can be seen also in Figure 1. Figure 2 presents that ANN has an excellent prediction.

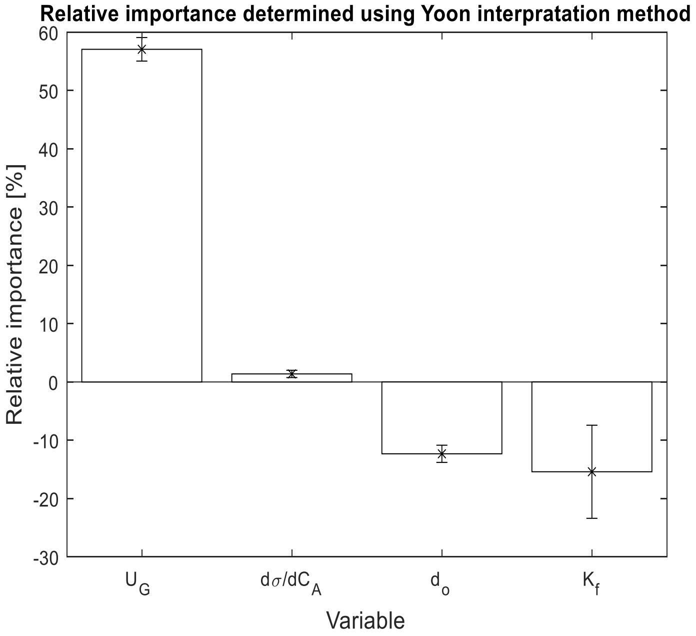


Figure 1. Relative importance of operating parameters using Yoon interpretation method for bubbly regime

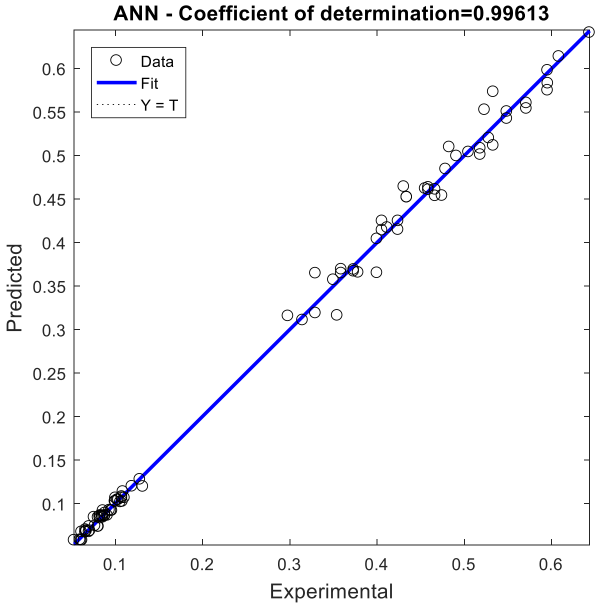


Figure 2. Parity plot of the experimental and predicted values for εG and Wld for bubbly regime

Relative importance of working parameters in the churn turbulent regime

The ANN topology was 4-10-1 for turbulent regime, R^2 was 0.9991. It is interesting to notes from Figure 3 that the surface tension gradient has greater influence than the orifice diameter of the gas distributor. This can be explained that at gas velocities corresponding to the bubble flow, coalescence did not appear. On the other hand, at high gas velocities corresponding to the churn turbulent flow, coalescence was much stronger and the effect of the alcohols to hinder the coalescence was more noticeable. Influence of the superficial gas velocity and the membrane resistance was the same as in the bubble regime.

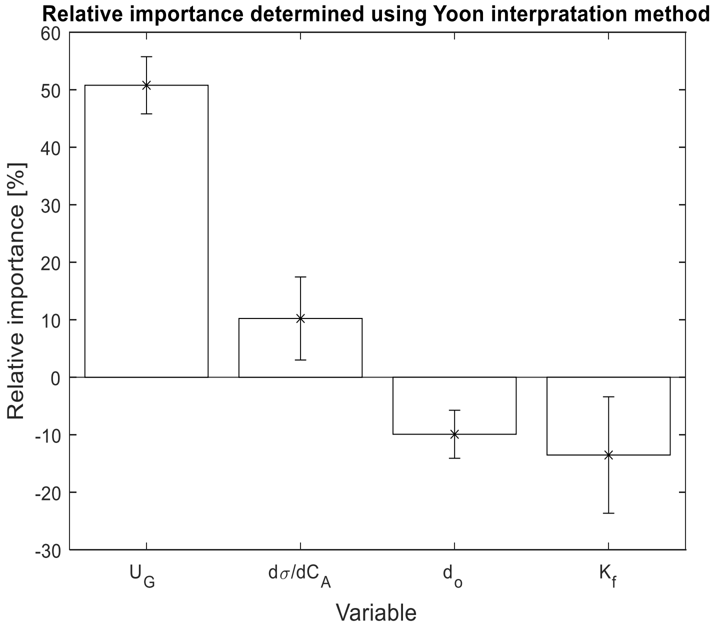


Figure 3. Relative importance of operating parameters using Yoon interpretation method for turbulent regime

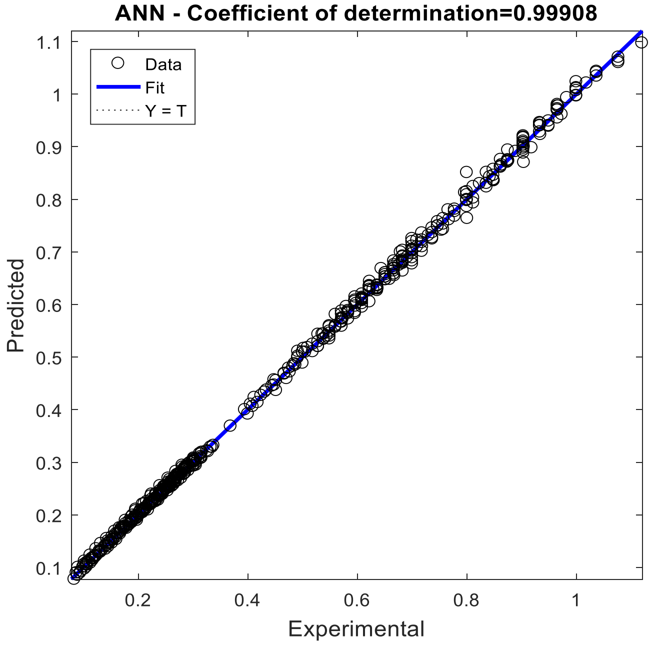


Figure 4. Parity plot of the experimental and predicted values for εG and Wld for turbulent regime

Conclusion

ANN coupled with Yoon's interpretation model showed that can be successfully used to determine relative importance of operating parameters such as superficial gas velocity, surface tension gradient, orifice diameter of gas distributor and the membrane inserted into the downcomer on the gas holdup and downcomer liquid velocity. Results from this study are very important for the scale up and understanding the phenomena that occur in the external loop airlift reactors with and without the membrane.

Acknowledgment

This research was supported by the Ministry of Education and Science and Technological Development of the Republic of Serbia. (Project No. 172025).

References

1. Liu, R., Huang, X., Wang, C., Chen, L., Qian, Y., Study on hydraulic characteristics in a submerged membrane bioreactor process. *Process Biochem*. 2000, 36, 249-254
2. Futselaar, H., Schonewille, H., de Vente, D., Broens, L., NORIT AirLift MBR: side-stream system for municipal waste water treatment. *Desalination* 2007, 204, 1-7
3. Chisti, M.Y., *Airlift bioreactors*, Elsevier Applied Science, London, 1988.
4. Bello, R.A., Robinson, C.W., Moo-Young, M., Liquid circulation and mixing characteristics of airlift contactors. *Can. J. Chem. Eng*. 1984, 62, 573-577
5. Bentifraouine, C., Xuereb, C., Riba, J.-P., Effect of gas liquid separator and liquid height on the global hydrodynamic parameters of an external loop airlift contactor. *Chem. Eng. J*. 1997, 66, 91-95

6. Rujiruttanakul, Y., Pavasant, P., Influence of configuration on the performance of external loop airlift contactors. *Chem. Eng. Res. Des*. 2011, 89, 2254-2261
7. Kojić, P.S., Tokić, M.S., Šijački, I.M., Lukić, N.L., Petrović, D.L., Jovičević, D.Z., Popović, S.S., Influence of the Sparger Type and Added Alcohol on the Gas Holdup of an External-Loop Airlift Reactor. *Chem. Eng. Technol*. 2015, 38, 701-708.
8. Verlaan, P., *Modelling and characterization of an airlift-loop bioreactor*, Wageningen University, Wageningen, Netherlands, 1987.

Cathodic protection of carbon steel in 3%NaCl by Mg doped AlZnSnSi sacrificial anode

C. Oulmas[1, 2], Z. Mekhalif[1], J. Delhalle[1], D. Boughrara[2], S. Boutarfaia[3] & A. Kadri[2]

[1]Laboratoire de Chimie et d'Electrochimie des Surfaces, Université de Namur, 61, Rue de Bruxelles, 5000, Namur, Belgique

[2]Laboratoire de Physique et Chimie des Matériaux, Université Mouloud MAMMERI de Tizi-Ouzou, BP 17 RP, Tizi-Ouzou 15000, Algérie1

[3]Centre de Recherche CRND / COMENA, BP 43, Sebala, Draria, Alger 16050, Algérie

Abstract

AlZnSnSi alloy was prepared using different contents of Mg to be used as anode for cathodic protection of steel (A60) in 0.1M NaCl.

The influence of Mg on the corrosion behavior of AlZnSnSi anode in natural chloride solution were investigated by potentiodynamic measurements, scanning electron microscopy and X-ray energy dispersion. The main precipitates in AlZnSnSiMg alloy are Mg_2Zn *and* Mg_2Si*. The addition of Mg to AlZnSnSi alloy shift the corrosion potential towards more negative direction and gave a good cathodic protection after one month. SEM images show that the presence of Mg in AlZnSnSi alloy produce better and uniform dissolution. RP results confirm that the presence of Mg in the alloy improves the uniform corrosion and the anodic dissolution of AlZnSnSi alloy by reducing polarization resistance values (Rp).*

Keywords: *Cathodic protection, Aluminum alloy, uniform corrosion.*

Introduction

Cathodic protection is the main technique for preventing corrosion on external surfaces of carbon steel parts in the submerged zones of ships, harbor installations and offshore structures that operate in direct contact with seawater [1]. Such protection is used also for internal parts of marine equipment in which seawater flows such as tanks, filters, pumps, valves even if made of corrosion resistant alloy. The combination of cathodic protection and corrosion resistant alloys can be a convenient solution. The cathodic protection of stainless steel can avoid localized corrosion induced by chlorides and makes possible the utilization of alloys with lower contents of chromium and molybdenum compared to the levels needed for the corrosion resistance in seawater, thus allowing the use of less expensive steels.

Aluminum alloys [1,2] are preferentially used in cathodic protection technology of steel because of their properties due to their low cost, low density and theoretical specific capacity ($2980 Ah.Kg^{-1}$). Often aluminum alloys are inhibited by the presence of a passive oxide film, which limits their practical applications [3]. Indeed, the presence of oxides on the surface of these materials induces localized corrosion, which reduces their efficiency. A possible solution is to make it active by the addition of elements such as zinc [4] tin [5], silicon [6], magnesium [7], indium [8], etc. Different microstructures such as grain size, dislocation density and precipitates have various effects on the corrosion behavior of these alloys.

Muller et al. [9] reported that alloying aluminum with 5% Zn results in high activation. Hence, the presence of Sn as an alloying element increases the rates of corrosion. In a more recent work [10, 11], it has been reported that the presence of Sn leads to a more homogenous corrosion. The addition of Mg to Al improves its mechanical properties such as hardness and strength [12].

According to J.Wen et al.[13], the formation of Mg_2Si in the AlZnInMgTi alloy by adding 0.1(wt.%) of Si, causes a higher current efficiency, lower fluctuation of the cathodic current protection (CCP) values and more uniform corrosion compared to the Al-5Zn-0.03In-1Mg-0.05Ti (wt.%) anode.

In this work, the influence of Mg addition to AlZnSnSi alloy is considered for the first time to the elaboration of an alloy with anodic precipitates distributed in the Al matrix. This leads to more uniform dissolution of the anode and then improves the cathodic protection of carbon steel in sodium chloride medium.

Mg_2Si precipitate in chloride environment is very anodic compared to the solid solution. Since Mg_2Si reacts with water to form SiO_2 and MgO [19]. Mg_2Zn precipitates can act as corrosion center and cause the propagation of the corrosion [7]. Therefore, the aim of this work is to combine the generation of both of precipitates to improve the protection of steel in 0.1M NaCl.

Experimental procedure

A. Materials preparation

The aluminum alloys used in this study were elaborated from the pure elements (99.99% Heraeus-GMBH) with the chemical composition, 5% wt. of Zn, 0.25% wt. of Sn, 0.1% wt. of Si, 1.6% wt. of Mg and balance of Al. The elaboration was carried out in a graphite crucible under argon gas at 660°C ± 50°C until the fusion of all the elements, followed by 20 min cooling. Before any characterization, the as-cast aluminum alloys ($\mathrm{S} = 0.63\mathrm{cm}^2$) were mechanically polished (Buehler EcoMet ™ 300 polishing machine) with SiC emery paper up to 1200 grade, then under monocrystalline diamond paste with a particle size of 9 µm, 3 µm and 1 µm on a nylon belt. The substrates are cleaned first with ultrapure water, then with denatured ethanol under ultrasound and finally dried under nitrogen flow. Scanning Electron Microscope (SEM) (JOEL 7500 F) was used to study the alloys microstructures. The structures of the specimens surfaces were identified by XRD using PANALYTICAL X'PERT PRO diffractometer with monochromatic CuKα radiation. (λ=1.5406 Å). The surface roughness (Ra) was measured using a Dektak 08 apparatus controlled by the Dektak 32 software, with a scanning rate of $0.02\mathrm{mm}.s^{-1}$ and a distance measurement of $2.62\mathrm{mm}$.

Cathodic protection tests of steel (S_{steel} (cm) =1/3 S_{anode} (cm)), have been carried out in 0.1M NaCl solution. Anode (alloys) and cathode (steel) are weighted before immersion and coupling in the corrosion environment during 1 month. After the test, the corrosion products are removed and cleaned; samples are weighted again to determine weight loss. One month is adequate to generate sufficient weight loss for accurate measurement.

B. Electrochemical measurements

The electrochemical measurements were performed using a PGSTAT30-AUTOLAB system in a conventional three-electrode cell. A specific software (Autolab Software version 4.8) controls the experimental sequences, acquisition and processing of digital data. Ag-AgCl and Pt were used as the reference and counter electrodes, respectively.

Polarization resistance tests of alloys are obtained according to Ohm's law,$E = Rp \times i$, $\pm 10\, mV/ AgAgCl$.Vs OCP (open circuit potential), therefore the polarization resistance is determined from the slope $\Delta E \,/\, \Delta i\ (\Omega \,/\, cm^2)$, while potentiodynamic polarization tests were obtained at $\pm 200\ mVAgAgCl$ .Vs OCP with a scanning rate of 1 mV/s.

Results and discussions

Microstructure

AlZnSnSi alloy was polished and prepared for physical surface characterization by SEM. EDX analysis has been carried out to determine the chemical composition in (Fig.1). The alloy exhibits a dendric structure with the existence of bright irregular shape spot spread all over the alloy surface. The bright spots are attributed to Zn and Sn elements located at the grain boundary of aluminum matrix. EDX spectra show the presence of elements such as Zn and Sn from the bright spot area (Fig.1. (b-1)), while Al, Zn were detected from the dark spot area (Fig.1.(b-2)). Sn has a low solid solubility in aluminum [14]. It has a tendency to be rejected to interdendrite structure and to diffuse preferentially at the grain boundaries.

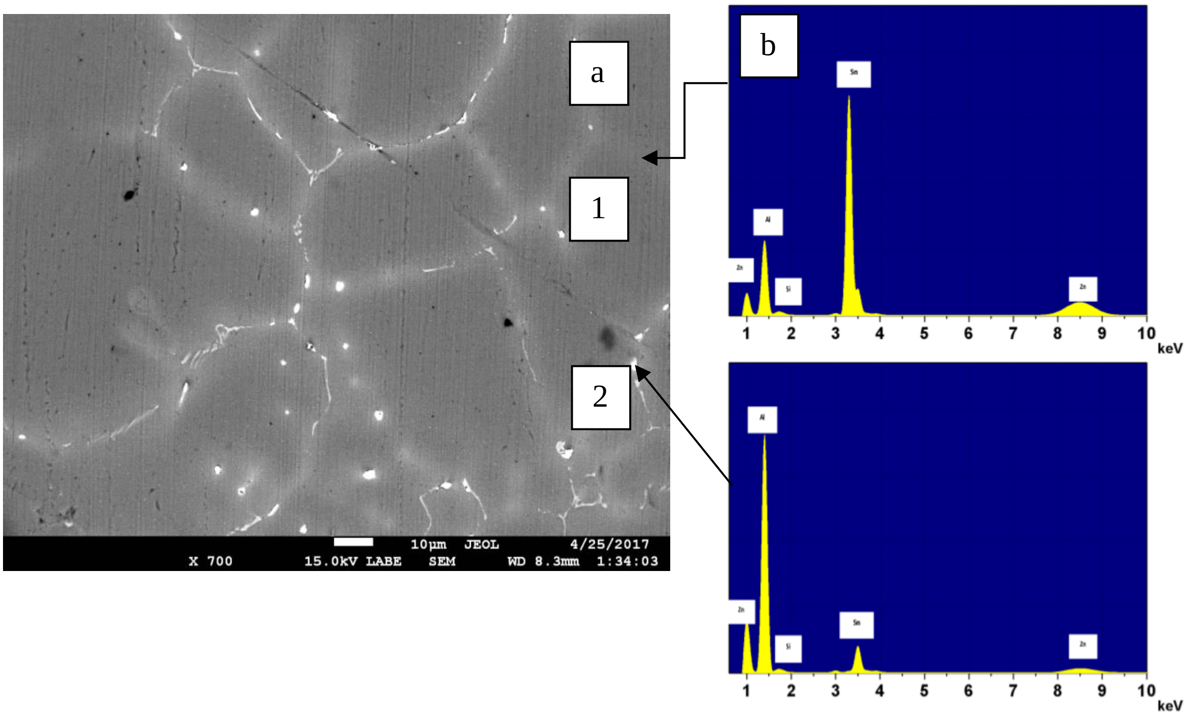


Figure.1.SEM image for (a) polished surface of AlZnSnSi alloy, (b) representative EDX spectra at spot (1) and (2) EDX at spot (2)

The addition of Mg (wt.%) to the alloy decreases the bright precipitates at grain boundaries, which may suggests a good distribution of the Mg atoms in the α-Al solid solution, and cause a phenomenon of uniform corrosion of the surface. According to Jingling et **al. [15]**, the addition of Mg reduces the precipitates, refines the grain, and increases the concentration of Zn in the α-Al matrix.

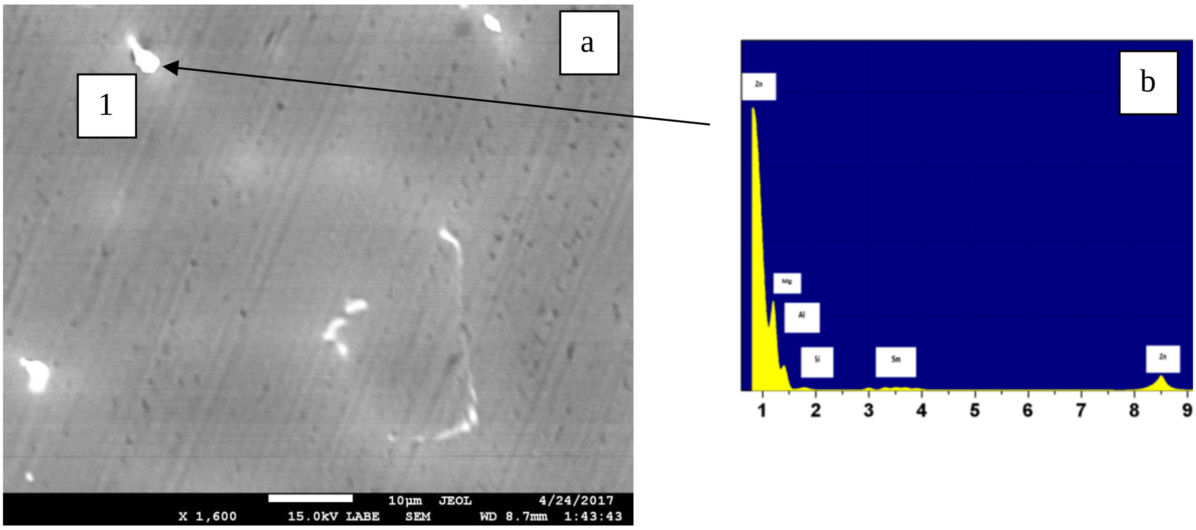


Figure.2. SEM image for (a) polished surface of AlZnSnSiMg alloy and (b) EDX spectra in (b) of Fig 2.a

B. X-ray diffraction analysis

X-ray diffraction analysis pattern indicate the presence of two crystallized intermetallic phases in addition to the α-aluminum matrix, with a magnesium addition in the alloy under consideration. Sn related peaks are not detected which is probably due to its low concentration. By way of illustration, (Fig. 3), shows the X-ray diffraction pattern obtained for the AlZnSnSi and AlZnSnSiMg alloys. These intermetallic phases can be indexed as the intermetallic phases Mg_2Si [16], Zn_2Mg [17].

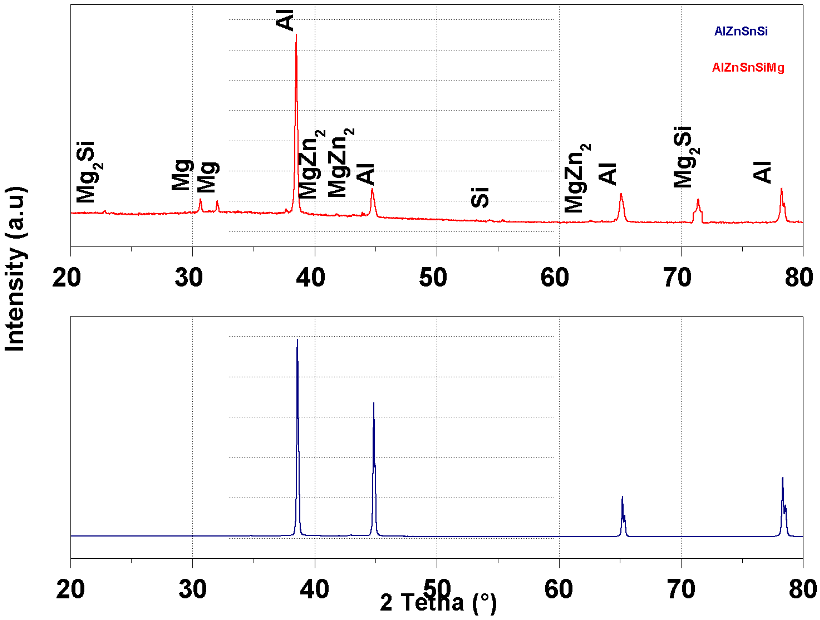


Figure 3:X-ray diffraction pattern of the alloys

As it can be seen in the XRD patterns, there are two kinds of intermetallic precipitates formed in the AlZnSnSiMg alloy.

Silicon, according to the principle of metal solidification, can increase the fluidity of the alloy because it has not only the same crystal structure of face-centered cubes as aluminum. In the other hand, the elements with low melting point such as Zn or Mg are enriched in the liquid ahead of solid-liquid interface during the solidification process, forming the precipitates regions [18].

C. Surface topography study

The surface roughness parameter (Ra) was used to identify the specific topography of surface before and after exposition to corrosive environment.

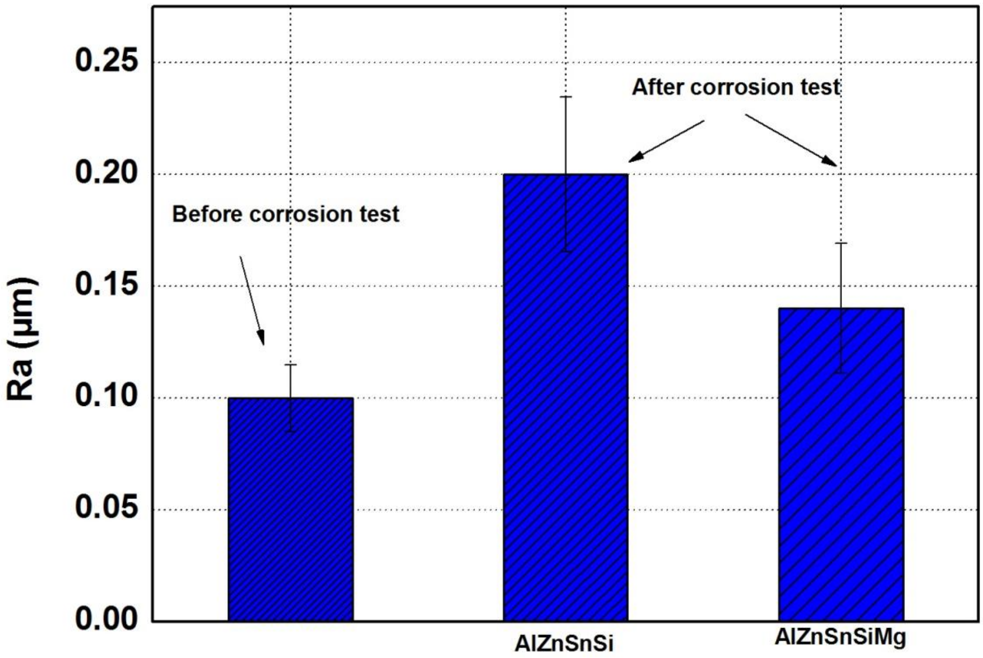


Figure 4: Surface roughness before and after 24 hours of immersion in 3% NaCl aqueous solution

(Figure 4) shows the surface roughness parameter before corrosion test (i.e. after polishing surface), where Ra is similar for both alloys (AlZnSnSi and AlZnSnSiMg).

After corrosion attack, the average surface roughness is comparatively lower with Mg addition to the alloy (AlZnSnSiMg). Mg integrates well in the alloy and contributes to a better dissolution process by the formation of Mg_2Si and $MgZn_2$ with favor a better dissolution process by creating a more homogenous galvanic current.

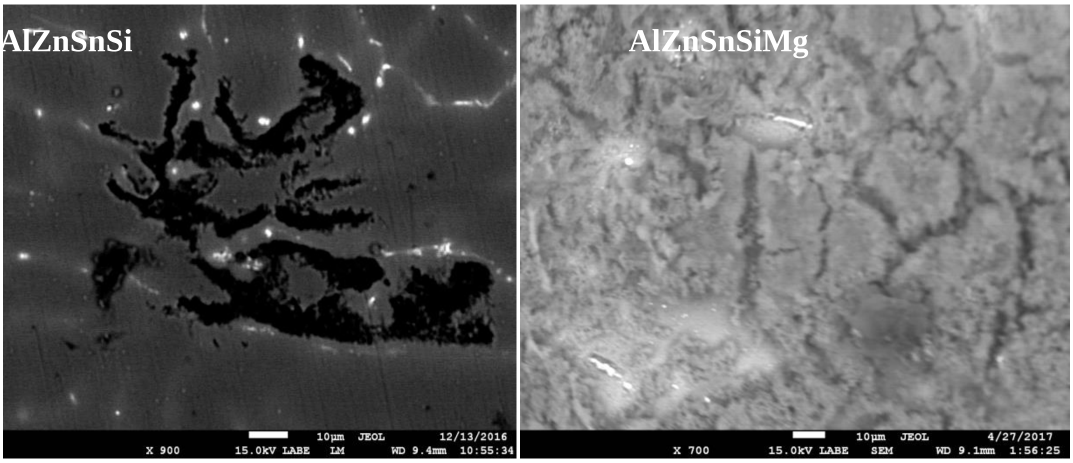


Figure 5: SEM images of the alloys after 24 hours of immersion in 3%NaCl

D. Polarisation Resistance measurements (PR)

The value of the polarization resistance PR of AlZnSnSi and AlZnSnSiMg from the I-E curves after 24 hours of immersion are given in the (Fig. 6).

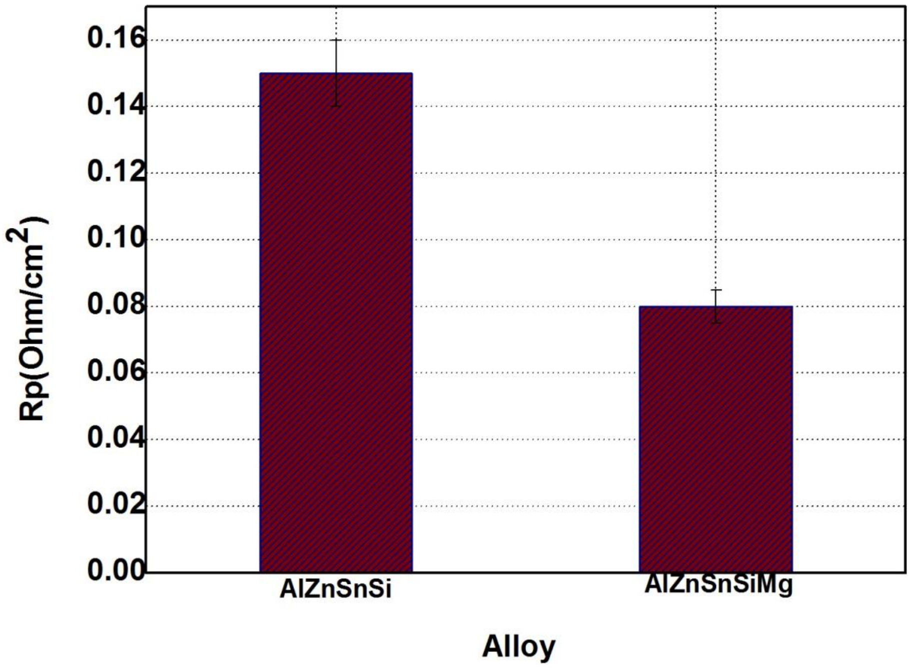


Figure 6: Polarization resistance values after 24 hours of immersion in 3%NaCl aqueous solution

By adding Mg to the alloy, RP decreases from 0.15 Ω/cm^2 to 0.08 Ω/cm^2. For AlZnSnSi, it can be seen that the polarization resistance is larger than the AlZnSnSiMg. This is can be attributed to the anodic behavior of the precipitates formed after the heat treatment which lead to the corrosion of the anode and decrease its polarization resistance in the grain boundary unlike with AlZnSnSiMg where the precipitates are anodic and then their dissolution is done in islets. This low value of RP indicates that Mg plays an activating effect on the alloy by the formation of anodic precipitates.

E. Galvanic Coupling

In order to evaluate the cathodic protection of steel by aluminum anodes, calculations of the anode efficiency have been carried out [19], using measurements of current protection and weight loss of the anode.

$$\boldsymbol{CC_A} = \frac{\boldsymbol{I_g\ \Delta t}}{\mathrm{Wm}} \qquad (\mathbf{1})$$

$$\boldsymbol{Ef_A}(\%) = \frac{\boldsymbol{CC_A}}{\boldsymbol{CC_{th}}} \times \mathbf{100} \quad (\mathbf{2})$$

Table 1: Open circuit potential of alloys measured after 24 hours (OCP), cathodic current and potential protection (CPP, CCP respectively), current capacity and efficiency of the alloys after one moth of immersion in 0.1M NaCl.

	OCP (V/AgAgCl)	**CPP (V/AgAgCl)**	**CCP (μA/cm^2)**	**Current capacity (Ah/Kg)**	**Efficiency (%)**
AlZnSnSi	-0.88	-0.86	100	1000	35.98
AlZnSnSiMg	-1.10	-0.90	130	1800	64.57

Where:

$\mathbf{I_g\ \Delta t = Q = \int_0^t I\ dt}$ A.sec = 1/3600 A.h

Wm: Weight loss of the anode samples

$\mathbf{CC_A}$**:** Actual current capacity

$\mathbf{CC_{th}}$**:** Theoretical current capacity

The addition of Mg and Si displaces the galvanic potential to very electronegative values and above all to the protection potential of the carbon steel (-800 mV / Ag-AgCl, according to the NACE criterion), confirming that these anodes are more active than pure Al and can be used as sacrificial anodes for the protection of carbon steel.

Conclusion

The results presented in this work showed that the addition of Mg and Si in the AlZnSn alloy influence significantly its electrochemical behavior and improve its uniform corrosion. The corrosion potential of AlZnSnSiMg alloy is found more electronegative than without AlZnSnSi.

The current efficiency and capacity of AlZnSnSiMg are higher than AlZnSnSi alloy. The main precipitates in AlZnSnSiMg alloy are Mg_2Si and $MgZn_2$.

Perspectives

Elaboration, of Mg_2Si and Mg_2Zn precipitates, study of their corrosion behavior compared to the Al-Sn matrix, to distinguish the most anodic precipitate and thus which contributes mostly to the sacrificial anode protection of steel in 0.1NaCl medium.

References

1. H. Sun, L. Liu, Y. Li, L. Ma, Y. Yan , Corrosion Science, 77 (2013) 77–87
2. T. Prosek, D. Persson, J. Stoulil, D. Thierry, Corrosion Science, 86 (2014) 231–238
3. S.Lameche-Djeghaba, A.Benchettara, Arab J sci Eng, 39 (2014), 113-122
4. A. E. Ares, L. M. Gassa, Corrosion Science, 59, (2012) 290–306.
5. M.C. Isa, M.Y. Ahmad, A.R. Daud, and M. Daud, Key Engin. Mater, 442 (2010), 322–329
6. L. L. Li, B. Zhang, B. Tian, Y. Zhou, J.Q.Wang, E. H. Han, W. Ke, Journal of Electro chem Soc, 164, (2017),6, 240-249
7. Jingling M, Jiuba W, Wenxia Z, Quanan L, Materials characterization, 65, (2012), 86–92
8. A.G. Munnoz, S.B. Saidman, J.B. Bessone, Corrosion Science 44, (2002) 2171–2182
9. I.L. Muller, J.R. Galvele, Corros. Sci., 17, (1977) 995–1007
10. S. Gudić, I. Smoljko, M. Kliškić, J. Alloys and Comp., 505 (1) 27, (2010) 54–63
11. S.Khireche, D. Boughrara, A. Kadri, L. Hamadou, N. Benbrahim, Corros. Sci., 87, (2014) 504-516
12. Gupta RK, Zhang R, Davies CHJ, Birbilis N, Corrosion (2013); 69:1081e7
13. Jiuba W, Junguang H, Xianwen L, Corrosion Science 53, (2011), 3861–3865.
14. S. L. Erricker and J. D. Scantlebury, Mater. Sci., Forum, 623, (1995) 192-194
15. M. Jingling, W. Jiuba, L. Xudong, Z. Shengli, Y. Yanfu, Rare Metals, 28, (2009) 187-192
16. L. L. Li, B. Zhang,B. Tian, Y. Zhou, J. Q. Wang, E. H. Han and W. Kea, Journal of The Electrochemical Society, 164, (2017), 6, 240-249
17. S. D. Wang1,2, D. K. Xu1, B. J. Wang, L. Y. Sheng, E. H. Han & C. Dong, Scientific reports, Nature, 2017
18. L.F.Mondolfo, Aluminum alloys, structure and properties, Butterworth, New York, 1976
19. EE.Stansbury, R.A.Buchanan, Fundamentals of electrochemical corrosion, 2000

Correlation between crystal orientation and morphology of silver powder particles obtained by different methods of synthesis and conditions of electrolysis

Uzajamna veza između orijentacije kristala i morfologije čestica praha srebra dobijenih različitim metoda sinteze i uslova elektrolize

N. D. Nikolić[1], Lj. Avramović[2], V. M. Maksimović[3], M. M. Pavlović[1], M. Vuković[4], J. S. Stevanović[1], M. G. Pavlović[1]

[1]ICTM-Department of Electrochemistry, University of Belgrade, Njegoševa 12, Belgrade, Serbia

[2]Mining and Metallurgy Institute, Zeleni bulevar 35, Bor, Serbia

[3]Vinča Institute of Nuclear Sciences, University of Belgrade, Belgrade, Serbia

[4]Institute for Multidisciplinary Research, University of Belgrade, Kneza Višeslava 1a, Belgrade, Serbia

[1]IHTM-Centar za elektrohemiju, Univerzitet u Beogradu, Njegoševa 12, Beograd, Srbija

[2]Institut za rudarstvo i metalurgiju, Zeleni bulevar 35, Bor, Srbija

[3]Institut za nuklearne nauke "Vinča", Univerzitet u Beogradu, Beograd, Srbija

[4]Institut za multidisciplinarna istraživanja, Univerzitet u Beogradu, Beograd, Srbija

Abstract

Morphologies of silver powder particles obtained by chemical and electrochemical processes of synthesis were correlated with their crystal structure. Reduction with hydrazine was used for the synthesis of Ag powder by the chemical process. The different kinds of electrolytes (the nitrate and the ammonium ones), regimes of electrolysis (the galvanostatic and the potentiostatic ones) and overpotentials of the electrodeposition were used for production of Ag powders by electrolysis. Morphologies of synthesized particles strongly depended on the method of synthesis and conditions of electrolysis. Agglomerates of approximately spherical grains were formed with hydrazine as the reducing agent. In the dependence of conditions and regimes of electrolysis, various forms of dendritic particles, such as the needle-like, fern-like and pine-like dendrites, were formed. The preferred orientation of Ag particles changed from the strong (111) preferred orientation for the Ag particles obtained by the electrolysis from the nitrate electrolyte in the galvanostatic regime and at the overpotential outside plateau of the limiting diffusion current density to almost random oriented Ag crystallites for chemically synthesized particles and the pine-like particles obtained from the ammonium electrolyte by the galvanostatic and those produced by the potentiostatic regime outside plateau of the limiting diffusion current density.

Izvod

Morfologije čestica praha srebra dobijene hemijskim i elektrohemijskim procesima sinteze su povezane sa njihovom kristalnom strukturom. Proces redukcije sa hidrazinom je bio korišćen za hemijsku sintezu praha srebra. Različite vrste elektrolita (nitratni i amonijačni), režimi elektrolize (galvanostatski i potenciostatski) i prenapetosti elektrohemijskog taloženja su korišćene za proizvodnju praha srebra elektrolizom. Aglomerati približno sferičnih zrna su bili formirani sa hidrazinom kao redukcionim sredstvom. U zavisnosti od uslova i režima elektrolize, različite forme dendritičnih čestica, kao što su igličasti dendriti i oni nalik paprati i boru, su bili formirani.

Preferencijalna orijentacija čestica srebra se menjala od stroge (111) preferencijalne orijentacije za čestice dobijene elektrolizom iz nitratnog elektrolita galvanostatskim režimom i na prenapetosti izvan platoa granične difuzione gustine struje do skoro slučajno orijentisanih kristalita srebra kod hemijski sintetizovanih čestica i onih nalik boru dobijenih iz amonijačnog elektrolita galvanostatskim režimom i potenciostatskim režimom na prenapetosti izvan platoa granične difuzione gustine struje.

The presence and importance of removing the present emissions of gasses as a byproduct of wastewater

Prisustvo i značaj uklanjanja prisutnih štetnih gasova kao nus proizvod otpadnih voda

Nataša Lukić, Milan Radoičić

PUC Belgrade Waterworks and Sewerage, Kneza Miloša 27, Belgrade, Serbia

JKP Beogradski vodovod i kanalizacija, Kneza Miloša 27, Beograd, Srbija

Abstract

The protection and improvement of the environment is one of the most important goals to be achieved by countries, nations, companies and individuals. Realizing the importance of the environment JKP BVK recognized anthropogenic sources of air pollution and about to take measures to reduce the degree of air pollution in urban areas. The goal is to highlight the impact of emissions compounds into the atmosphere from the accumulated waste water gases in facilities of BKS (KCS, sewer manholes, WWTP). Therefore we propose measures for successful resolution of air protection in order to preserve the air as natural values of general interest. Filtration of waste gases prevents their impact on human health and / or the environment. We eliminate emissions into the atmosphere and reducing the vulnerability of the microclimate of the city and the environment. The paper suggests that designers and investors should be to select and apply these methods and devices in the facilities of the sewage system, where they are present and where they are treated sanitary waste water utilities.

Key words: *sewage, municipal waste water, waste gases, ozonation, biomass, mechanical - chemical filter,environment*

Izvod

Zaštita i unapređenje životne sredine je danas jedan od najvažnijih ciljeva koji se postavljaju pred države, narode, kompanije i čoveka. Shvatajući važnost životne sredine JKP BVK je prepoznao antropogene izvore zagađenja vazduha i preduzima mere u cilju smanjenja stepena zagađenosti vazduha u urbanoj sredini. Cilj rada je da se ukaže na uticaj emisije štetnih gasova-jedinjenja u atmosferu iz akumulirane otpadne vode u objektima BKS (KCS, kanalizacioni šahtovi, PPOV). Predlažu se mere za uspešno rešavanje zaštite vazduha u cilju očuvanja vazduha kao prirodne vrednosti od opšteg interesa. Filtracijom otpadnih gasova sprečava se njihov štetan uticaj na zdravlje ljudi i životnu sredinu. Eliminiše se njihova emisija u atmosferu i smanjuje uticaj na ranjivost mikroklime grada i životne sredine. U radu je ukazana i potreba projektanata i investitora za izbor i primenu predloženih postupaka, mera i uređaja u objektima kanalizacionog sistema gde su prisutne ili se tretiraju otpadne vode (komunalne i tehnološke).

Ključne reči : *kanalizacija, komunalne otpadne vode, štetni gasovi, ozonizacija, biomasa, mehaničko – hemijski filter, životna sredina*

Effects of inorganic inhibitors on corrosion properties Al-Mg alloys in 0.5M solution of NaCl

Uticaj neorganskih inhibitora na korozione osobine Al-Mg legura u 0,5M rastvoru NaCl

Dragan Radonjić, Jelena Šćepanović, Darko Vuksanović

University of Montenegro, Faculty of Metallurgy and Technology, Podgorica, Montenegro

Univerzitet u Crnoj Gori, Metalurško-tehnološki fakultet, Podgorica, Crna Gora

Abstract

In this paper was investigated the possibility of inhibiting the corrosion of the Al-Mg alloy alloys with inorganic inhibitors in a 0.5 M NaCl solution at room temperature. Solutions used as corrosion inhibitors are $NaNO_2$ *i* K_2CrO_4*. Their influence on corrosion of Al-Mg alloys was investigated by determining electrochemical parameters by the method of linear polarization and the potentiodynamic method. From the value of the corrosion current density determined by the measurements, the efficiency in the solution with and without the presence of the inhibitor was calculated. The use of inhibitors led to the improvement of corrosion characteristics, which was the aim of this paper.*

Keywords: *corrosion inhibitors, corrosion of metals, aqueous solutions, current density*

Izvod

U ovom radu je ispitana mogućnost inhibicije korozije legure Al-Mg legura neorganskim inhibitorima u 0,5M rastvoru NaCl na sobnoj temperaturi. Kao inhibitor korozije korišćeni su rastvori $NaNO_2$ *i* K_2CrO_4*. Njihov uticaj na koroziju Al-Mg legura ispitivan je određivanjem elektrohemijskih parametara metodom linearne polarizacije i potenciodinamičkom metodom. Iz vrijednosti gustina struje korozije određenih mjerenjima izračunata je efikasnost u rastvoru sa i bez prisustva inhibitora. Korišćenjem inhibitora dovelo je do poboljšanja korozionih karakteristika, što je bio i cilj ovog rada.*

Ključne riječi: *inhibitori korozije, korozija metala, vodeni rastvori, gustina struje*

Uvod

Aluminijumske legure sa magnezijumom kao glavnim legirajućim elementom, serije 5xxx, predstavljaju važnu grupu komercijalnih Al legura koje imaju najveću primjenu u automobilskoj, transportnoj, industriji ambalaže, avioindustriji i raketnoj tehnici.

Glavni doprinos čvrstoći ovih legura daju rastvarajuće ojačavanje i hladna deformacija, a manje ojačavanje granicama zrna i teksturom. Rastvarajuće ojačavanje se postiže prisustvom supstitucijski rastvorenih atoma Mg u čvrstom rastvoru Al. Pored Mg koji je glavni legirajući element i koji ima veliku rastvorljivost u čvrstom rastvoru, ove legure sadrže i druge legirajuće i prateće elemente (Mn, Fe, Si, Cr, Zn, Cu, Ti, Ni), koji zbog ograničene rastvorljivosti grade nerastvorne intermetalne faze. Ovi elementi manje utiču na povećanje čvrstoće od Mg, ali imaju značajnu ulogu na promjene u strukturi koje nastaju u toku zagrijavanja Al-Mg legura, tj. imaju veliku ulogu u kontroli veličine i homogenosti raspodjele zrna, utiču na fizička svojstva i korozionu postojanost. Legure sistema Al-Mg pokazuju odličnu korozionu postojanost i dobru zavarljivost.

Ovaj tip legura bio je predmet velikog broja istraživanja, korišćenjem kako neorganskih, tako i organskih inhibiora korozije u različitim rastvorima. Rezultati polarizacionih mjerenja pokazali su da gentisinska kiselina deluje kao katodni inhibitor legure Al-2,5 Mg u rastvoru NaCl koncentracije 0,5 M [1]. Inhibiciona efikasnost primjenjenog inhibitora najveća je u stanju mirovanja i pri najnižoj temperaturi koja se ispituje, a smanjuje sa povećanjem brzine rotacije elektrode i povećanjem temperature elektrolita. Sinapinska kiselina je proučavana za moguću primenu kao inhibitor korozije Al-2.5 Mg u rastvoru NaCl od 0,5 M [2]. Rezultati polarizacionih mjerenja su pokazali da sinapinska kiselina djeluje kao katodni inhibitor legure Al-2,5 Mg u 0,5 M rastvoru NaCl. Inhibitna efikasnost se smanjuje sa povećanjem temperature elektrolita. Istraživanja [3] su dokazala inhibitorno djelovanje fenolne frakcije vodenog ekstrakta ruzmarina na koroziju legure Al-2,5 Mg u 3% rastvoru NaCl. Dokazano je da je efikasnost aditiva kao inhibitora korozije Al-2,5 Mg legure vrlo dobra, ali postoje razlike u ponašanju inhibicije pojedinih frakcija. Ovo se može pripisati činjenici da svaka od ovih frakcija sadrži različita jedinjenja koja treba identifikovati i objasniti njihov uticaj.

Sprovedena istraživanja u ovom radu imala su cilj da pokažu uticaj hemijskog sastava ispitivanih legura (sa 2,5% Mg i 4,4% Mg) na koroziono ponašanje, kao i da se kvantifikuje brzina korozije praćenjem vrijednosti gustine struje korozije i izračuna efikasnost zaštite u prisustvu primijenjenih neorganskih inhibitora.

Eksperimentalni dio

Legure sistema Al-Mg dobijene su topljenjem u elektrootpornoj peći snage 5,5 kW, čija radna temperatura je 1100 °C. Nakon topljenja u elektrootpornoj peći vršeno je livenje u metalnu kokilu i hlađenje na vazduhu.

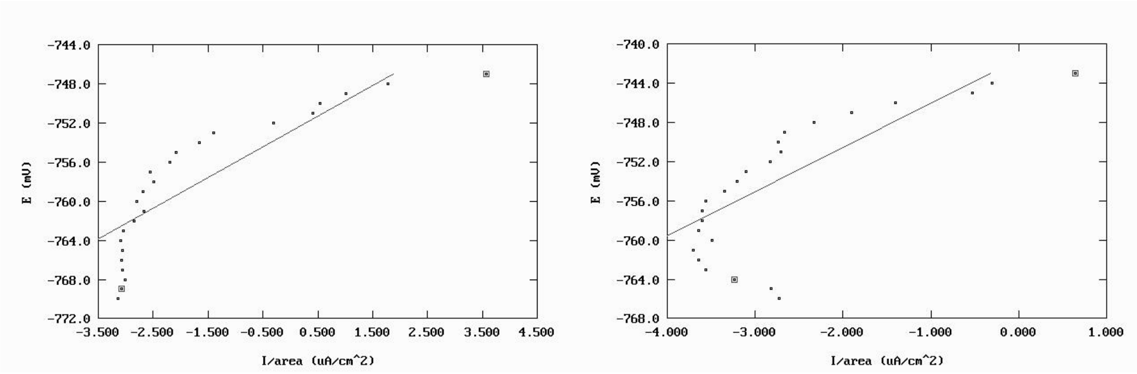
Koroziona i elektrohemijska ispitivanja vršena su na opremi za ubrzana ispitivanja-sistem PAR koji čine: potenciostat-galvanostat model 273, diferencijalni elektrometar, koroziona ćelija K0047, standardna zasićena kalomel elektroda, pomoćne elektrode-valjkasti elektrografit, računar sa korozionim softverom SOFTCORR 352 II i štampač.

U korozioniom istraživanjima korišćene su metode:

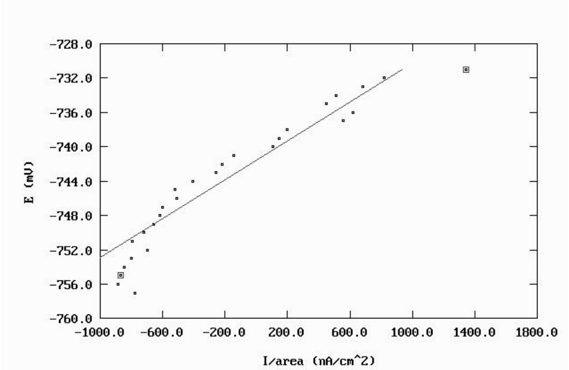
- metoda linearne polarizacije i
- potenciodinamička metoda.

Rezultati i diskusija

Linearnom polarizacijom su dobijeni eksperimentalni dijagrami za legure Al-2,5Mg i Al-4,4Mg u 0,5 M rastvoru NaCl bez inhibitora i sa dodatkom $NaNO_2$ i K_2CrO_4 kao inhibitora korozije u koncentraciji 10^{-4} M. Na slikama 1 i 2 dati su prikazani dijagrami za legure Al-2,5Mg i Al-4,4Mg.



a) *b)*



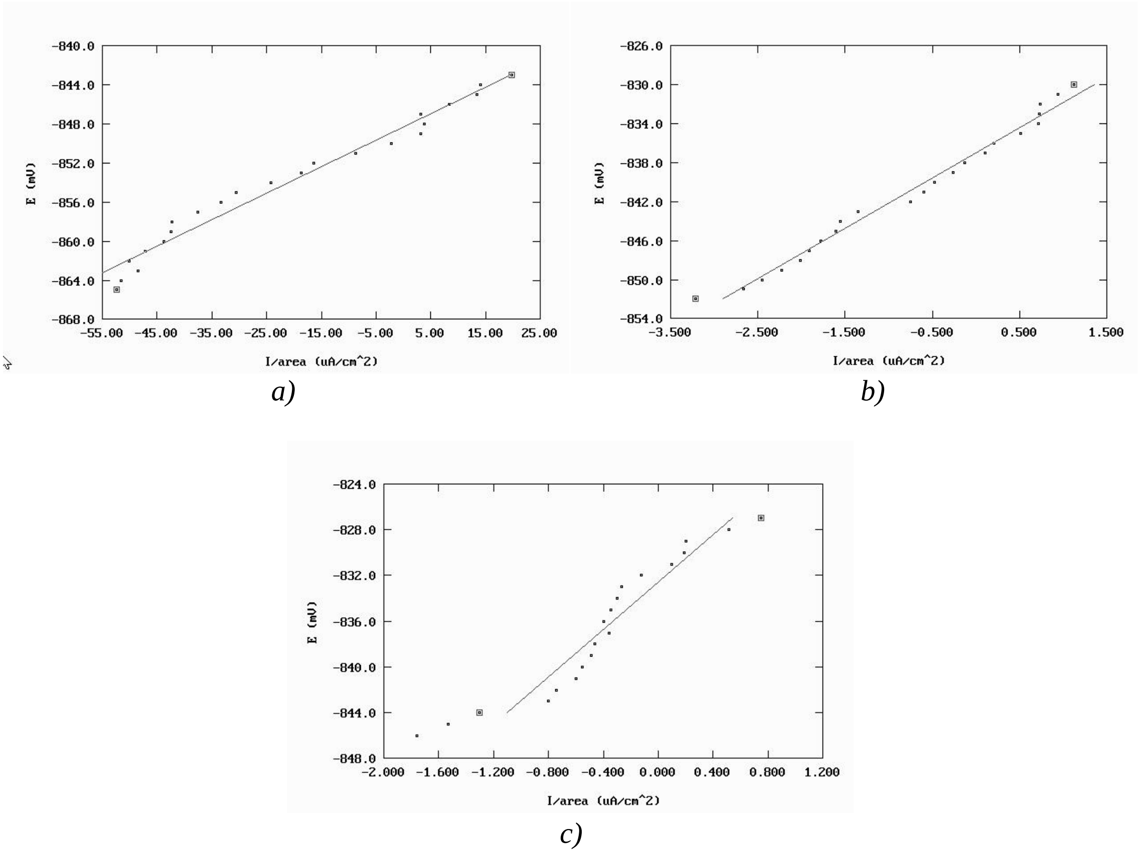
c)

Slika 1. Linearne polarizacije legure Al-2,5Mg:

a) bez dodatka inhibitora

b) u prisustvu 10-4M $NaNO_2$

c) u prisustvu 10-4M K_2CrO_4



a) *b)*

c)

Slika 2. Linearne polarizacije legure Al-4,4Mg:

a) bez dodatka inhibitora

b) u prisustvu 10-4M $NaNO_2$

c) u prisustvu 10-4M K_2CrO_4

Na osnovu prethodno prikazanih linearnih polarizacija, kod obije ispitivane legure, primjetno je pomjeranje potencijala prema pozitivnijim vrijednostima u prisustvu inhibitora, u odnosu na linearnu polarizaciju u rastvoru bez dodatka inhibitora, što pokazuje da dodatak inhibitora utiče je na smanjenje brzine korozije.

U tabelama 1 i 2 prikazane su eksperimentalne vrijednosti polarizacionog otpora (R_p), gustine struje korozije (j_{corr}), potencijala e(j=0) u 0,5M rastvoru NaCl.

Tabela 1. Vrijednosti Rp, j_{corr} i e(j=0) dobijene metodom polarizacionog otpora u prisustvu inhibitora $NaNO_2$

Legura	**Bez inhibitora**			**10^{-4} M $NaNO_2$**		
	e(j=0) [mV]	**Rp [kΩ]**	**j_{corr} [μA/cm^2]**	**e(j=0) [mV]**	**Rp [kΩ]**	**j_{corr} [μA/cm^2]**
Al-2,5Mg	-752,9	3,136	6,924	-741,5	4,517	4,807
Al-4,4Mg	-848,3	0,271	80,11	-837,0	5,176	4,196

Tabela 2. Vrijednosti Rp, j_{corr} i e(j=0) dobijene metodom polarizacionog otpora u prisustvu inhibitora K_2CrO_4

Legura	**Bez inhibitora**			**10^{-4} M K_2CrO_4**		
	e(j=0) [mV]	**Rp [kΩ]**	**j_{corr} [μA/cm^2]**	**e(j=0) [mV]**	**Rp [kΩ]**	**j_{corr} [μA/cm^2]**
Al-2,5Mg	-752,9	3,136	6,924	-741,5	11,28	1,924
Al-4,4Mg	-848,3	0,271	80,11	-832,6	10,37	2,095

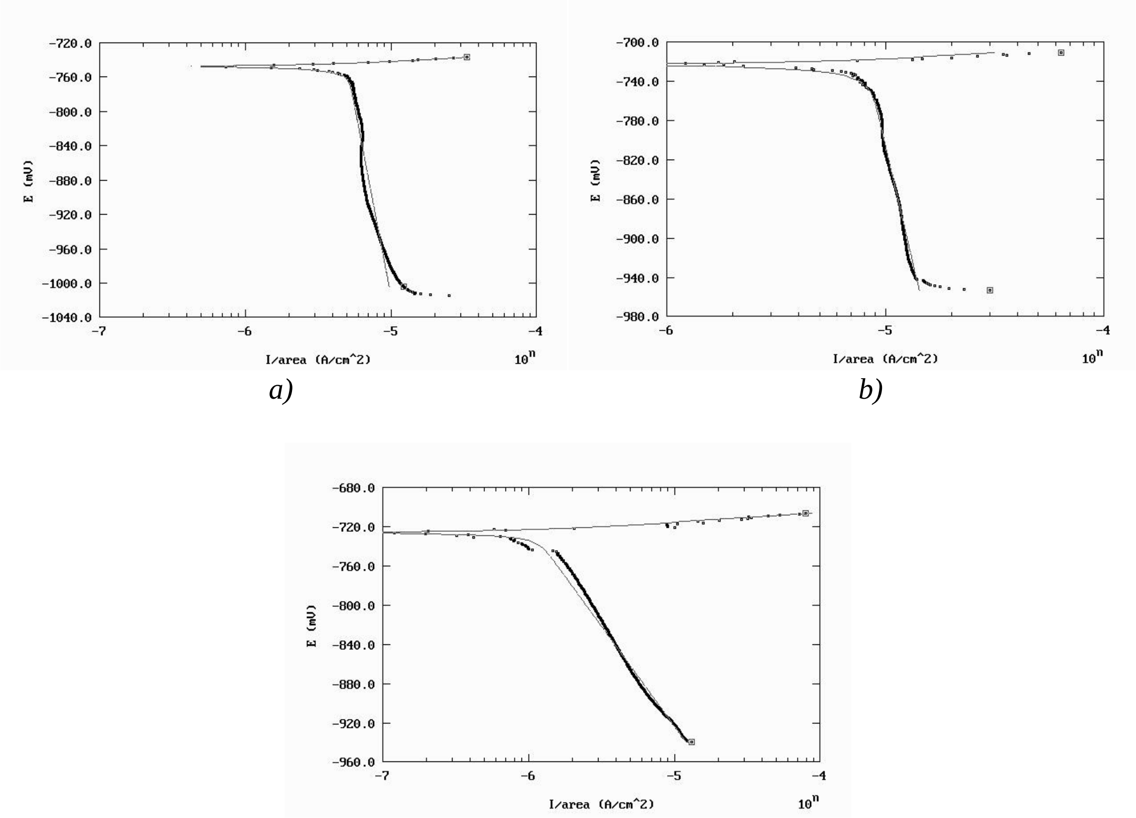
Na osnovu dobijenih vrijednosti gustine struje korozije i polarizacionog otpora legura sistema Al-Mg uočeno je da dodatak inhibitora u osnovni rastvor utiče na povećanje vrijednosti Rp i smanjenje vrijednosti j_{corr}. Efikasnost zaštite izračunata je iz eksperimentalnih rezultata prikazanih u tabelama 1 i 2, prema jednačini [4]:

$$\eta = \frac{j_{corr} - (j_{corr})_{inh}}{j_{corr}}$$

Tabela 3. Efikasnost zaštite ispitivanih Al legura u prisustvu organskih inhibitora, osnovni rastvor 0,5M NaCl

Legura	**10^{-4}M $NaNO_2$**	**10^{-4}M K_2CrO_4**
Al-2,5Mg	30,57%	72,21%
Al-4,4Mg	94,76%	97,38%

Na slikama 3 i 4 prikazane su potenciodinamičke katodne i anodne polarizacione krive ispitivanih legura sistema Al-Mg u 0,5M rastvoru NaCl bez inhibitora i sa dodatkom inhibitora u koncentraciji 10^{-4} M.



a) *b)*

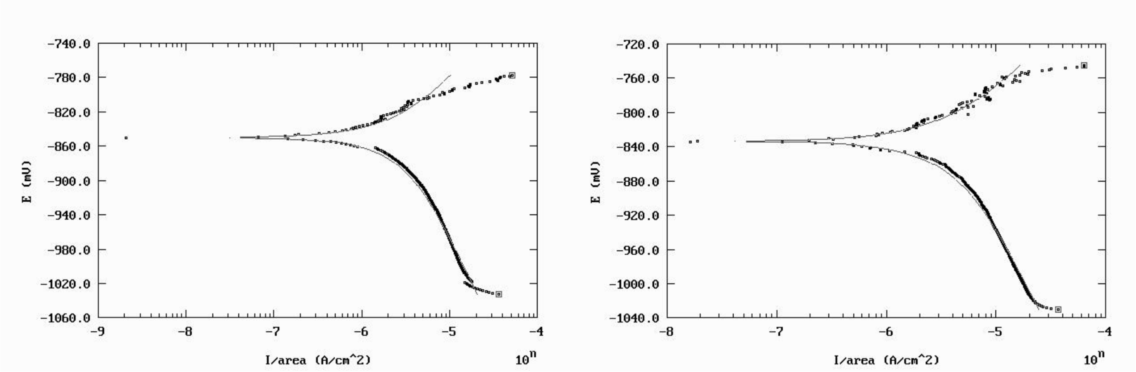
c)

Slika 3. Potenciodinamičke katodne i anodne polarizacione krive legure Al-2,5Mg:

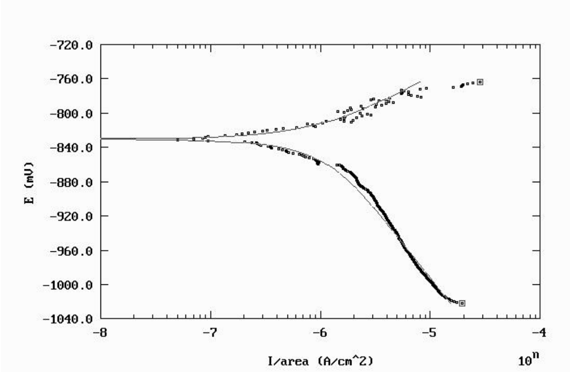
a) bez dodatka inhibitora

b) u prisustvu 10-4M NaNO$_2$

c) u prisustvu 10-4M K$_2$CrO$_4$



a) *b)*



c)

Slika 4. Potenciodinamičke katodne i anodne polarizacione krive legure Al-4,4Mg:
a) bez dodatka inhibitora
b) u prisustvu 10^{-4}M $NaNO_2$
c) u prisustvu 10^{-4}M K_2CrO_4

Kinetički parametri ispitivanog korozionog procesa: korozioni potencijal, katodni i anodni Tafelov nagibi bez prisustva inhibitora kao i u prisustvu inhibitora određeni na osnovu potenciodinamičkih krivih. Eksperimentalni rezultati pokazuju da dodatak oba inhibitora pomjera E_{corr} ka pozitivnijim vrijednostima usled smanjenja brzine anodne reakcije. Ova činjenica ukazuje da su ispitivani inhibitori adsorbovani na anodnim mjestima površine legure, usled čega sprečavaju reakciju rastvaranja legure i na taj način kontrolišu proces korozije [5]. Inhibitor može biti klasifikovan kao katodni ili anodni tip inhibitora ukoliko su promjene u vrijednostima E_{corr} veće od 85 mV [6]. Ekpperimentalni rezultati pokazuju da su promjene korozionog potencijala znatno manje, (do 25 mV) pa su $NaNO_2$ i K_2CrO_4 inhibitori mješovitog tipa. Neznatne promjene vrijednosti anodnih Tafelovih nagiba, b_a u prisustvu oba inhibitora govore da korišćeni inhibitori ne mijenjaju mehanizam anodne reakcije, vec adsorpcijom na povšini legure regulišu brzinu korozionog procesa [7,8]

Tabela 5. Kinetički parametri korozionog ponašanja Al legure u prisustvu $NaNO_2$

	Bez inhibitora			**10^{-4} M $NaNO_2$**		
Legura	**E_{corr} [mV]**	**b_k (mV/dec)**	**b_a (mV/dec)**	**E_{corr} [mV]**	**b_k (mV/dec)**	**b_a (mV/dec)**
Al-2,5Mg	-747,4	886,7	11,4	-723,3	953,0	17,93
Al-4,4Mg	-849,6	213,5	120,8	-833,4	254,3	136,8

Tabela 6. Kinetički parametri korozionog ponašanja Al legure u prisustvu K_2CrO_4

	Bez inhibitora			**10^{-4} M K_2CrO_4**		
Legura	**E_{corr} [mV]**	**b_k (mV/dec)**	**b_a (mV/dec)**	**E_{corr} [mV]**	**b_k (mV/dec)**	**b_a (mV/dec)**
Al-2,5Mg	-747,4	886,7	11,4	-726,9	203,8	10,58
Al-4,4Mg	-849,6	213,5	120,8	-730,0	162,2	71,47

Zaključak

Koroziona istraživanja legura Al-2,5Mg i Al-4,4Mg u vodenom rastvoru NaCl bez i sa uticaja korišćenih inhibitora pokazuju da je hemijski sastav ispitivanih uzoraka pravilno odabra, naročito za leguru Al-4,4Mg.

Najveću efikasnost zaštite pokazala je Al-4,4Mg (97,38%) sa dodatkom K_2CrO4 kao inhibitora. Uzimajući u obzir sve rezultate, može se zaključiti da veću prosječnu efikasnost ima K_2CrO4, u odnosu na $NaNO_2$. Uticaj korišćenja inhibitora naročito je izražen kod legure Al-4,4Mg, kod koje je prosječna efikasnost zaštite oko 96 %.

Na osnovu prethodno iznesenog, uticaj korišćenih inhibitora je veoma pozitivan na smanjenje brzine korozionog procesa u ispitivanom rastvoru NaCl.

Literatura

1. L. Vrsalović, M. Kliškić, S. Gudić, I. Smoljko, Corrosion inhibition of Al-Mg alloy by genttisic acid, Indian Journal of Chemical Technology, Vol. 17, March 2010, pp. 89-94.
2. L. Vrsalović, M. Kliškić, J. Radošević, S. Gudić, Sinapinic acid as Al–2.5Mg alloy corrosion inhibitor in sodium chloride solution, Journal of Applied Electrochemistry, March 2007, Volume 37, Issue 3, pp 325–330.
3. M. Kliškić, J. Radošević, S. Gudić, V. Katalinić, Aqueous extract of Rosmarinus officinalis L. as inhibitor of Al–Mg alloy corrosion in chloride solution, Journal of Applied Electrochemistry, July 2000, Volume 30, Issue 7, pp 823–830.
4. A.R.Despić, J. Radošević, M. Kliskić, Inhibition of cathodic corrosion of aluminium, 7th European Symposium on Corrosion Inhibitors, N. 9, 1990, p 1119-1124.
5. S.A. Umoren, I. B. Obot, E.E.Ebenso, P. C. Okafor, O.Ogbobe and E. E. Oguzie, “Gum Arabic as potential corrosion inhibitor for aluminum in alkaline medium and its adsorption characteristics”,Anti - Corrosion Methods & Materials, vol. 53, pp. 277- 282 , 2006.
6. Liu, F.G.; Du, M.; Zhang, J.; Qiu, M. Electrochemical behavior of Q235 steel in saltwater saturated with carbon dioxide based on new imidazoline derivative inhibitor. Corros. Sci. 2009, 51, 102–109.
7. Magda Ameer, Azza Ghoneim, Amany Fekry, Electrochemical Corrosion Inhibition of Al -Alloy in Phosphoric Acid , Chemistry and Materials Research, ISSN 2225-0956 , Vol 2, no.1, 2012
8. Ivana Jevremović, Vesna Misković-Stanković, The Inhibitive effect of ethanolamine on corrosion behavior of aluminium in NaCl solution saturated with CO, Association of Metallurgical Engineers of Serbia, UDC: 620.193/.196:669.711 ; 620.197.

Effect of corrosion propagation in industrial aggressive environment and in salt chamber onto strength of axially tensioned element

Uticaj propagacije korozije u industrijski agresivnim sredinama i u slanoj komori na nosivost aksijalno zategnutih elemenata

Jelena Stanković[1], Zoran Mišković[2], Miomir Pavlović[3], Dragica Jevtić[2], Zlatko Marković[2]

[1]Mining and Metallurgy Institute Bor, Zeleni Bulevar 35, 19210 Bor, Serbia

[2]University of Belgrade, Faculty of civil engineering, Bulevar kralja Aleksandra 73,Belgrade, Serbia

[3]University of Belgrade, Faculty of Technology and Metallurgy, Karnegijeva 4, Belgrade, Serbia

[1]Institut za rudarstvo i metalurgiju u Boru, Zeleni Bulevar 35, 19210 Bor, Srbija

[2]Univerzitet u Beogradu, Građevinski fakultet, Bulevar kralja Aleksandra 73, Beograd, Srbija

[3]Univerzitet u Beogradu, Tehnološko-metalurški fakultet, Karnegijeva 4, Beograd, Srbija

Izvod

U ovom radu je prikazana degradacija materijala usled korozije građevinskog čelika, u prisustvu korozionih agenasa u neposrednoj blizini industrijskog kompleksa RTB-a u Boru, kao i uporedna analiza sa rezultatima dobijenih iz slane komore. Ispitivanje opšte korozije sprovedeno je blizu fabrike sumporne kiseline i pored stanice automatskog monitoring kvaliteta vazduha u Boru u vremenu od 6 meseci, kao i u slanoj komori u trajanju od 120h i 240h. Rezultati su upoređeni sa etalonskim uzorcima čuvanim u laboratoriji. Za procenu korozione otpornosti materijala korišćena je metoda zasnovana na merenju gubitka mase. Uzorci su pravaougaoni, dimenzija usvojenih na osnovu standard EN 10002-1. Korišćeni čelik je S235, a njegove mehaničke karakteristike su dobijene iz testa zatezanja.

Ključne reči: *opšta korozija, gubitak mase, sumporna kiselina, slana komora*

Abstract

The aim of this paper is deterioration of physical and mechanical properties of structural steel due to corrosion caused by the presence of corrosive agents in the industrial complex of RTB Bor and also comparative analysis with the results obtained from the salt chamber. Testing of general corrosion in atmosphere were close to the sulfuric acid factory and next to station of automatic monitoring of air quality in Bor. Time of exposure were 6 months. Testing in salt chamber were 120h and 240h. The results would be compared with the etalon samples. For the evaluation of corrosion resistance of metals can be used methods which are based on measuring mass loss. Investigations were carried out on test pieces of rectangular cross section, whose dimensions were adopted according to EN 10002-1. The material used is a commercial steel S235. Its mechanical properties are obtained by tensile tests.

Keywords: *general corrosion, mass loss, sulfuric acid, salt chamber*

Uvod

Pod korozijom se podrazumeva postepeno razaranje metala usled interakcije metal-sredina. Ovaj proces u opštem slučaju zavisi od sledećih faktora: od vrste metala, odnosno od sastava i strukture legure, od hemijske prirode sredine, tj. od procentualnog sadržaja agresivnih supstanci u njoj i od temperature sredine. Za ocenu korozione otpornosti metala najčešće se koriste metode koje se zasnivaju na merenju gubitka mase ili na merenju dubine korozionog razaranja uzoraka koji su bili izloženi delovanju agresivne sredine tokom određenog vremena. Stepen korozione otpornosti metala može se vrlo pouzdano utvrditi i ispitivanjem mehaničkih svojstava metala. Postupak se svodi na upoređivanju pojedinih mehaničkih karakteristika dve grupe uzoraka: grupe uzoraka koji su bili izloženi delovanju određenih agresivnih agenasa i grupe uzoraka koji nisu bili izloženi ovom delovanju. Prema karakteru korozione sredine razlikuju se atmosferska, podvodna, zemljišna i druge vrste elektrohemijske korozije. Atmosferska korozija je značajan problem usled uništavanja različitih materijala, naročito metala i njihovih legura. Istraživanje korozije u industrijski zagađenim sredinama je jako bitno, pošto je korozija faktor koji utiče na nosivost i trajnost čeličnih konstrukcija, čime izaziva i ogromne troškove na održavanju konstrukcija. [4]

Korozioni proces se najbrže razvija u toku zimskih meseci usled povećanja koncentracije zagađivača u vazduhu, kao što su SO_2, CO_2, hloridni joni i prašina. Razne kombinacije ovih faktora su tipične za industrijsku sredinu. Najbitniji klimatski faktori koji utiču na korozioni proces su relativna vlažnost vazduha, broj sunčanih sati, temperatura vazduha i metalne površine, brzina vetra i trajanje i frekvencija kiše, rose i magle. Kondenzacija se smatra važnim uzročnikom korozije metala. Njeno formiranje zavisi od relativne vlažnosti i od promene temperature. Kondenzacija ne pere metalne površine, tako da je koncentracija zagađenja relativno visoka i može biti agresivnija od kiše. Kiša izaziva povećano formiranje tankog sloja vode i korozionih agenasa kao što su H^+ i SO_4^{2-}, ali takođe može oprati kontaminirane površine. Atmosferska korozija metala je značajna kada su inhibitori korozije prisutni u slojevima vode, čime se povećava njena agresivnost. Hloridni joni i SO_2 su najčešći i najbitniji atmosferski korozioni agensi. Standard ISO 9223 se zasniva na određivanju nivoa ova dva kontaminirajuća agensa kako bi se klasifikovala atmosferska korozija. [1]. Na karakter i brznu korozije, pored navedenih činilaca, mnogo utiče i naponsko stanje posmatranog metalnog elementa. Ispitivanja su pokazala da naponi zatezanja posebno imaju velikog uticaja na ubrzanje korozionog procesa. Ovo se objašnjava razaranjem zaštitne prevlake oksida i obrazovanjem mikroprslina. U takvim slučajevima se govori o naponskoj koroziji.

Sva koroziona razaranje utiču na nosivost čeličnih konstrukcija, pa samim tim povećavaju troškove održavanja. Laboratorijska ispitivanja imaju zadatak da daju približne rezultate kao i ispitivanja korozije na atmosferskim stanicama, samo za ubrzano vreme. Cilj je dobiti iste rezultate za kraće vreme, čime se postižu velike uštede u ceni koštanja procesa i njegovog praćenja u industrijskim postrojenjima.

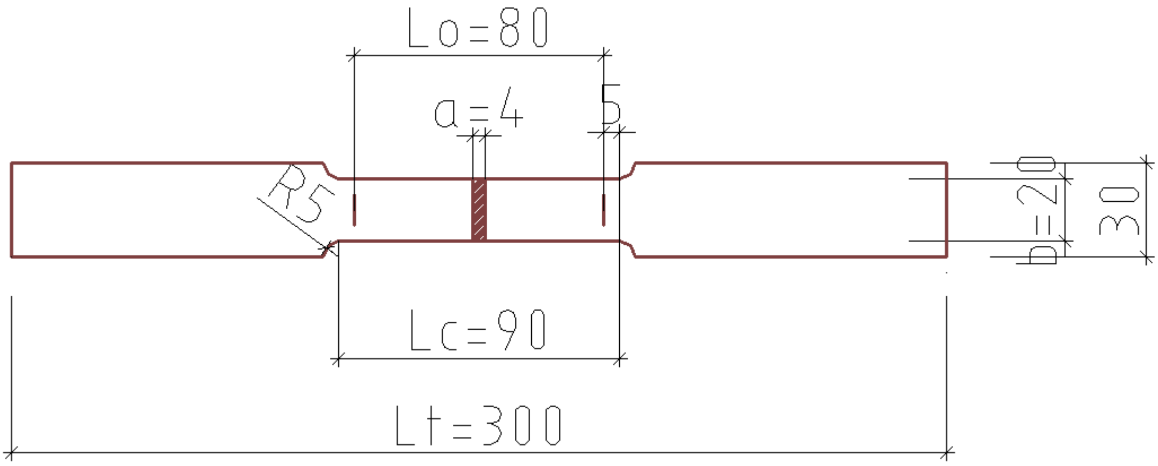
Slika 1 – Postavljanje uzoraka na terenu

Eksperiment

Predmet istraživanja su fizičko-mehanička svojstva konstrukcionog čelika usled propagacije korozije izazvane prisustvom korozionih agenasa u industrijskoj sredini kao što je neposredna okolina RTB-a Bor. Ispitivanje opšte korozije se vrši na terenu, u odabranim atmosferskim korozionim stanicama. U ovom eksperimentu izabrane su lokacije u blizini fabrike sumporne kiseline i pored stanice automatskog monitoringa kvaliteta vazduha u Boru (slika 1). Izlaganje uzoraka (čeličnih epruveta) je trajalo 6 meseci. Uzorci su postavljeni na drvenom ramu tako da najmanjom površinom naležu na njega. Postavljeni su pod uglom od 45° u odnosu na teren, kao horizontal, i okrenuti prema jugu, što se u velikom broju ispitivanja smatra kao položaj u kome je najveća površina uzorka zahvaćena korozijom u najdužem vremenskom interval [2].

Takođe, određeni broj uzoraka je ispitivan u komorama za ubrzano starenje (slane komore). Izlaganje NSS testu (test sa neutralnim sprejem) na osnovu standard ISO 9227 je trajalo 120h i 240h. Ovaj standard se primenjuje na metale i njegove legure, a vreme ispitivanja je izabrano analizom predhodnih sličnih istraživanja, sprovedenih u sredinama sa povećanim sadržajem sumpora u vazduhu, sa ciljem da se razultati uzoraka izloženi atmosferskim uticajima poklope sa rezultatima iz slane komore. Svi uzorci su upoređeni sa etalonskim uzorcima koji su čuvani u laboratorijskim uslovima, u eksikatoru sa silika-gelom. Za ocenu korozione otpornosti metala koristiće se metode koje se zasnivaju na merenju gubitka mase uzoraka koji su bili izloženi delovanju agresivne sredine tokom određenog vremena.

Ispitivanja su izvedena na čeličnim epruvetama, čije su dimenzije usvojene na osnovu standarda EN 10002-1 (slika 2). Materijal koji se koristi je komercijalni čelik S235. Njegove mehaničke karakteristike su dobijene ispitivanjem zatezanjem. Uopšeno, nakon 6 meseci izlaganja [3], sve epruvete su bile 100% prekrivene koroziom.



Slika 2 – Dimenzija uzorka

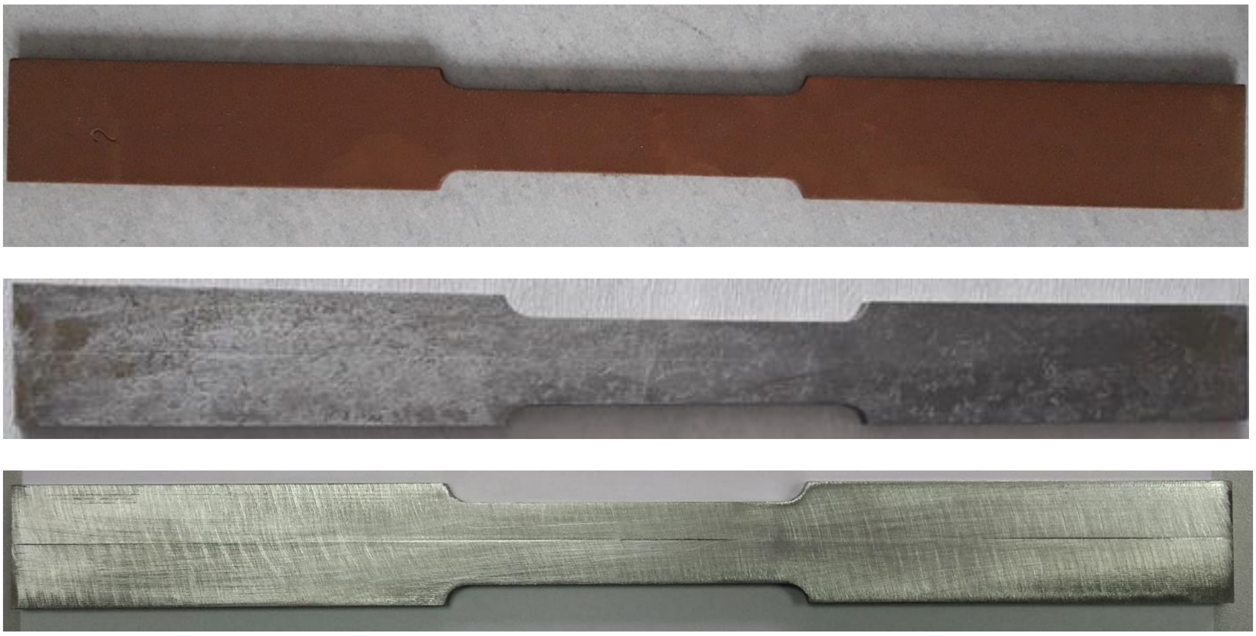
Analiza rezultata

Nivo degradacije mehaničkih karakteristika i promena mase usled korozije na uzorcima nakon 6 meseci izlaganja atmosferskim uticajima u Boru, na dva lokaliteta, zatim na uzorcima izloženim 120h i 240h u slanoj komori i na uzorcima čuvanim u laboratorijskim uslovima su prikazani u Tabeli 2. Uzorci sa oznakom 1 su debljine 4mm, 3 su 6mm, a 5 su 8mm (tabela 1). Oznaka E označava etalonske uzorke, MP su uzorci pored stanice automatskog monitoringa kvaliteta vazduha (kako bi se u daljem istraživanju izvela korelacija između nivoa korozije i procentualnog sadržaja korozionih inhibitora u vazduhu). Uzorci AF su smešteni u neposrednoj blizini fabrike sumporne kiseline. SSI je oznaka uzoraka izloženih NSS testu u trajanju od 120h, a SSII izloženih 240h.

Svi navedeni uzorci su predhodno mereni, izlagani odgovarajućim agresivnim sredinama i ponovo mereni, kako bi se odredila promena mase. Produkti korozije sa svih uzoraka, kao i sa kontrolnih, etalonskih, su skidani po standardu SRPS C.A5.005 u rastvoru hlorovodonične kiseline, heksametiltetraamina i destilovane vode. Na epruvetama izlaganim atmosferskim uticajima prvo su produkti skidani mehaničkim putem, a nakon toga i hemijskim, u trajanju definisanim u standardu. Etalonski uzorci su povinuti istom postupku, kako bi se uračunali i gubici mase, usled eventualnog dejstva na osnovni materijal.

Tabela 1 – Klasifikacija uzorka

Oznaka	**Lokacija uzorka**	**Period izlaganja**	**Oznaka uzorka**					
E	Etalon (laboratorija)	6 meseci	E1	E2	E3	E4	E5	E6
AF	Fabrika sumporne kiseline	6 meseci	AF1	AF2	AF3	AF4	AF5	AF6
MP	Stanica automatskog monitoringa kvaliteta vazduha u Boru	6 meseci	MP1	MP2	MP3	MP4	MP5	MP6
SSI	Uzorci iz slane komore	120h	SSI-1	SSI-2	SSI-3	SSI-4	SSI-5	SSI-6
SSII	Uzorci iz slane komore	240h	SSII-1	SSII-2	SSII-3	SSII-4	SSII-5	SSII-6



Slika 3 – Površina uzorka nakon 6 meseci izlaganja pored fabrike sumporne kiseline, nakon 240h u slanoj komori i etalonskog uzorka (gledano odozgo na dole)

Iz navedenih rezultata (tabela 2), uočljivo je da je procentualni gubitak mase uzoraka pored fabrike sumporne kiseline daleko veći nego na uzorcima smeštenim pored merne stanice, koja je 4 kilometara udaljena od fabrike. Samim tim, sila koju ove epruvete mogu da prime je manja. Ovaj rezultat je očekivan, jer je u blizini fabrike sumporne kiselina procentualni sadržaj ove supstance u vazduhu najveći, dok se sa udaljavanjem smanjuje.

Takođe, iz ove tabele je uočljivo da je gubitak mase kod epruveta izloženih atmosferskim uticajima znatno veći, nego kod istih uzoraka izloženih uticajima u slanoj komori, za približno iste vrednosti sile kidanja koju ove epruvete mogu da prime. Ovaj podatak nedvosmisleno pokazuje da je kod uzoraka izloženih atmosferskim uticajima naglašena uniformna korozija, što je i očekivano, dok su kod uzoraka iz slane komore prisutni i drugi tipovi korozije, kao što je pitting ili tačkasta korozija, što je uočljivo na samom izgledu površine uzoraka (slika 3).

Tabela 2 – Uporedne vrednosti promene mase i sile kidanja na uzorcima iz etalona, izlaganim atmosferiliji i u slanoj komori

Oznaka uzorka		**Debljina uzorka (mm)**	**Masa pre izlaganja (g)**	**Masa posle izlaganja (g)**	**Razlika u promeni mase (g)**	**Razlika u procentima**	**Sila kidanja (N)**
E	E1	4	254,654	254,570	0,084	3,299%	32158
	E3	6	387,606	387,563	0,043	1,109%	51727
	E5	8	521,467	521,440	0,027	0,518%	63597
AF	AF 1	4	254,398	247,911	6,487	2,550%	30291
	AF 3	6	383,004	375,612	7,392	1,930%	48012
	AF 5	8	519,034	511,258	7,776	1,498%	61680
MP	MP 1	4	256,429	254,315	2,114	0,824%	31164
	MP 3	6	385,095	382,778	2,317	0,602%	50174
	MP 5	8	521,210	518,870	2,340	0,449%	63303
SSI	SSI 1	4	256,108	254,603	1,505	0,588%	30417
	SSI 3	6	386,304	384,944	1,360	0,352%	51963
	SSI 5	8	522,374	521,100	1,274	0,244%	62563
SSII	SSII-1	4	255,815	254,178	1,637	0,640%	31094
	SSII-3	6	384,556	382,349	2,207	0,574%	50296
	SSII	8	507,020	505,051	1,969	0,388%	60053

	-5						

Međutim, na osnovu sila kidanja, može se zaključiti da vremenu izlaganja od 6 meseci u industrijskoj sredini sa povećanim sadržajem SO_2 u vazduhu odgovara period izlaganja u slanoj komori sa neutralnim rastvorom (NSS test) između 120h i 240h, pošto se između ovih vrednosti može izvesti dobra korelacija. Ovim se dokazuje da u tačno dirigovanim laboratorijskim uslovima, sa većom ili manjom tačnošću, može se simulirati atmosferska korozija industrijskih sredina, čime se eksperimentalni proces pojednostavljuje i ubrzava.

Zaključci

Dobijeni rezultati i podaci iz ovog rada treba da daju doprinos u sagledavanju i proučavanju problema nosivosti i trajnosti korozijom oslabljenih čeličnih konstrukcija u industriskim sredinama, gde postoje mnogobrojni inhibitori atmosferske korozije. Pre svega, potrebno je u realnim uslovima eksploatacije proveriti laboratorijske ubrzane metode korozije, čime bi se smanjilo vreme potrebno za izvođenje eksperimenata.

Zahvalnica:

Rad je proizašao iz projekta broj TR 37001: Uticaj rudarskog otpada iz RTB-a Bor na zagađenje vodotokova sa predlogom mera i postupaka za smanjenje štetnog dejstva na životnu sredinu, koji je finansiran sredstvima Ministarstva za prosvetu, nauku i tehnološki razvoj Republike Srbije.

Literatura

1. Mendoza, F. Corvo, Outdoor and indoor atmospheric corrosion of carbon steel, Corrosion Science 41 (1999) 75-86
2. S. P. Parekh, A. V. Pandya, H. K. Kadiya, Progressive atmospheric corrosion study of metals like mild steel, zinc and aluminum in urban station of Ahmedabad district, International Journal of ChemTech Research, CODEN (USA), Vol. 4, No. 4, Oct-Dec 2012, pp. 1700-1774
3. Mendoza, F. Corvo, Outdoor and indoor atmospheric corrosion of carbon steel, Corrosion Science 41 (1999) 75-86
4. M. Pavlović, D. Stanojević, S. Mladenović, Korozija i zaštita materijala, 1. Izd,Tehnološki fakultet Zvornik, 2012

Synthesis of waterborne alkyd resins

Ivan Ristić[1], Florijan Morovic[1], Tamara Erceg[1], Suzana Cakić[2], Darko Manjenčić[1], Jaroslava Budinski-Simendić[1]

[1] Faculty of Technology Novi Sad, University of Novi Sad

[2]Faculty of Technology Leskovac, University of Niš

Abstract

Today, almost the one half of synthetic binders in organic coatings are based on alkyd resins. Vegetable oils in their structure classified alkyd resins as bio-based materials. In order to put complete lyfe cycle of alkyd coatings in ecological framework, organic solvent is replaced by water in formulation of waterborne coatings. In this work, alkyd resins are modified by maleic anhydride in order to improve their affinity to water. Synthesis of water dispersible alkyd resins were carried out in two ways: by the reaction of direct polyesterification of glycerol, phtalic anhydride and modificated ricinoleic acid and by the subsequent modification of synthesized alkyd resins. For the formation of film on the substrate surface, two pathways were used: enamelling and curing by styrene. The modified alkyd resin can be dispersed in water up to 30 wt%. Structures of obtained modified resins were confirmed by FTIR method. According to the results of physico-mechanical testing was shown that obtained alkyds are suitable for various applications as coatings.

1. Introduction

Organic coatings cover a large part of polymer materials market, because, it is almost impossible to imagine any long-time use product without organic coating applied on its surface. These materials are applied to a substrate primarily due to their protective and decorative purpose. The protective purpose includes making a barrier against external agents such as water, air, acids, alkalis, organic liquids, but also fire, mechanical abrasion, depending on substrate nature and conditions of its use. The decorative function of organic coatings is manifested through their colour, transparency, gloss, texture and combination of these properties. Polymer resins are the main component of organic coatings, where they perform function of binder.

The use of volatile organic solvents as diluents in organic coatings formulations has contributed to increasing of atmospheric pollution. Organic emissions derived from organic solvents and using the fossil fuels based ingredients make organic coatings environmentally harmful and expensive materials. The concept of applying eco-friendly manufacturing practice in production of organic coating implies several items:

- reducing the amount of solvent in coating formulations by development of low-solvent and solvent – free coatings;
- using the natural renewable resources for extraction and design of eco-friendly ingredients for synthesis of coatings.

The level of used organic solvent for the coatings preparation can be reduced by preparation of high solid coatings, powder coatings and waterborne coatings. Waterborne coatings are environmental friendly coatings in which the main solvent is water. That implies the fact that the used binder must be resin soluble or dispersible in water. Therefore, waterborne coatings are divided into two categories – water soluble coatings and aqueous dispersions. Among wide range of different renewable resources, vegetable oils and carboxyhidrate products as eco-friendly, non-toxic, biodegradable and cost effective materials have found their purpose in organic coatings [1]. From the chemical point of view, vegetable oils are saturated or unsaturated fatty acids or tryglicerides extracted mainly from the plant seed [2]. Vegetable oils are ingredients of alkyd resins, which are defined as oil modificated polyesters, extensively used as binders in paints formulations. Alkyd resins can be obtained via following synthesis pathways:

- direct esterification of polyhydroxyl alcohol, dicarboxylic acids (or their anhydrides) and monofunctional fatty acids,
- alcoholysis of oil by glycerol, resulting in obtaining of mono- and diglycerides which then react with dicarboxylic acid or its anhydride [3].

Applied on substrate surface, coatings form film in process named drying. According to the way of film formation, or according to the fatty acid type incorporated in their structure, alkyd resins are categorized as drying, semi-drying and non-drying. Alkyd resins those contain enough unsaturated bonds in oil component in their backbone, tend to form films at room temperature in process of solidifying by air oxygen, are defined as drying ones. Non-drying alkyd resins contain saturated fatty acids or oil component with insufficiently number of double bonds in their structure. Semi-drying alkyd resins are between those two categories according to the level of unsaturation.

Non-drying and semi-drying alkyd resins form insoluble film by curing at high temperatures or by mediation of crosslinking agent (amino resins for example) at high temperatures [4].

Motivated by cost and ecological requirements, alkyd resins coatings industry is shifting toward waterborne systems. Waterborne alkyd resins are polymer systems with a high acid number (above 50) [5] which enables dispersibility or solubility in water. Alkyd resins with affinity to water can be prepared by modification of fatty acid or glyceride by hydrophilic monomer.

The aim of this work is synthesis of alkyd resins with potential to form water dispersions and investigation the properties of formed films.

2. Experimental part

2.1. Materials

Glycerol, phthalic anhydride, maleic anhydride, ricinoleic acid, initiator azobisisobutyronitrile (AIBN) and styrene were procured from Sigma Aldrich (Figure 1).

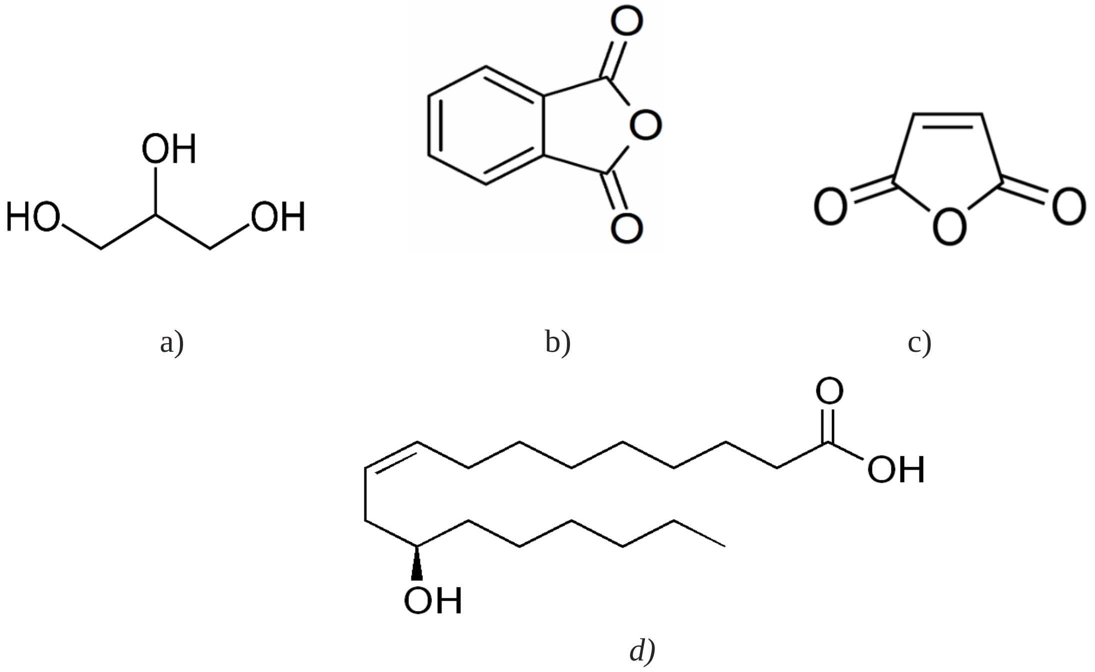


Figure 1. a) glycerol, b) phtalic anhydride, c) maleic anhydride, d) ricinoleic acid.

2.2. Methods

2.2.1. Synthesis of modificated alkyd resins

Modified alkyd resins were synthesized via two pathways:

- direct polyesterification of glycerol, phtalyc anhydride and modificated ricinoleic acid (**Method I**),
- subsequent modification of synthesised alkyd resins (**Method II**).

The first method is a two-step procedure, in which modified ricinoleic acid is added to the mixture of glycerol and phtalyc anhydride. Modification of ricinoleic acid was carried out by the reaction of free-radical polymerization with maleic anhydride at temperature of 70 °C, for 3 hours, using a AIBN as initiator. After addition of all components, polyesterification was carried out at temperature of 110-120 °C, until reaching the gel point.

Subsequent modification implied the synthesis of alkyde resins using the same molar ratios of glycerol, phtalic anhydride and ricinoleic acid as in first method. Maleic anhydride and AIBN were added after a certain time of polyesterification. Polyesterification was carried out at temperature of 110-120 °C. After increasing of reaction mixture viscosity, modificator maleic anhydride and initiator AIBN were added to the resin, and the reaction between ricinoleic acid (incorporated in alkyd structure) and maleic anhydride was carried out via free-radical polymerization, at lower temperature of 70 °C, for 3 hours.

The resulting modified resins were dispersed in water using an inverse dispersion process comprising first dissolving the resin in acetone and then slowly adding this solution to water heated at 50 °C with intensive stirring. The modified alkyd resin can be dispersed in water up to 30 wt%.

One part of obtained resins was applied directly on the glass plate, and the other one were mixed with styrene as crosslinking agent before applying on the glass plate and exposure to high temperatures in dryer.

The resins samples marks and description are listed in Table 1.

Table 1. The labels of prepared alkyd systems.

Sample	**Description**
AR-E-I	Alkyd resin synthesized by Method I and cured by enamelling
AR-CS-I	Alkyd resin synthesized by Method I and cured by styrene at high temperature
AR-E-II	Alkyd resin synthesized by Method II and cured by enamelling
AR-CS-II	Alkyd resin synthesized by Method II and cured by styrene at high temperature

2.2.2. Characterisation of modificated alkyd resins

Modification of alkyd resins was confirmed by Fourier Transform Infrared Analysis (FTIR). Alkyd resins films were deposited on KBr discs and FTIR spectra were recorded using a Bruker's Alpha spectrometer.

The level of curing was estimated by solvent resistant test, which is carried out by dragging of wool soaked by methyle ethyl ketone (MEK) over the film of alkyd resins deposited on the glass substrate, until the appearance the first signs of film dissolving.

In addition, physical and mechanical properties (hardness, gloss, adhesion) of resulting alkyd films were tested. Films cast by 100 μm applicators from the water solutions onto a phosphated mild steel panel (7 cm × 2 cm) to obtain a dry film thickness of 25–30 µm. König pendulum hardness of cured films determined with a BYK-Gardner pendulum hardness tester and the values are reported in seconds (ASTM D4366). The adhesion performance of the enamel was tested with commercial cello tape according to the cross-cut adhesion test method (ASTM D3359). The results are presented using a rating of 0 for a poor adhering coating through 5B for a very good adhering coating. The gloss characteristics of the films were determined according to ASTM D 523, with a glossometer "BYK micro gloss 60°", over a resin-coated mild steel panel at an angle incidence of 60°.

3. Results and discussion

Prepared non-cured systems have shown a certain dispersibility in water, due to the carboxylic groups originated from maleic acid units, incorporated in alkyde resins structure. Non-modificated resins are extremely lipophilic.

FTIR spectrums of synthesized resins are shown in Figure 2 and 3. A broad peak at around 3440 cm^{-1} is atributed to vibration of OH group. Aliphatic symmetric and asymmetric vibrations appear as sharp peaks at 2926 and 2865 cm^{-1}. Intensive peak at around 1728 (modified resins) and 1723 cm^{-1} (non-modificated resins) correspond to streching of C=O group from polyester backbone. Sharp peak at 1719 cm^{-1}, detected in spectrum of modified resin is allocated to carboxyl group originated from maleic anhydride. The absence of C=C double bond peak, from ricinoleic acid, at around 3030 cm^{-1} in the spectrum of modified resin (Figure 3) indicates that modification were successfully done via free-radical polymerization between ricinoleic acid (in alkide structures) and maleic anhydride.

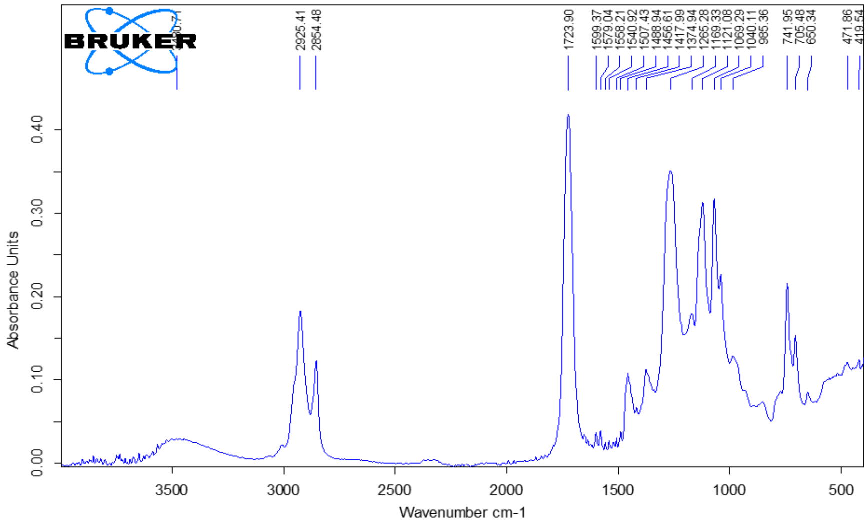


Figure 2. FTIR spectrum of non-modified alkyd resin.

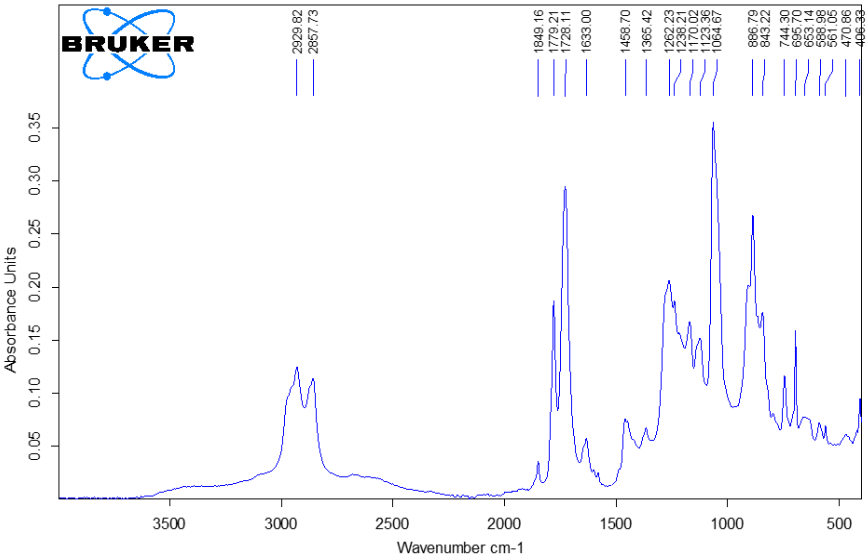


Figure 3. FTIR spectrum of modified alkyd resin by Method II.

The results of solvent resistant test and mechanical properties are shown in Table 2. It can be concluded that both type of drying (enamelling or curing with styrene) gave the films with the same resistant to MEK. Also, both methods of alkyd modification had not significant influence on the MEK resistance results.

Table 2. Properties of cured modified alkyd resins.

Sample	**Number of dragging**	**Hardness (s)**	**Gloss (%)**	**Adhesion**
AR-E-I	20	98	91-93	5B
AR-CS-I	24	102	91-92	5B
AR-E-II	19	85	91-92	5B
AR-CS-II	22	96	90-92	5B

In Table 2 physical and mechanical properties of coating are given. These results indicate that obtained films based on modified alkyd resins have a high gloss. Adhesion test, according to ASTM D3359, was designed to assess the adherent strength of the cured film. Obtained results in Table 2 shown that adhesions of modified alkyd films are good for application as coatings. Curing of modified alkyd with addition of styrene resulted in higher value of final product hardness.

4. Conclusion

Alkyd resins have been extensively used in protective coatings and paints. The use of renewable resources as feedstock for preparation of alkyd resins ingredients as well as possibility of wide applications, make those polymers significant from the ecological and economical point of view. Interest for alkyd resins has increased with development of waterborne coatings based on them. In this work, modification of alkyd resins has carried out by maleic anhydride in order to achieve dispersibility of alkyd resins in aqueous systems. The presence of double bond in ricinoleic acid was used as center for modification by maleic anhydride via free-radical reaction. FTIR spectrums confirmed that modification had carried out successfully. According to the results of physico-mechanical properties of cured modified resins shown that obtained alkyds are suitable for various applications as final coatings.

Acknowledgements

The authors would like to thank the Ministry of Education, science and technological development of Republic of Serbia (project III45022)

References

1. Samarath, N.B., Mahanwar, P.A., Modified vegetable oil based additives as a future polymeric materials-Review, *Open J. Organic Polym. Mater*, 2015, 5, 1-22.
2. Hasnat, A., Modified Alkyd Resins as the Versatile Coating Materials derived from Vegetable Oils, *Archives of Applied Science Research - Scholars Research Library*, 2017, 9, 7-12.
3. Onukwli, O.D., Igbokwe, P.K., Production and characterization of castor oil-modified alkyd resins, *J. Eng. Appl. Sci*., 2008, 3, 161–165.
4. Kalenda, P., Kalendová, A., Possibilities of affecting the chemical resistances of the coatings formed by reaction of amino resins with alkyd resins, *Pigm. Res. Techn*., 2002, 31, 27–32.
5. Stoye, D., Freitag, W., Paints, coatings and solvents, Wiley-VCH Weinheim,1998 pp. 45-46.

The effect of the alkyl substituents on the inhibitory efficiency of imidazole based ionic liquids

Uticaj dužine alkil supstituenta na inhibitorsku efikasnost jonskih tečnosti na bazi imidazola

Đenđi Vaštag, Slobodan Gadžurić, Milan Vraneš, Nebojša Zec

University of Novi Sad, Faculty of Sciences, Trg D. Obradovića 3, Novi Sad, Serbia

Univerzitet u Novom Sadu, Prirodno-matematički fakultet, Trg D. Obradovića 3, Novi Sad, Srbija

Izvod

U ovom radu je ispitan uticaj dužine bočnih alkil nizova jonske tečnosti na njena inhibitorska svojstva pri zaštiti bakra od korozije u kiselo-sulfatnoj sredini (pH=3). Kao ekološki pogodna jedinjenja u odnosu na konvencionalne organske korozione inhibitore, proučavane su jonske tečnosti na bazi 1-alkil-3-alkil-imidazolijum–bromida (alkil = etil, butil, oktil), kao potencijalni inhibitori korozije bakra. Rezultati elektrohemijske impedansne spektroskopije i potenciostatskih polarizacionih merenja ukazuju da ispitivana jonska tečnost pri datim uslovima poseduje inhibitorska svojstva u odnosu na koroziju bakra u kiseloj sredini, a da joj se efikasnost menja u funkciji primenjene koncentracije kao i dužine oba alkil supstituenta. Uočeno je da kod 1-etil-3-alkil-imidazolijum–bromida porast dužine alkil niza u položaju N-3 dovodi do porasta inhibitorske efikasnosti, konstante adsorpcije (K_{ads}) kao i promene slobodne energije adsorpcije ($-\Delta G_{ads}$), za razliku od 1-butil-3-alkil-imidazolijum–bromida kod kojeg porast dužine alkil niza izaziva smanjenje K_{ads} i $-\Delta G_{ads}$.

Abstract

In this study the effect of the alkyl chain length on the inhibitory efficiency of 1-alkyl-3-alkyl-imidazolium bromide against *copper corrosion in acidic sulphate solution (pH=3) was investigated. Ionic liquids based on 1-alkyl-3-alkyl-imidazolium bromide (alkyl = ethyl, butyl, octyl) were tested as potential inhibitors of copper corrosion and compared to conventional organic inhibitors. The results of electrochemical impedance spectroscopy and potentiostatic polarization measurements indicate that investigated* ionic liquids in the given conditions possess favorable inhibitory properties against copper corrosion, which *efficiency depends on the applied concentration as well as the length of both alkyl substituents. It was observed that in the 1-ethyl-3-alkyl-imidazolium bromide the increase of the alkyl chain length in the position N-3 leads to an inhibitory efficiency increase, the adsorption constant (K_{ads}) and the change in the free energy of adsorption ($-\Delta G_{ads}$), unlike of 1-butyl-3-alkyl imidazolium bromide in which case the increase of the alkyl chain length causes a decrease of the K_{ads} and $-\Delta G_{ads}$.*

Application of beet molasses in hard sugar cubes: effect on nutritional profile and storage behavior

Rada Jevtić-Mučibabić[1], Bojana Filipčev[1], Olivera Šimurina[1], Branislav Bogdanović[2], Biljana Bogdanović[2]

[1]University of Novi Sad, Institute of Food Technology in Novi Sad, Blvd. cara Lazara 1,
Novi Sad, Serbia
[2]AD "Šajkaška", Sugar factory, 21230 Žabalj, Čuruški put 3, Serbia

Abstract

Hard sugar cubes were enriched by adding various levels of sugar beet molasses (2, 2.3, 3, 4, 5, 10%). Molasses addition affected the quality of hard sugar cubes. Basic quality parameters were all increased and exceeded the limits set by current national regulation. Sugar cubes enriched with molasses had considerably higher content of minerals. Potassium content increased 17.5-41.3 times, sodium content 80-472 times, calcium 8.4-37 times, magnesium 12.5-38.7 times, iron 4-31 times, zinc 11.4-44 times, depending on the enrichment level (2-10%), respectively. Betaine content in the enriched sugar cubes ranged from 63.97 mg/100 g to 260.47 mg/100 g while it was not detected in the control cubes. Molasses contributed to significant hardening of sugar cubes. During storage, molasses-enriched sugar cubes packaged in cardboard box tended to absorb moisture from ambient air and significantly softened after 45 days of storage. This was due to highly hygroscopic nature of molasses. It is recommended to use packaging material with lower moisture permeability to avoid moisture migration in hard sugar cubes enriched with molasses.

Key words: *macroelements, microelements, betaine, hardness, shelf-life.*

Izvod

Kocke šećera su obgaćivane dodatkom različitih koncentracija melase šećerne repe (2, 2.3, 3, 5, 10%). Dodatak melase je uticao na paramtere kvaliteta šećera u kocki. Osnovni parametri kvaliteta su imali tendenciju rasta i bili su van opsega definisanog važećim pravilnikom. Zabeležen je izrazit porast u sadržaju mineralnih materija u kockama šećera obogaćenim melasom. Sadržaj kalijuma je bio viši 17.5-41.3 puta, natrijuma 80-472 puta, kalcijuma 8.4-37 puta, magnezijuma 12.5-38.7 puta, gvožđa 4-31 puta i zinka 11.4-44 puta, zavisno nivoa obogaćivanja (2-10%), respektivno. Sadržaj betaina u šećeru u kocki obogaćenim melasom se kretao u opsegu 63.97-260.47 mg/100 g dok u kontrolnom uzorku betain nije detektovan. Dodatak melase je doprineo izrazitom otvrdnjavanju kocki šećera neposredno nakon dodatka melase. Tokom skladištenja, kocke šećera zapakovane u kartonske kutije su pokazale značajno manju tvrdoću nakon 45 dana, što je posledica upijanja vlage iz okolnog vazduha zbog izrazite higroskopnosti melase. Preporučuje se da se kocke šećera obogaćene melasom pakuju u materijale manje propusnosti na vlagu kako bi se sprečila migracija vlage između proizvoda i ambijentalnog vazduha.

Ključne reči: *makroelementi, mikroelementi, betain, tvrdoća, trajnost*

INTRODUCTION

Molasses is a byproduct from the processing of sugarcane or beet which remains after successive crystallization of sugar crystals from thick juice. Apart from sugar, it contains many valuable nutrients such as micro (Fe, Mn, Zn, Se) and macrominerals (K, Na, Mg, Ca), B group vitamins and a range of bioactive compounds.

Molasses has been recently shown to possess remarkable "pro-health" potential which will probably allow its classification as a functional ingredient in near future. It exerts marked antioxidant activity due to presence of high spectrum of phenolic and flavonoid compounds, melanines, melanoidines and caramellization products. Moreover, molasses contains a range of important bioactive compounds such as B group vitamins, betaine (only beet molasses), choline, alantoine, purine, cytosine, guanosine, cytidine, aminoacids, lactic acid, etc. Positive health effects of molasses have been confirmed in several studies. Phenolic extracts from beet molasses exhibited strong antitumor activities [1,2]. Protective antioxidative effect of molasses without cytotoxic effects of molasses in *in vitro* study was confirmed by Valli et al. [3]. Immunomodulatory effects of cane molasses on human whole blood cell cultures was reported by Rahiman and Pool [4]. Antidiabetes effects of cane molasses extracts were shown by Wright et al. [5]. Actually, the addition of filtered concentrate made from cane molasses proved effective in reducing glycaemic index of enriched food product which imply on the potential of molasses to modify carbohydrate metabolism [5]. A product similar to molasses in nature is non-centrifugal sugar or jaggery or black sugar, which is obtained by evaporating water in sugar cane juice. Jaggery has been scientifically confirmed to have multiple health effects like antitoxic, immunological, cytoprotective, anticarcinogenic, antidiabetes and antihypertension [6,7]. These effects are mainly related to mineral composition (presence of Fe and Cr) and antioxidants in jaggery. In contrast to jaggery, molasses contains less sugar and all the non-sugar constituents that passed the refining process. It is reasonable to expect that some health effects of jaggery will be retained in molasses.

These results suggest that molasses is an ingredient with high capacity to add functional properties and nutritional value to a food product which may serve as a relatively affordable ingredient to enhance food quality. In several studies, it was investigated the possibility to enrich different food (bread, various types of biscuits, meat products) with beet molasses [8,9,10,11]. The main objective of this work was to determine quality attributes (basic quality, nutritional composition, textural properties) of hard sugar cubes enriched with various levels of beet molasses. Secondary objective was to monitor the evolution of texture changes during storage of sugar cubes for 90 days.

MATERIAL AND METHODS

Basic quality parameters of hard sugar cubes, content of minerals were determined according to methods described in the Handbook for the laboratory control of sugar processing [12]. The methods are harmonised with the regulations guided by the International Commission for Uniform Methods of Sugar Analysis [13].

Betaine determination

Betaine analysis was performed using a HPLC system Agilent (Agilent Technologies Inc.,USA) equipped with a Kine-tex®HILIC (Phenomenex, Germany) column (2.6μm, 100 x 2.1 mm) and ELSD detector.

Measurement of sugar cube hardness

Sugar cube hardness was measured by cutting on a texture analyzer TA-XTplus (Stable Micro Systems Godalming, England) using a blade set with knife. The following settings were applied: test speed: 2 mm/s, distance: 6 mm, trigger force 25 g. A load cell of 50 kg was used. Maximum cutting force extracted from the force-time curves represented hardness of the sugar cubes. Ten measurements were made per each batch. Evolution of hardness was monitored over 90 days of storage. Sugar cubes were packaged in cardboard boxes normally used to package classic hard sugar cubes in retail.

Statistical analysis

The obtained data were processed using statistical software Statistica 12 (StatSoft, Inc, Tulsa, OK). One-way ANOVA procedure was used. All analyses were done in duplicate unless otherwise stated.

RESULTS AND DISCUSION

Basic quality parameters for hard sugar cubes made from refined (white) sugar are defined by the current national rulebook and involves the following parameters: polarization, ash content, reducing compound content and moisture content. Increasing molasses content caused an increase in polarization, ash content, reducing compounds contents and moisture content. Therefore, the basic quality attributes of sugar cubes enriched with all tested doses were over the limits set by the regulation. However, this was expected since the regulation sets the values for refined sugar. Consequently, if sugar cubes enriched with molasses are to become a viable product on market, new ranges for quality parameters should be included as well as additional quality attributes that better describe the novel product should be defined. Higher ash content in the molasses-enriched sugar cubes is an indicator of higher mineral content.

Table 1. Basic quality parameters of hard sugar cubes before and after enrichment with molasses

Sugar cubes	**Parameter (%)**			
	Polarisation	**Ash**	**Reducing matters**	**Moisture**
From refined sugar	99.93^a	0.010^a	0.007^a	0.01^a
enriched with 2% molasses	99.89^b	0.095^b	0.134^b	0.13^b
enriched with 2.3% molasses	99.87^b	0.097^b	0.153^b	0.14^b
enriched with 3% molasses	99.81^b	0.099^b	0.179^c	0.16^b
enriched with 4% molasses	98.71^c	0.158^c	0.181^c	0.21^c
enriched with 5% molasses	98.67^c	0.163^c	0.183^c	0.23^c
enriched with 10% molasses	97.58^d	0.279^d	0.194^d	0.42^d

a,b,c,d Means followed by different letters are significantly different ($p<0.05$).

As expected, addition of molasses substantially increased the content of macro and microelements in the sugar cubes in comparison to the control (refined sugar) (Table 2). This favourably affects the nutritional profile of molasses enriched sugar cubes. According to Wright et al. (2014), minerals such as Mg, Ca and K are important for the efficient functioning of insulin and their deficiency has been associated with increased risk of diabetes occurrence. It was suggested that the “anti-diabetes” effect of filtered molasses concentrate is partially due to its mineral content apart from the presence of phenolics and organic acids.

Table 2. Mineral content of sugar cubes before and after enrichment with molasses

Sugar cubes	**Elements (mg/kg)**							
	K	**Na**	**Ca**	**Mg**	**Fe**	**Mn**	**Cu**	**Zn**
From refined sugar	34.7^{a}	2.8^{a}	20.4^{a}	0.99^{a}	0.65^{a}	< 0.25^{a}	<1^{a}	0.29^{a}
enriched with 2% molasses	610.4^{b}	223.4^{b}	172.3^{b}	12.36^{b}	2.57^{b}	0.43^{b}	<1	3.32^{b}
enriched with 2.3% molasses	699.5^{b}	230.4^{b}	186.6^{b}	13.05^{b}	3.52^{b}	0.57^{b}	<1	4.41^{b}
enriched with 3% molasses	745.8^{b}	268.5^{b}	202.0^{b}	17.88^{c}	3.93^{b}	0.63^{b}	<1	10.37^{c}
enriched with 4% molasses	1355^{c}	461.4^{c}	322.9^{c}	19.1^{c}	3.98^{b}	0.91^{c}	<1	10.51^{c}
enriched with 5% molasses	1383^{c}	497.8^{c}	378.0^{c}	19.7^{c}	5.30^{c}	1.01^{c}	<1	11.66^{c}
enriched with 10% molasses	1432^{d}	1323^{d}	753.9^{d}	38.3^{d}	20.15^{d}	1.55^{d}	2.72	12.55^{d}

a,b,c, d Means followed by different letters are significantly different ($p<0.05$).

Unlike cane molasses, beet molasses contains betaine. Betaine is not an essential nutrient; however it has been deficient in the diet of general population [14]. Since it was proven to lower the level of blood homocysteine levels, its intake became interesting for food nutritionist [15]. Betaine was not detected in the sugar cubes from refined sugars. Increasing molasses levels increased betaine content (Fig. 1). In cubes enriched with 2% molasses, the betaine content was around 65 mg/100 g. It increased almost four-fold when molasses level was increased to 10%.

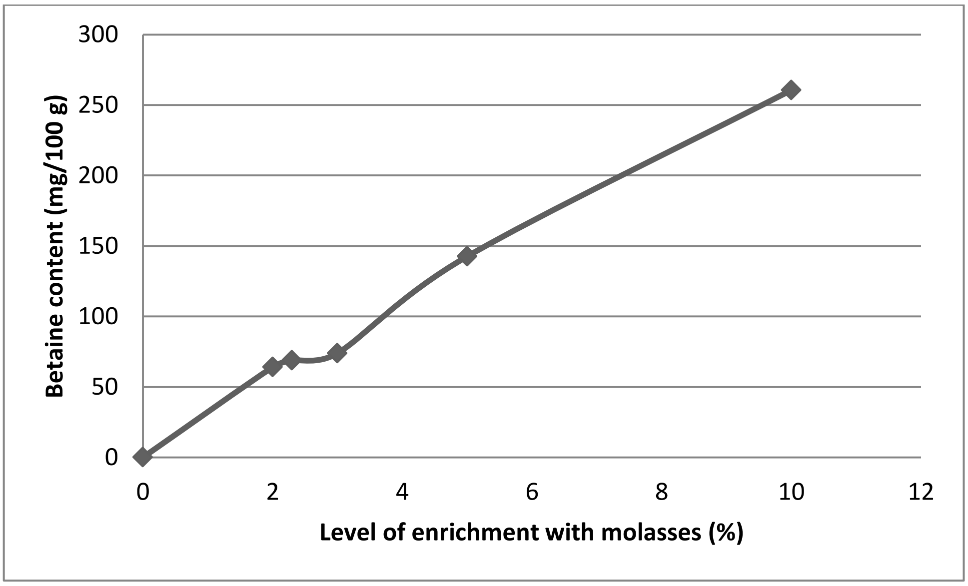


Figure 1. Betaine content in sugar cubes as affected by molasses addition

Inclusion of molasses to sugar cubes at various levels affected its hardness (Fig. 2). Increasing molasses levels significantly increased hardness and contributed to development of more compact and cohesive structure of sugar cubes. However, after 45 days, a significant decrease in hardness was observed with formation of gritty structure in the sugar cubes enriched with beet molasses. After 90 days of storage, the hardness of sugar cubes did not significantly change. Hardness of control sugar cubes did not significantly change over the storage period. Molasses is hygroscopic in nature. Sugar cubes are packaged in cardboard boxes which are permeable to water vapour so higher relative moisture content of ambient air caused increased water absorption and decreased the textural parameters. After reaching the equilibrium moisture, hardness of sugar cubes did not significantly change. Since the hardness of control sugar cubes remained similar during storage, it can be concluded that molasses-enriched sugar cubes are more sensitive to changes in relative humidity of ambient air. Therefore, using packaging materials with better barrier properties to moisture is recommended.

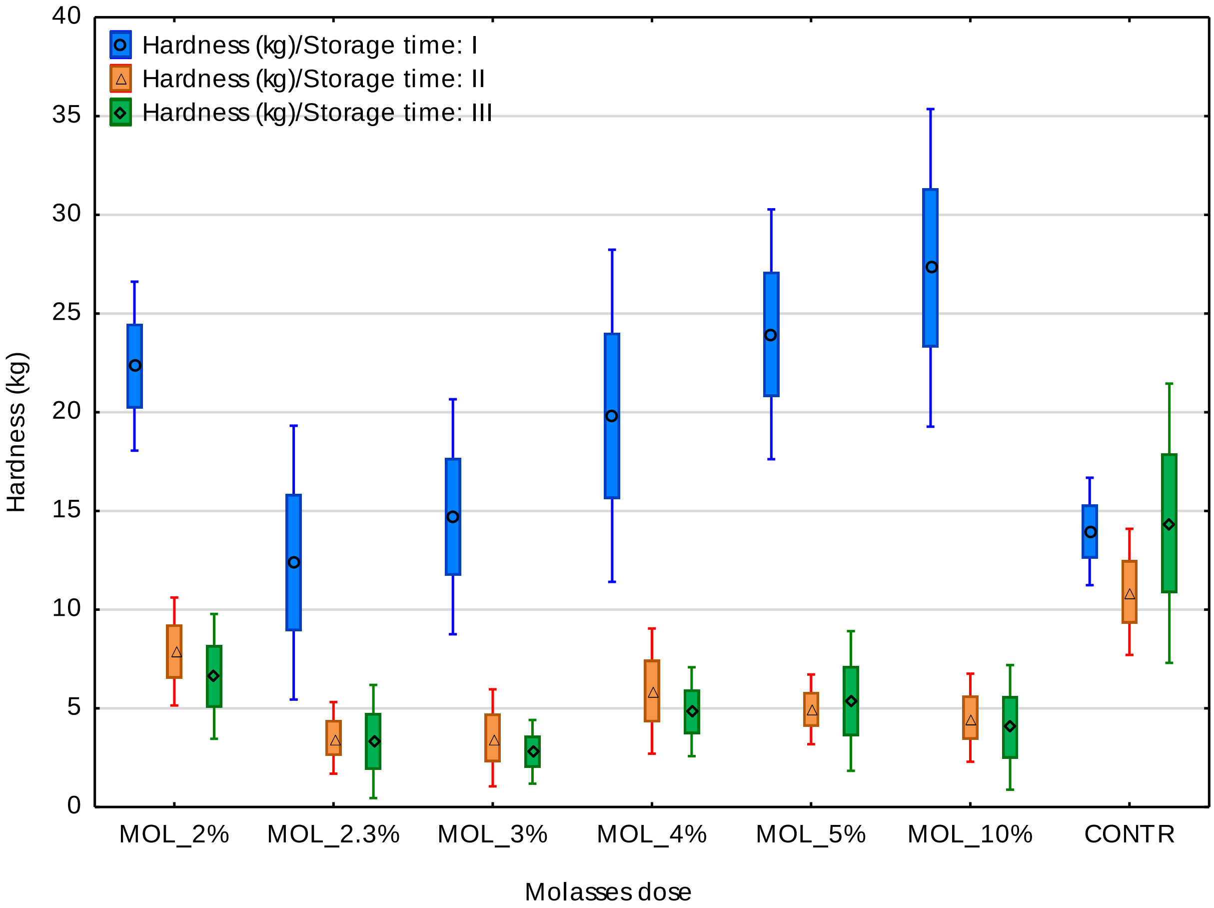


Figure 2. Dependence of sugar cube hardness on molasses enrichment level (%) and storage time (I-1day; II-45 days; III-90 days).

CONCLUSIONS

Sugar beet molasses provides a natural, abundant and affordable source of a range of valuable plant-derived bioactive compounds and minerals. The work described here demonstrates that it can be used for enrichment of classical sugar cubes made from refined sugar. Rising molasses enrichment levels caused substantial improvement in mineral composition of sugar cubes, and contributed to the presence of betaine. Basic quality attributes were also changed: enriched sugar cubes had higher values for all parameters (ash, polarization, reducing matters and moisture) which were out of the limits set by the national rulebook.

Addition of beet molasses to sugar cubes affects their textural and structural properties as well as shelf-life. Molasses almost linearly increased the compactness and hardness of the sugar cubes upon enrichment. During storage, it was observed that molasses enriched sugar cubes were more sensitive to moisture migration from ambient air. Due to high hygroscopic nature of molasses, enriched sugar cubes absorbed moisture and developed less hard and gritty structure. To prevent similar changes during storage, use of materials with better barrier properties to moisture than cardboard is recommended.

ACKNOWLEDGEMENTS

The authors gratefully acknowledge the financial support from the Ministry of Education, Science and Technological Development of The Republic of Serbia (Project III46005 and TR 31055, 2011-2014).

REFERENCES

1. Chen, M., Zhao, Y., Yu, S. (2015a). Optimisation of ultrasonic assisted extraction of phenolic compounds, antioxidants, and anthocyanins from sugar beet molasses. Food Cheemistry, 172, 543-550.
2. Chen, M., Meng, H., Zhao, Y., Chen, F., Yu, S. (2015b). Antioxidant and in vitro anticancer activities of phenolics isolated from sugar beet molasses. BMC Complementary & Alternative Medicine, 15 (1), 1-8.
3. Valli, V., Gómez-Caravaca, A.M., Di Nunzio, M., Danesi, F., Caboni, M.F., Bordoni, A. (2012). Sugar cane and sugar beet molasses, antioxidant-rich alternatives to refined sugar. Journal of Agricultural and Food Chemistry, 60, 12508-12515.
4. Rahiman, F., Pool, E,J. (2010). The effects of Saccharum ifficinarium (sugar cane) molasses on cytokine secretion by human blood cultures. Journal of Immunoassay and Immunochemistry, 31, 148-159.
5. Wright, A.G., Ellis, T.P., Ilag, L.L. (2014). Filtered molasses concentrate from sugar cane:natural functional ingredient effective in lowering the glycaemic index and insulin response of high carbohydrate foods. Plant Foods for Human Nutrition, 69, 310-316.
6. Jaffé, W.R. (2012). Health effects of non-centrifugal sugar (NCS): A review. Sugar Tech, 14 (2), 87-94.
7. Harish Nayaka, M.A., Sathisha, U.V., Manohar, M.P., Chandrashekar, K.B., Dharmesh, S.D. (2009). Cytoprotective and antioxidant activity studies of jaggery sugar. Food Chemistry, 115, 113-118.
8. Filipčev, B., Lević, Lj., Bodroža-Solarov, M., Mišljenović, N., Koprivica, G. (2010). Quality characteristics and antioxidant properties of breads supplemented with sugar beet molasses-based ingredients. International Journal of Food Properties, 13 (5),1035-1053.
9. Filipčev, B., Bodroža-Solarov, M., Šimurina, O., Cvetković, B. (2012). Use of sugar beet molasses in procesing of gingerbread type biscuits: effect on quality characteristics, nutritional profile, and bioavailability of calcium and iron. Acta Alimentaria Hungarica, 41, 494-505.
10. Filipčev, B., Mišan, A., Šarić, B., Šimurima O. (2016). Sugar beet molasses as an ingredient to enhance the nutritional and functional properties of gluten-free cookies, International Journal of Food Sciences and Nutrition, 67 (3), 249-256.
11. Filipović, V., Ćurčić, B., Nićetin, M., Plavšić, D., Koprivica, G.M. (2012). Nass transfer and microbiological profile of pork meat dehydrated in two different osmotic solutions. Hemijska Industrija, 66 (5), 743-748.
12. Milić, M., Karadžić, V., Obradović, S. (1992). Metode za laboratorijsku kontrolu procesa proizvodnje fabrika šećera, Tehnološki fakultet, Zavod za tehnologiju šećera, Novi Sad.
13. ICUMSA (2003). Methods Book, Dr. Albert Bartens KG, Berlin.
14. Ross, A., Zangger, A., Guiraud, S. (2014). Cereal foods are the major source of betaine in the Western diet - Analysis of betaine and free choline in cereal foods and updated assessments of betaine intake. Food Chemistry, 145, 859-865.
15. Craig, S.A.S. (2004). Betaine in human nutrition. *American Journal Clinical Nutrition,* 80, 539-548.

High temperature corrosion in biomass-fuelled power plant boilers

Visokotemperaturna korozija u energetskim kotlovima za sagorevanje biomase

Andrijana Stojanović[1], Srđan Belošević[1], Dragoljub Živković[2]

[1]University of Belgrade, Institute of Nuclear Sciences Vinca, Laboratory for Thermal Energy and Engineering, 11 000 Belgrade

[2]Faculty of Mechanical Engineering, University of Nis, 18 000 Nis, Serbia

Abstract

Biomass plants, apart from producing energy, help to reduce CO_2 *(g) emissions. One of the biggest problems for their development is superheater corrosion due to fuel corrosivity, especially of the straw. This limits both the temperature of the vapour and also the effectiveness of the plant. In this paper, the corrosion mechanisms that can occur in biomass-fueled power plant boilers were described.*

Apstrakt

Elektrane koje koriste za sagorevanje biomasu, ne samo da proizvode energiju, već pomažu smanjenju emisije CO_2*. Jedan od najvećih problema za njihov dalji razvoj je korozija pregrejača koja je uslovljena korozivnošću samog goriva, posebno slame. Ovaj problem ograničava temperaturu pare, kao i efikasnost same elektrane. U ovom radu su opisani mehanizmi korozije koji se mogu javiti u visokoenergetskim kotlovima za sagorevanje biomase.*

Introduction

Currently, much attention has been drawn towards the burning of biomass for power production. One of the main reasons for this is the concern regarding the global warming caused by carbon dioxide (CO_2) emissions. Biomass that is produced at the rate it is consumed is considered CO_2 neutral because during growth it accumulates the same amount of CO_2 (g) by photosynthesis as it releases during combustion.

Biomass includes a large variety of different fuels with different chemical composition and combustion characteristics. Wheat straw contains large amount of pottasium and chlorine, which are very undesirable due to their high corrosion power, so straw combustion is associated with some corrosion problems which are not encountered in coal-fire plants. During combustion, potassium chloride and SO_2 are released in the flue gas and through the condensation and deposition processes that will result in the formation of superheater deposits rich in potassium chloride and potassium sulphate. The operating conditions of different boilers (temperature, flue gas composition, fly ash, etc.) depend on the fuels and the process parameters, and may vary inside the boiler. The burning of difficult fuels, such as biomass and solid recovered fuel, leads to vary harsh conditions and may cause fouling, slagging, and high temperature corrosion of the metalic heat exchanger surfaces [1-5]. Corrosion can cause severe material damage and tube leakage, leading to severe operational problems and expensive consequences such as unplanned plant shutdowns, high maintenance costs, reduced availability of the plant and shortedned lifetime of the boiler tubing [6]. In addition, the demand for higher efficiency of electricity and heat generation requires an increase in steam temperatures, which in turn raises the material temperatures of boiler tubes, and may lead to even more severe corrosion problems especially in economizer and/or superheater areas. The material temperatures are planned to raise up to 750 - 800°C in advanced ultra super-critical power plant boilers in future. Schematic images of biomass-fuelled circulating fluidized bed (CFB) boilers are presented in Figure 1.

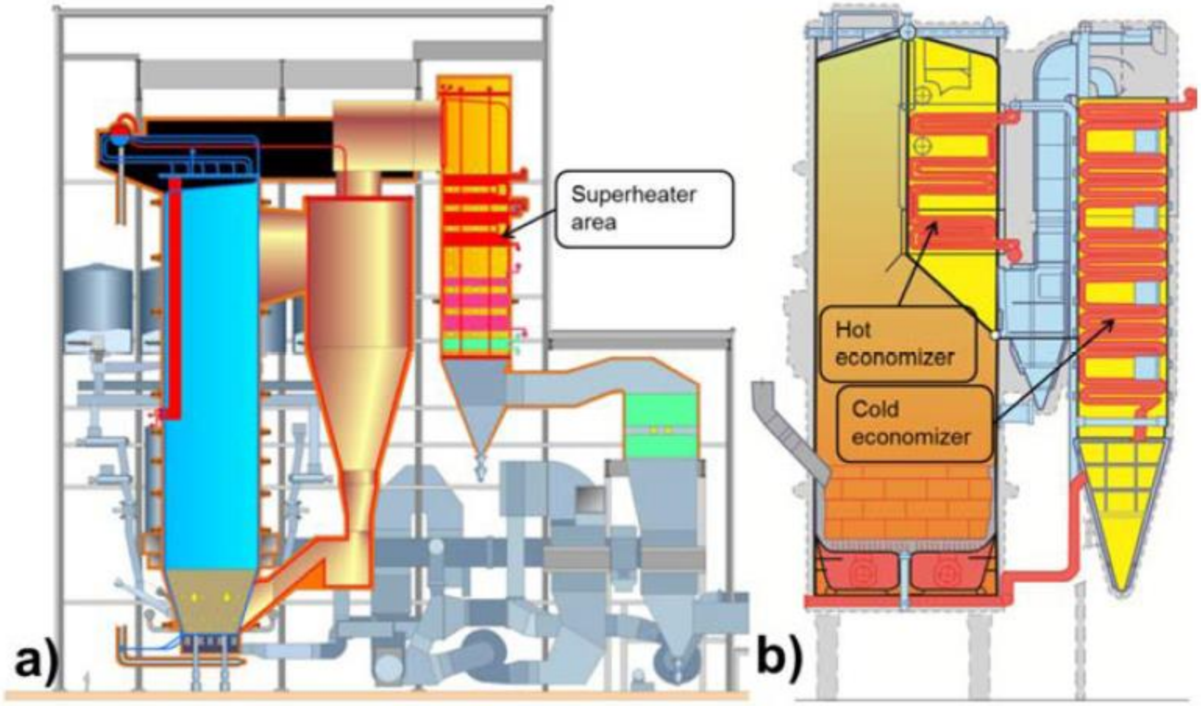


Figure 1. Schematic illustrations of circulating fluidized bed boilers. a) 550 MWth co-firing biomass boiler and b) 40 MWth district heating unit

There are several high temperature corrosion mechanisms that can occur in power plant boilers operating on chlorine-containing fuels, including biomass and waste-to energy boilers. In the superheater area, corrosion derives from the reactions between fly ash, gaseous components, and cooler metal surfaces, on which a deposit is formed. The corrosion reactions derive from combustion gas containing low-melting-point salts such as chlorides. Chlorine-induced active corrosion is detrimental to steels, and the corrosion starts almost immediately after introduction of chlorine-containing contamination into the environment [7]. Chlorine is able to penetrate and destroy the metal oxide layer, probably through cracks in the scale, and at the metal-scale interface the chlorine reacts with chromium and iron to form volatile metal chlorides [8]. Severe corrosion of the boiler tubes occurs especially due to molten phases [9-11], and one of the extremly demaging corrosion mechanisms in biomass and waste-to-energy boilers is molten salt attack due to low melting temperature compounds such as alkali metal chlorides (NaCl, KCl) and zinc, copper or lead chlorides [12-16].

The aim of this literature survey is to describe the knowledge of chlorine-associated, high temperature corrosion and the potential corrosion problems associated with burning biomass fuels either alone or in blends with coal, for electricity production. Chlorine-based corrosion is affected by the temperature and concentrations of chlorine, sulfur, alkali metals, and oxygen. The rest of this review focuses on the mechanisms of corrosion, citing literature from coal-, waste-, and biomass combustion to illustrate these mechanisms.

Potential corrosion problems in biomass-fired boilers

Several high temperature corrosion mechanisms prevail in power plant boilers utilizing chlorine-containing fuels including chlorine-induced active oxidation, selective chlorine corrosion, hot corrosion by eutectic melts and sulfidation [6,8,17]. Type II hot corrosion is caused by gas phase acid fluxing or sulfidation and occurs typically at 600-800°C. Sulfur dioxide and sulfates cause accelerated corrosion as a gaseous reaction as well as in deposits. Type II hot corrosion forms typically pitting, which results from the formation of mixtures of e.g. Na_2SO_4 and $NiSO_4$, which may have low melting temperature. For the Type II corrosion reactions to occur, a high partial pressure of SO_3 is required. Deposit formation and factors influencing corrosion rate are described in Figure 2 [18]. In the superheater area, corrosion derives from the reactions between fly ash, gaseous components, and cooler metal surface, on which a deposit is formed. The corrosion reactions are due to combustion gas containing HCl or deposited ash containing low-melting-pont salts such as chlorides.

The corrosion problems related to biomass combustion have been reported mainly to be caused by chlorine as stated earlier. Sulfidation has not been reported to be that serious problem in boiler conditions. In some cases, additional sulfur has been added to combustion with fuels with high chlorine content, e. g. biomass or recovered fuel, in order to prevent chlorine induced corrosion. Sulfur addition to decrease chlorine corrosion into the corrosion process has been studied and made also commercially available. [19, 20].

When the flue gas passes through the convective pass of a boiler, it is cooled and some of the alkali metals condense on the heat exchanger tubes. Part of the alkali metals may condense on fly ash particles, which later may impact on the heater exchanger tubes. The alkali metals may either condense as chlorides or sulfates. The alkali metal of major concern in biomass is potassium. Henriksen et al. [21] report selective chlorine corrosion when co-firing with straw in a circulating fluidized bed. The probes show selective corrosion, where mainly chromium and to some extent iron was removed from the metal grains and particularly from the grain boundaries, leaving these areas enriched in nickel. Chlorides were found in the degraded zone. The authors suggested that alkali chlorides are deposited on the tubes, sulfated by SO_2 thus releasing Cl_2 close to the metal surface. However, Henriksen et al. did not find any signs of selective corrosion when the same proportions of straw were added to suspension-firing of coal. The authors suggested that in the suspension-firing system, the temperature in the combustion zone is high enough for the volatilized alkali metals to react with silicates and herby be captured in a solid phase. This means that the alkali metals are no longer able to condense and thus being present on the heat exchanger tubes.

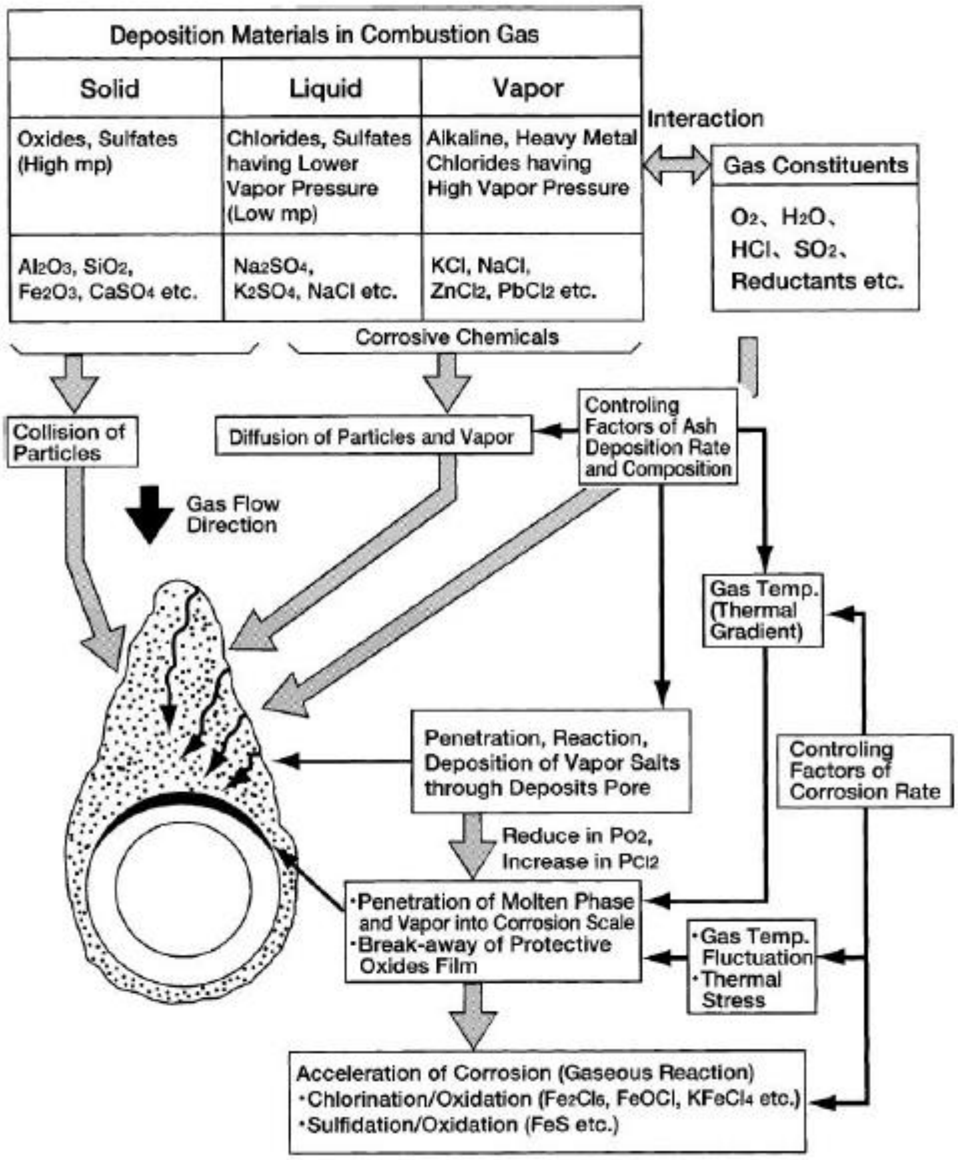


Figure 2. Main factors of ash deposition and corrosion rate

Chlorine induced corrosion

Chlorine and chlorides are especially detrimental to iron and low-alloy steels as they prevent the formation of protective oxide layers or degrade already formed layers. Corrosion starts almost immediately after introduction of chlorine-containing contamination into the environment [22]. Chlorine contamination may be low; e.g. Bramhoff et al. [23] have shown that an addition of 250-3000 vppm HCl(g) into oxidizing atmosphere leads to accelerated catastrophic corrosion of a low-alloy steel.

Active oxidation occurs in the presence of alkali chlorides in deposits and hydrogen chloride in the atmosphere [8]. Chlorine gas or chlorine ions penetrate the oxide-metal interface, where they react with the alloy components, typically forming $FeCl_2$. The metal chloride evaporates and, during its diffusion to the scale surface, is oxidized in the area with higher oxygen vapour pressure forming a non-protective oxide scale. The chlorine released in the reaction is able to participate again in the corrosion reaction, thus enhancing it. The active oxidation reaction circuit induced by chlorine is depicted schematically in Figure 3. Outward diffusion of $FeCl_2$(g) through the oxide scale is the rate controlling mechanism for the active oxidation process [8]. The reactions are similar for high-chromium alloys. Chlorine reacts with $FeCr_2O_4$ or Cr_2O_3. However, mainly $FeCl_2$ is formed due to the lower Gibbs free energy of $FeCl_2$ compared to $CrCl_2$ [8].

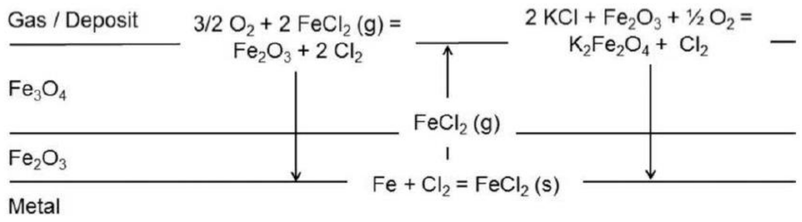


Figure 3.Schematic illustration of the active oxidation reaction circuit caused by chlorine [8]

High temperature corrosion due to molten phases

Chlorine is especially detrimental to heat exchanger surfaces because it forms compounds with low melting point and high volatility in boiler conditions. One important corrosion mechanism in biomass and waste-to-energy boilers is molten salt attack due to low-melting compounds such as alkali metal chlorides (NaCl and KCl); calcium, potassium, and sodium sulfates; and zinc, copper or lead chlorides [24]. Molten phases in the deposits may result in oxide scale fluxing and, hence, strong corrosion when the protective oxide scale is damaged and formation of new scale is hindered. Copper in the presence of chlorine has been reported to act detrimentally in boiler conditions, strongly accelerating the corrosion of iron- and nickel-based alloys [25]. Some reactions that may occur in the presence of chlorine, heavy metals and sulfates are presented in approximate Equation 1 adapted from [12], Equation 2 [25] and Equation 3 [8].

$$ZnCl_2(l) + 2Fe_2O_3 = (Zn, Fe)O + Fe_3O_4 + Cl_2 + 1/2O_2 \qquad (1)$$

$$2\ CuCl_2 + O_2\ \rightarrow 2\ CuO + 2\ Cl_2 \qquad (2)$$

$$(Na, K)_2SO_4 +\ SO_2 + \frac{1}{2}O_2 =\ (Na, K)_2S_2O_7 \qquad (3)$$

Chlorine also plays an important role in the formation of fine particles and the deposits [26]. Alkali metal chlorides of biomass combustion have high vapour pressures and therefore condensate at low temperatures in the flue gas. On the other hand, sulfur reacts with alkali metal (sodium or potassium) chlorides and hydroxides by sulfation reactions [27], as presented in Equations 4-5 [28]. In the sulfation reaction, chlorine of the metallic chloride is released as HCl, which hes been found to significantly reduce deposit formation and corrosion in power plants operating with chlorine-rich fuels [29].

$$2\left(\frac{Na}{K}\right)OH\ + SO_2 + \frac{1}{2}O_2\ \leftrightarrow\ (\frac{Na}{K})_2SO_4 +\ H_2O \qquad (4)$$

$$2\left(\frac{Na}{K}\right)Cl + H_2O + SO_2 + \frac{1}{2}O_2\ \leftrightarrow\ (\frac{Na}{K})_2SO_4 +\ 2HCl \qquad (5)$$

Zink has high influence on the corrosion mechanism, especially when waste wood is used for combustion [6]. When burning biomass or waste, for instance the following low-melting compounds are formed $ZnCl_2$, $FeCl_2$ and $FeCl_3$, with melting points of 318°C, 676°C and 303°C , respectively [15, 25]. Lead and copper have the same detrimental effect on the corrosion behavior of stainless steels [17]. According to thermodynamic equilibrium calculations by Otsuka [29], vapour condensation of KCl, NaCl, Na_2SO_4, as well as lead and zink salts takes place on the tubes surfaces below 350°C. Montgomery [30] has reported on the occurrence of pitting corrosion at low temperatures (300°C) due to chlorides and sulfates present as heavy metal salts in a melt or semi-melt phase. Catastrophic corrosion rates can occur in the presence of molten chlorides on heat exchanger surfaces even at 250°C [31]. Skrivfars et al. [32] have shown that enhanced corrosion can occur even below the first melting point of alkali sulfate and alkali chloride salts. It is assumed that water vapour accelerates the breakdown of the protective layer. Ehlers et al. [33] have shown that under the conditions of high $H_2O(g)/O_2$ ratios the penetration of water vapour molecules triggers enhanced oxidation and sustains high growth rates of the poorly protective Fe-rich oxide scale formed in the atmospheres.

Conclusions

In summary, it is clear that chlorine under some conditions may cause accelerated corrosion resulting in increased oxidation, metal wastage, internal attack, void formations, and loose non-adherent scales. The corrosion caused by chlorine is closely connected to alkali metals, especially when present in the deposits.

Severe corrosion may occur when chlorine is present in the deposits which are in direct contact with the metal scale. The corrosion may be severe in air, but can be further enhanced by SO_2, which may cause intra-deposit sulfation of alkali chlorides releasing HCl(g) or $Cl_2(g)$ close to the metal surface. Furthermore, alkali chlorides may react with the metal scale or with chromium carbide to form gaseous HCl or Cl_2 close to the metal. In case the metal temperature becomes high enough for the deposit to form molten phases, the corrosion, may be further enhanced. Small concentrations of alkali chlorides may increase the corrosion rate caused by molten sulfates in the case of co-combustion of straw and coal.

All of the corrosion mechanisms which are reviewed here may take place in combustion systems. Which mechanism is dominant one will depend on the combustion environment, combustion temperature, metal temperature and the presence of other elements such as alkali metals, sulfur, silicon, and aluminum.

Acknowledgements

This work has been supported by the Ministry of Education, Science and Technological Development of the Republic of Serbia (grant TR-33018)

References

1. Nielsen, H. P., Frandsen, F.J., Dam-Johansen, K., Baxter, L.L., The implications of chlorine-associated corrosion on the operation of biomass-fired boilers. Progress in Energy and Combustion Science 26 (2000), pp. 283-298.
2. Frandsen, F.J., Utiliziniomass and waste for power production-a decade of contributing to the understanding, interpretation nad analysis of deposits and corrosion products. Fuel 84 (2005), pp. 1277-1294
3. Persson, K., Brostrom, M., Carlsson, J., Nordin, A., Backman, R., High temperature corrosion in a 65 MW waste to energy plant. Fuel Processing Technology 88 (2007), pp. 1178-1182
4. Vaidya, A., Srinivasan, V., Streibl, T., Friis, M., Chi, W., Sampath, S., Process maps for plasma spraying of yttria-stabilized zirconia: An integrated approach to design, optimization and reliability. Mater. Sci. Eng. 2008., 496, pp. 239-253.
5. Zhang, W., Sampath, S., A., Universal method for representation of in-flight particle characteristics in thermal spray processes. J. Therm. Spray Technol., 2009, 18, pp. 23-34.

6. Otsuka, N., Chemistry and melting characteristics of fireside deposits taken from boiler tubes in waste incinerators. Corrosion Science 53 (2011), pp. 2269-2276.
7. Schofield, M. J., Corrosion, Plant Engineer's Reference Book, 2nd Edition, D. A. Snow, Elsevier, 2002, pp.9.
8. Grabke, H. J., Reese, E. and Spiegel, M., The effect of chlorides, hydrogen chloride and sulfur dioxide in the oxidation of steels below deposits. Corrosion Science 37 (1995), pp. 1023-1043.
9. Zahs, A., Spiegel, M., Grabke, H. J., Chloridation and oxidation of iron, chromium, nickel and their alloys in chloridizing and oxidizing atmospheres at 400-700°C. Corrosion Science 42 (2000), pp. 1093-1122.
10. Nielsen, H. P., Frandsen, F. J., and Dam-Johansen, K., Lab-scale investigations of high-temperature corrosion phenomena in straw-fired boilers. Energy & Fuels 13 (1999), pp. 1114-1121.
11. Ishitsuka, T., Nose, K., Stability of protective oxide films in waste incineration environment-solubility measurements of oxides in molten chlorides. Corrosion Science 44(22) (2002), pp. 247-263.
12. Spiegel M., Salt melt induced corrosion of metallic materials in waste incineration plants. Materials and Corrosion 50 (1999), pp. 373-393.
13. Michelsen, H. P., Frandsen, F., Dam-Johansen, K., and Larsen, O. H., Deposition and high temperature corrosion in a 10 MW straw fired boiler. Fuel Processing Technology 54 (1998), pp. 95-108.
14. Nakagawa, K., Matsunga, Y., The effect of chemical composition of ash deposit on the corrosion of boiler tubes in waste incinerators. Materials Science Forum, 251 (1997), pp. 535-542.
15. Amand, L-E., Leckner, B., Eskilsson, D., Tullin, C., Deposits on heat transfer tubes during co-combustion of biofuels and sewage sludge. Fuel 85 (2006), pp. 1313-1322.
16. Vainikka, P., Bankiewicz, D., Frantsi, A., Silvennoinen, J., Hannula, J., Yrjas, P., Hupa, M., High temperature corrosion of boiler waterwalls induced by chlorides and bromides. Part 1: Occurrence of the corrosive ash forming elements in a fluidized bed boiler co-firing solid recovered fuel. Fuel 90 (2011), pp. 2055-2063.
17. Antunes R. A., Lopes de Oliviera, M. C., Corrosion in biomass combustion: A materials selection analysis and its interaction with corrosion mechanisms and mitigation strategies. Corrosion Science 76 (2013), pp. 6-26.
18. Kawahara, Y., High temperature corrosion mechanisms and effect of alloying elements for materials used in waste incineration environment. Corrosion Science 44 (2002), pp. 223-245.
19. Henderson, P., Szakalos, P., Petterson, R., Andersson, C., Hogberg, J., Reducing superheater corrosion in wood-fired boilers. Materials and Corrosion 57 (2006), pp. 128-134.
20. Aho, M., Yrjas, P., Taipale, R., Hupa, M., Silvennoinen, J., Reduction of superheater corrosion by co-firing risky biomass with sewage sludge. Fuel 89 (2010), pp 2376-2386.
21. Henriksen N., Larsen O. H., Blum, R., Inselman S., High-temperature corrosion when co-firing coal and straw in pulverized coal boilers and circulating fluidized bed boilers. VGB Conference. Corrosion and Corrosion Protection in Power plants. Essen, November 29-30, 1995.
22. Grabke, H., J., Proceedings of the International Conference on Fireside problems while incinerating municipal and industrial waste, 8-12. 10. 1989. FL, USA, pp. 161-176.
23. Bramhoff, D., Grabke, H. J., Reese, E., Schmidt, H. P., Einfluss von HCl und Cl_2 auf Hochtemperaturkorrosion des 2 1/4Cr1Mo-Stahls in Atmospharen mit hohen Sauerstoffdrucken. Werkstoffe und Korrosion 41(1990), pp. 303-310 (in German).
24. Galetz, M. C., Bauer , J. T., Schutze, M., Noguchi, M., Takato, C., Cho, H., The influence of copper in ash deposits on the corrosion of boiler tube alloys for waste-to-energy plants. Materials and Corrosion 63 (2012), pp. 1-8.
25. Lind, T., Kauppinen, e., Hokkinen, J., Jokiniemi, J.K., Orjala, M., Aurela, M., Hillamo, R., Effect of chlorine and sulfur on fine particle formation in pilot scale CFBC of biomass. Energy and Fuels 20 (2006), pp. 61-68.
26. Hansen, L.A., Nielsen, H.P., Frandsen, F.J., DamJohansen, K., Horlyck, S., Karlsson, A., Influence of deposit formation on corrosion at a straw-fired boiler. Fuel Processing Technology 64 (2000), pp. 189-209.
27. Sippula, O., Lind, T., Jokiniemi, J., Effects of chlorine and sulphur on particle formation in wood combustion in a laboratory scale reactor. Fuel 87 (2008), pp. 2425-2436.

28. Liu, K., Xie, W., Ll, D., Pan, W. P., Riley, J.T., Riga, A., The effect of chlorine and sulfur on the composition of ash deposits in a fluidized bed combustion system. Energy and Fuels 14 (2000), pp. 963-972.
29. Otsuka, N., A thermodynamic approach on vapour-condensation of corrosive salts from flue gas on boiler tubes in waste incinerators. Corrosion Science 50 (2008), pp. 1627-1636
30. Montgomery, M., Biede, O., Larsen, O.H., Experiences with Inconel 625 in biomass and waste incineration plants. Material Science Forum 522-523.
31. Spigel, M., Zahs, A., Grabke, H.J., Fundamental aspects of chlorine induced corrosion in power plants. Materials at high temperatures 20 (2003), pp. 153-159
32. Skrifvars, B. J., Western-Karlson, M., Hupa, M., Salmenoja, K., Corrosion of super-heater steel materials under alkali salt deposits. Part 2: SEM analyses of different steel materials. Corrosion Science 52 (2010), pp. 1011-1019.
33. Ehlers, J., Young, D. J., Smaardijk, E. J., Tyagi, A.K., Penkalla, H. J., Singheiser, L., Qudakkers, W.J., Enhanced oxidation of the 9%Cr steel P91 in water vapour containing environments. Corrosion Science 48(2006), pp. 3428-3454.

Influence of the school's information capacity on the implementation of the international program Eco-school

Uticaj informatičkih kapaciteta škole na implementaciju međunarodnog programa Eko-škole

Dragan Soleša, Radovan Vladisavljević

Faculty of Economics and Engineering Management in Novi Sad, University Business Academy in Novi Sad

Fakultet za ekonomiju i inženjerski menadžment u Novom Sadu, Univerzitet privredna akademija u Novom Sadu

Abstract

The scope of the paper is to present the results of research related to the impact of information capacities of educational institutions in the process of implementation of the international Eco School program. In the last few decades, education for sustainable development has become one of the more important topics in the education reform process. This topic is important for two reasons, the first reason is related to raising awareness about the problems of sustainable development. Another reason is the education of future experts in the field of environmental protection and sustainable development. The results of the research show us that in our country, much more must be done to change existing paradigms in education in the field of environmental protection and sustainable development. The good side is that an increasing number of educational institutions are involved in some form of education in the field of environmental protection and sustainable development.

Key words: *education for environmental protection and sustainable development, education system, information systems, international program Eco School*

Rezime

Cilj rada je prikaz rezultata istraživanja vezanih za uticaj informatičkih kapaciteta obrazovnih ustanova u procesu implementacije međunarodnog programa Eko škole. U poslednjih nekoliko decenija obrazovanje za održivi razvoj postaje jedna od važnijih tema u procesu reforme obrazovanja. Ova tema je važna iz dva razloga, prvi razlog je vezan za povećanje svesti o problemima održivog razvoja dok je drugi razlog obrazovanje budućih stručnjaka u oblasti očuvanja životne sredine i održivog razvoja. Rezultati istraživanja nam pokazuju da se u našoj državi mora još dosta raditi na promeni postojećih paradigmi u obrazovanja u oblasti očuvanja životne sredine i održivog razvoja. Dobra strana je ta što se sve veći broj obrazovnih ustanova uključuje u neki oblik obrazovanja u oblasti očuvanja životne sredine i održivog razvoja.

Ključne reči: *obrazovanje za očuvanje životne sredine i održivog razvoja, obrazovni sistem, informacioni sistemi, međunarodni program Eko škola*

Uvod

Cilj rada je prikaz rezultata istraživanja vezanih za informatičku podršku prilikom uvođenja programa Eko škole u naš obrazovni sistem. Osnovna premisa je da informacioni sistem ima veliku ulogu u kreiranju pozitivne klime prilikom uvođenja programa Eko škole. U osnovi Eko škola je deo nove obrazovne paradigme orijentisane ka obrazovanju za održivi razvoj.

Kroz rad prikazaćemo zašto je pomenuta programa važna i to ne samo na lokalnom već i na međunarodnom nivou. Naglasak je na tome što veliki broj zemalja sveta ulaže značajne napore u izmeni zakona i pravila vezanih za zaštitu životne sredine i održivog razvoja. U ovim krupnim društvenim promenama obrazovanje igra značajnu ulogu, naročito u segmentu održivosti.

Istraživanje je rađeno za potrebe praćenja osnovnih parametara implementacije programa Eko škole. Ono što se mora naglasiti jeste da prikazano istraživanje u ovom radu predstavlja samo izvod iz šireg istraživanja. Izabrali smo nekoliko pitanja iz upitnika koji je imao više baterija pitanja. S obzirom na temu naučnog skupa i zahteve koji su predstavljeni autorima, rad je fokusiran na tehničko tehnološki segment implementacije programa Eko škole

Održivi razvoj

U osnovi misija održivog razvoja je usmerena ka kreiranju društvenog modela koji omogućava ekonomski, tehnološki i društveni razvoja bez žrtvovanja životne sredine. Naglasak je na zaštiti budućih generacije uz uvažavanje potreba sadašnjeg društva. „Politike koje podstiču obrazovanje, znanje, kreativnost i veštine i stvaraju uslove za interakciju između različitih zainteresovanih strana stvaraju know-how, koji podstiče razvoj održivih inovacija“ (Krozer, Y., *Theory and Practices on Innovating for Sustainable Development*, Springer, London, 2016, pp. 184).

„U narednim decenijama, od inženjera će se očekivati da nadograđuju, redizajniraju i inoviraju nove proizvode i usluge koji brzo ispunjavaju povećane ekološke i socijalne kriterijume“ (Desha, C., Hagroves, K., *Higher Education and Sustainable Development: A model for curriculum renewal*, Routledge, London, 2014, pp. 33). Drugim rečima još u segmentu formiranja novog proizvoda mora se voditi računa o uticaju na životnu sredinu.

„Inovativnost u upravljanju životnom sredinom odnosi se na sva nova i primenjena institucionalna i organizaciona rešenja za rešavanje sukoba oko ekoloških resursa“ (Carrillo-Hermosilla J., González, P. Könnölä, T., Eco-Innovation: when Sustainability and Competitiveness Shake Hands, Palgrave MacMillan, Hampshire, 2009, pp. 21). Ovo pitanje je od krucijalne važnosti iz velikog broja razloga. U vremenu industrijske revolucija osnova razvoja su bila prirodna bogatstva poput uglja i nafte. Moderna industrija se okreće ka alternativnim izvorima energije i znanju kao glavnom pokretaču tehnološkog i društvenog razvoja.

„Eko sistemi mogu biti podvrgnuti sukcesijama i periodičnih podmlađivanja“ (Rolston, H. A., New Environmental Ethics: The Next Millennium for Life on Earth, Routledge, New York, 2012, pp. 160). Što znači da priroda ima mogućnosti da se oporavi, „…važno je ispitati ponašanje u pogledu opcija koje mogu biti ograničene usled obrazovanja, profesionalnog treninga, grupnog pritiska“ (Bizer, K., Führ, M., Sustainable Behavioral Governance: Responsive Regulation for Innovation in Beckenbach, F., Kahlenborn, W. (ed.) New Perspectives for Environmental Policies through Behavioral Economics, Springer, Berlin, 2016, pp. 282). Pritisci društva moraju da se usmere ka održivom razvoju kako bi se kreiralo okruženje u kojem će se ciljevi održivosti biti mogući.

I samo znanje o prirodi i održivom razvoju je u stalnom fluksu, „…baza znanja nije statična, ona se kontinuirano razvija na osnovu promena uslova okoline i informacija dobijenih od drugih pojedinaca unutar i izvan zajednice“ (Falkowski, Martinez-Bautista, Diemont, 2015 :40). Tako da se ova tema konstantno razvija i proširuje.

Obrazovanje za održivi razvoj

Obrazovanje je ključna komponenata društava u celini bez koje je nemoguće zamisliti održivost na duže staze. Nažalost obrazovni sistemi širom sveta se teško prilagođavaju novim trendovima društva. „Obrazovanje treba da uključi kritičko shvatanje uticaja nauke na društvo. Zbog toga je važno sistematično uključiti pitanja zaštite životne sredine u rad sa učenicima“ (Krnel, D., Naglič, S., `Environmental literacy comparison between eco-schools and ordinary schools in Slovenia`, Science Education International, Vol.20, No.1/2, December, pp. 5-24, 2009, pp. 17). Upravo kritičko razmišljanje je komponenta koja nedostaje mnogima obrazovnim sistemima. Kontinualno preispitivanje uticaja tehnologije i nauke na životnu sredinu su pitanja od ključne važnosti.

„Obrazovanje za održivi razvoj dopušta svakom ljudskom biću da pribavi znanja, veština, stavove i vrednosti neophodne za oblikovanje održive budućnosti“ (UNESCO, 2014). Definicija obrazovanja za održivi razvoj je usmerena ka budućim potrebama društva uz naglasak da se ne ugrožava razvoj sadašnjeg društva. Platforma obrazovanja za održivi razvoj je „obrazovanje za odživi razvoj je zamišljen kao misaoni okvir koji naglašava značaj onih aspekata obrazovanja koja nisu deo formalnog kurikuluma“ (Bonnett, M., `Education for Sustainable Development: a coherent philosophy for environmental education?`, Cambridge Journal of Education, Vol. 29, No. 3, 2013, pp. 313 – 324,). Iz ovoga sledi da obrazovanje za održivi razvoj nije kalup po kojem se mora formirati obrazovni sistem, već je to platforma koja pruža veliku fleksibilnosti.

Problem ležu u nedovoljno struktuiranom procesu obrazovanja. „Nastava je neuredan posao, pun nagađanja i intuicije “(Riley, P. *Attachment Theory and the Teacher–Student Relationship: A practical guide for teachers, teacher educators and school leaders*, Routledge, London, 2011, pp. 109). „Međutim, neurednost nije lako dokumentovana, nastava se uči iskustvom, i to izgleda da opterećava mnoge političare i birokrate u obrazovanju“ (Riley, P. *Attachment Theory and the Teacher–Student Relationship: A practical guide for teachers, teacher educators and school leaders*, Routledge, London, 2011, pp. 109). Drugim rečima ono koji su van učionice teško mogu da razumeju problematiku obrazovanja. I najbolje politike i strategije obrazovanja ne mogu nadomestiti iskustvo koje se stiče u radu sa učenicima.

„U novom okruženju obrazovanja sa integrisanim (IKT – informaciono komunikacione tehnologije) u kurikulume učenje dobija novu dimenziju“ (Shopova, T., Digital Literacy of Students and its Improvement at the University, Journal on Efficiency and Responsibility in Education and Science, Vol. 7, No. 2, 2014, pp. 31). Deljenje informacija postaje daleko lakše i jednostavnije. Mediji prenosa znanja postaju daleko efikasniji, pristupačnija i kvalitetnija. Moderne tehnologije pružaju multimedijalne platforme na kojima se mogu graditi novi kurikulumi.

Program Eko škole

“Obrazovanje po svojoj prilici, međutim, nije garancija postizanja ciljeva ‘Održivog razvoja’ tako da su posrednici potrebni u formi zaposlenosti koja obezbeđuje sredstava za život, a samim tim i pristup materijalnim dobrima koji su toliko važni za savremeni život“ (Teng, P. S. P. Linking Education to Socially-Relevant Bio entrepreneurship for Sustainable Development’ in Kim, M. and Diong, H., C. (ed.) Biology Education for Social and Sustainable Development, Rotterdam: Sense Publisher, 2012, pp. 6). Iz ovog razloga formiran je program Eko škole koji ima podršku Ujedinjenih Nacija, okosnica programa je uključenje aktera van obrazovnog sistema. Na ovaj način svi dobijaju mogućnost da sarađuju i van programa Eko škole.

Popularnost ovog programa se može uočiti uključenjem većeg broja studenata/učenika. „Visok stepen uključenosti studenata i puno uvažavanja javnosti ukazuju na to da takvi događaji takođe generišu obrazovne spin-off-e koji podrazumevaju izgradnju kapaciteta za inovativne poteze u budućnosti“ (Krozer, Y., *Theory and Practices on Innovating for Sustainable Development*, Springer, London, 2016, pp. 57). Tako da program Eko škole predstavlja temelj za mnoge aktivnosti i projekte koji su deo vezani za održivi razvoj i ekološka pitanja. Sam program nije projektnog karaktera i vodi se drugačijom logikom nego što to zahtevaju projekti, ali program je visoko kompatibilan sa projektima Evropske unije, nacionalnog okvira ili lokalne zajednice.

„Inicijativa programa je naročito fokusirana na multisektorskoj i intersektorskoj kooperaciji za ispunjenje ciljeva (Ambasadori održivog razvoja i životne sredine, 2017):
Razvoj međusobne saradnje i saradnje sa relevantnim međunarodnim organizacijama iste i slične profesije; Razvoj svih oblika uspešne saradnje sa drugim profesionalnim organizacijama i udruženjima u interesu svojih članova; Iniciranje i podrška onim aktivnostima i inicijativama sa ciljem očuvanja životne sredine i prostornog planiranja; …; Saradnja sa relevantnim naučnim, stručnim, ekonomskim i drugim organizacijama i telima o realizaciji zadataka od zajedničkog interesa; Afirmacija i zaštita osnovnih vrednosti, interesa i pozicija održivog razvoja i životne sredine …“
Iz prethodnog pasusa se mogu videti osnovni ciljevi programa Eko škole i Ambasadora održivog razvoja i zaštite životne sredine kao tela koje administrira program. Ciljevi programa jasno ukazuju na proaktivni pristup i visokoj saradnji sa svim relevantnim akterima. Program je uspešno implementiran u velikom broju zemalja, a u Republici Srbiji preko trideset obrazovnih ustanova je uključena u program.

Istraživačke metode

Predmetno disciplinarno sužavanje istraživanja je sledeće: u najširem istraživačkom poduhvatu istraživaćemo obrazovanje, uže predmetno određivanje je vezano za obrazovanje u domenu zaštite životne sredine i održivog razvoja. Najuža oblast istraživanja je uticaj informacionih sistema na programe i projekte Eko škole u cilju poboljšavanja obrazovanja za zaštitu životne sredine i održivog razvoja.
Problem se može izraziti pitanjem: da li informatički kapaciteti obrazovnih ustanova utiču na implementaciju programa Eko škole?
Cilj istraživanja se ogleda u ispitivanju stavova ispitanika veznih za aktivnosti učenika/studenata u aktivnostima programa Eko škole. Učenici odnosno studenti su ključni činioci implementacionih napora, bez potpunog uključivanja studenata u program nije moguće upravljati osnovnim aktivnostima programa niti konkurisati za različite projekte vezane za program.
Za potrebe ovog rada izdvojili smo tri ključna pitanja iz šireg istraživanja rađenog za potrebe projekta Autonomne pokrajine Vojvodine pod naslovom „Eko-škole kao model i sredstvo obrazovanja za održivi razvoj“. Svrha ovog projekta je prikaz rezultata i iskustava prilikom implementacije međunarodnog programa Eko-škole. Istraživanje je rađeno na teritoriji Republike Srbije, učesnici su bile obrazovne ustanove koje su se priključile programu Eko-škole. Broj škola koje je učestvovalo u istraživanju je 35, ispitivani su zaposleni koji su uključeni u vođenju programa Eko-škole.
Kao nezavisnu varijablu koristili smo ocenu informatičkih kapaciteta. Ova ocena se kreće od najmanje ocene 1 koja označava vrlo slab informatički kapacitet, 2 koja označava slab informatički kapacitet, 3 koja označava dobar informatički kapacitet i 4 koja označava izuzetno dobar informatički kapacitet. Sama ocena je kompozitnog karaktera koja je sačinjena od ocena iz više oblasti. Prilikom istraživanja informatičkih kapaciteta ocenjivali smo web sajt ustanove, uređenje stranica na socijalnim mrežama („Facebook“, „Twitter“ i sl.) i dodatne usluge koje se nude od strane ustanova. Web sajt ustanove je važan ne samo za marketing već i za izgradnju određenog imidža organizacije. U mnogim slučajevima web sajt ustanove je način da se najjednostavniji način povežu sve zainteresovane stane. Sa druge strane socijalne mreže igraju veliku ulogu u povezivanju i integraciji svih zainteresovanih strana sa tom razlikom što ustanova ima daleko veću kontrolu. U eri rapidnog širenja Interneta i mobilnih platformi mnoge obrazovne ustanove mogu da pruže dodatne usluge poput elektronskog dnevnika/indeksa, dodatnih informacija, platforme za učenje na daljinu („distance learning systems“ – DLS) i sl.
Svaka od ovih stavki istraživači su ocenjivali sa ocenom od 1 do 4. Na kraju su izvučene aritmetičke sredine koje su zaokruživane i takve dodeljene varijabli informatičkih kapaciteta

ustanove. Na ovaj način dobijena je realna slika mogućnosti organizacija koje učestuju u programu Eko škole. Informatički kapaciteti su važni jer celokupna korespodencija sa partnerima u programu Eko škole se vrši elektronskim putem. Sa druge strane informacije o programu Eko škole moraju biti dostupni svima kako bi svi učesnici lakše mogli da se informišu. Ovo je važno jer program Eko škole je holističkog karaktera koji uključuje pored obrazovne ustanove i zainteresovane ustanove i individualce van obrazovnog sistema.

Glavni instrument istraživanja je upitnik sa većim brojem pitanja, za potrebe ovog rada izdvojili smo tri pitanja koja se odnose na angažovanje učenika u programu Eko škole. Pitanja su formulisana u obliku iskaza na koji su ispitanici odgovorili ocenjivanjem sa ocenom od 1 do 5. Ocena 1 je označavala da se ispitanici u potpunosti ne slažu sa iskazom, ocena 2 je označavala da se ispitanici ne slažu sa postavljenim iskazom, ocena 3 je označavala da se ispitanici i slažu i ne slažu sa iskazom, ocena 4 je označavala da se ispitanici slažu sa iskazom i na kraju ocena 5 je označavala da se ispitanici u potpunosti slažu sa postavljenim iskazom. Na ovaj način upitnik je formulisan u obliku Lirektove skale.

Prvo pitanje koje smo izdvojili je vezano za aktivnosti učenik i glasi: Učenici aktivno učestvuju u aktivnostima Eko-škole. Drugim pitanjem testirali smo u kojoj meri učenici sami preuzimaju inicijativu, ovo pitanje je glasilo: Učenici samostalno pokreću aktivnosti koje se mogu povezati sa svrhom Eko-škole. Treće pitanje je testiralo uključivanje učenika sa specijalnim potrebama, ovo pitanje je glasilo: Program Eko-škole pruža mogućnost afirmacije učenika s posebnim potrebama. Ovo poslednje pitanje je važno jer učenici sa posebnim potrebama su posebna kategorija koja se tradicionalno teško uklapa u obrazovni sistem koji je orijentisan na masovno obrazovanje. Ovde se mora naglasiti da u kategoriju učenika sa posebnim potrebama spadaju učenici sa smetnjama u razvoja ali i daroviti učenici. I jedna i druga grupa se teško uklapa u postojeće obrazovne sisteme, kod prve kategorije može biti problema u praćenju nastave zbog smanjene inteligencije, fizičkih i sličnih smetnji. Sa druge strane darovita deca koja najčešće imaju visok nivo inteligencije vrlo brzo gube motiv za učenje.

Na osnovu predmeta, problema i cilja istraživanja kao i izbora istraživačkih alata možemo kreirati istraživačka pitanja.

Istraživačko pitanje 1: Da li postoji statistički značajne razlike između informacionih kapaciteta obrazovnih ustanova i učestvovanja učenika u aktivnostima vezanim za program Eko škole?

Istraživačko pitanje 2: Da li postoji statistički značajne razlike između informacionih kapaciteta obrazovnih ustanova i samostalnih inicijativa učenika vezanih za program Eko škole?

Istraživačko pitanje 3: Da li postoji statistički značajne razlike između informacionih kapaciteta obrazovnih ustanova i afirmacije učenika sa posebnim potreban kroz program Eko škole?

Rezultati istraživanja

Prvi korak u obradi podataka dobijenih anketom je deskriptivni opis dobijenih rezultata. Na ocenu informatičkih kapaciteta škole rezultati su sledeći: od 35 škola koja su učestvovale u istraživanju njih 11 (31,4%) je dobilo ocenu 1 (vrlo slab), 11 (31,4%) škola je dobilo ocenu 2 (slab), 2 (5,8%) ocenu 3 (dobar), a 11 (31,4%) ocenu 4 (izuzetno dobar). Aritmetička sredina dobijenih rezultata je 2,37, medijana iznosi 2, standardna devijacija 1,239, a zakrivljenost 0,313.

Na pitanju „Učenici aktivno učestuju u aktivnostima Eko škole“ rezultat je sledeći: 3 (8,6%) ispitanika su iskaz ocenila ocenom 3 (i slažem se i ne slažem se), 14 (40%) ocenom 4 (slažem se), dok su 18 (51,4%) ispitanika ocenili iskaz ocenom 5 (u potpunosti se slažem). Srednja vrednosti rezultata je 4,43, medijana 5, standardna devijacija 0,655, a zakrivljenost -0,722.

Na drugom pitanju „Učenici samostalno pokreću aktivnosti koje se mogu povezati sa svrhom Eko škole“ rezultat je sledeći: 2 (5,7%) ispitanika je ocenila iskaz sa ocenom 2 (ne slažem se), 12 (34,3%) sa ocenom 3 (is slažem se i ne slažem se), 15 (42,9%) sa ocenom 4 (slažem se) i 6 (17,1%)

ispitanika ocenilo je iskaz sa ocenom 5 (u potpunosti se slažem). Srednja vrednosti rezultata je 3,71, medijana 4, standardna devijacija 0,825, a zakrivljenost -0,075.

Na poslednjem pitanju koje je glasilo „Program Eko-škole pruža mogućnost afirmacije učenika s posebnim potrebama“ rezultat je sledeći: 3 (8,6%) ispitanika ocenilo je iskaz sa ocenom 2 (ne slažem se), 11 (31,4%) sa ocenom 3 (i slažem se i ne slažem se), 13 (37,1%) sa ocenom 4 (slažem se) i na kraju 8 (22,9%) ispitanika ocenilo je iskaz ocenom 5 (u potpunosti se slažem). Srednja vrednosti rezultata je 3,74, medijana 4, standardna devijacija 0,919, a zakrivljenost -0,172.
Iz ovih rezultat može se videti da preovladaju pozitivni stavovi prema programu Eko škole. Međutim na osnovu deskriptivne statistike nemoguće je donositi validne zaključke. Kako bi došli do odgovora na naša istraživačka pitanja koristili smo se neparametarskim metodama analiziranja podatka, tražili smo statistički razlike između grupa. Neparametarske metode smo koristili kako bi umanjili problem malog uzorka, ovde je potrebno naglasiti da je i populacija relativno mala i broji manje od 50 ustanova različitog nivo obrazovanja. Prvo smo koristili Kruskal-Wallis test koji nam otkriva kod kojih pitanja može detektovati statističke razlike. Nažalost ovaj test nam ne daje kompletnu sliku o tome koje grupe se statistički značajno razlikuju. Za ovo smo koristili Mann-Whitney test, s obzirom da imamo kod nezavisne varijable 4 tako smo morali da svaki par analiziramo posebno. Takođe, zbog četvoro stepene nezavisne varijable morali smo da izvršimo Bonferonijeovo prilagođavanje nivo praga značajnosti tako da je novi prag značajnosti 0,05/4 = 0.0125.

Tabela 1. Kruskal-Wallis test

	Informatički kapacitet škole	N	Mean Rank
Učenici aktivno učestvuju u aktivnostima Eko-škole	vrlo slab	11	19,14
	slab	11	14,09
	dobar	2	26,50
	izuzetno dobar	11	19,23
	Total	35	
Učenici samostalno pokreću aktivnosti koje se mogu povezati sa svrhom Eko-škole	vrlo slab	11	19,95
	slab	11	17,14
	dobar	2	27,25
	izuzetno dobar	11	15,23
	Total	35	
Program Eko-škole pruža mogućnost afirmacije učenika s posebnim potrebama	vrlo slab	11	25,77
	slab	11	15,09
	dobar	2	15,00
	izuzetno dobar	11	13,68
	Total	35	

Tabel 2. Statistika testa $^{a, b}$

	Učenici aktivno učestvuju u aktivnostima Eko-škole	Učenici samostalno pokreću aktivnosti koje se mogu povezati sa svrhom Eko-škole	Program Eko-škole pruža mogućnost afirmacije učenika s posebnim potrebama
Chi-Square	4,088	3,324	10,311
df	3	3	3

Asymp. Sig.	,252	,344	,016

a. Kruskal Wallis Test

b. Grouping Variable: Informatički kapacitet škole

Kruskal-Wallis – ov test je otkrio statistički značajnu razliku informatičkih kapaciteta po pitanju mogućnosti programa Eko škole da afirmiše učenike sa posebnim potrebama C^2(2, n = 35) = 10,311, p = 0,016. S obzirom da imamo četiri stepena u pitanju vezanom za informatičke kapacitete, ovim testom ne možemo sa sigurnošću reći koja grupa je statistički značajnija. Iz ovog razloga pristupamo izradi Mann-Whitney testu.

Kod ostalih pitanja Kruskal-Wallis test nije otkrio statistički značajne razlike, stoga ova pitanja nećemo dalje obrađivati.

Tabela 3. Mann-Whitney test

	Informatički kapacitet škole	N	Mean Rank	Sum of Ranks
Program Eko-škole pruža mogućnost afirmacije učenika s posebnim potrebama	vrlo slab	11	15,41	169,50
	izuzetno dobar	11	7,59	83,50
	Total	22		

Tabela 4. Statistika testa a

	Program Eko-škole pruža mogućnost afirmacije učenika s posebnim potrebama
Mann-Whitney U	17,500
Wilcoxon W	83,500
Z	-2,988
Asymp. Sig. (2-tailed)	,003
Exact Sig. [2*(1-tailed Sig.)]	,003^b

a. Grouping Variable: Informatički kapacitet škole

b. Not corrected for ties.

Mann-Wihney test je otkrio statistički značajnu razliku između vrlo slabih informatičkih kapaciteta i izuzetno dobrih informatičkih kapaciteta, U = 17,500, z = -2,988, p = 0,003. S obzirom da smo imali četiri kategorije ocena informatičkih kapaciteta izvršili smo prilagođavanje praga značajnosti 0,05/4 = 0.0125.

Diskusija istraživanja i zaključak

Iz rezultata istraživanja možemo formulisati odgovore na postavljena istraživačka pitanja. S obzirom da kod prva dva pitanja nismo otkrili statistički značajne razlike po pitanju informatičkih kapaciteta odgovor odgovora na prva dva istraživačka pitanja su negativni. Sa druge strane kod trećeg istraživačkog pitanja detektovali smo statistički značajne razlike između nivoa informatičkog kapaciteta i nivoa afirmacije učenika sa posebnim potrebama. Iz ovog sledi da je odgovor na trećem pitanju pozitivan.

Ovakvi rezultati se mogu objasniti prirodom programa i umešnosti onih koji implementiraju isti. Prvo pitanje bilo vezano za aktivnosti učenika, velika većina ispitanika je dalo potvrdan odgovor, 18 (51,4%) ispitanika ocenili iskaz ocenom 5 (u potpunosti se slažem). Iz ovog može da se zaključi da i pored informatičkih kapaciteta učenici se rado uključuju u aktivnosti programa Eko škole. Razloga je mnogo, većina škola nažalost nema adekvatne informatičke kapacitete ali i pored toga je u stanju da se izbore sa relativno kompleksnim problemima u obrazovanju.

Drugo pitanje je bilo vezano za pokretanje samostalnih inicijativa učenika u programu Eko škole. Deskriptivna statistika nam daje uvid u to da je veći broj pozitivnih odgovora nego negativnih. Međutim, za razliku od prethodnog pitanja nemamo nadprosečnu većinu kod pozitivnih pitanja. Ovde se može postaviti pitanje da li bi poboljšanje informatičkih kapaciteta povećalo skor, naročiti u domenu bolje uređenje stanica na socijalnim mrežama. Ipak treba naglasiti da ni kod ovog pitanja nismo uočili statistički značajne rezultate.

Kod trećeg pitanja koje se bavilo uključivanjem učenika sa posebnim potreban u program Eko škole uočena je statički značajna razlika. Ove razlike su naročito izražene između ocena informatičkih kapaciteta škola u kategorijama vrlo slabo i izuzetno dobar kapacitet. Proverom statističkih sredina uočavamo da je kategorija vrlo slab iznosi MD = 15,41. Ovo nam govori sa stanovišta afirmacije učenika sa posebnim informatički kapaciteti su važni.

Ovakav rezultata može se objasniti činjenicom da sam termin deca sa posebnim potrebama uključuje širok spektar. Na jednom kraju spektra nalaze se deca sa smetnjama u razvoju, a sa druge strane darovita deca. Međutim, za obe grupe dece dodatne informacije su od velike važnosti. Deca ometena u razvoju imaju potrebe za dodatnim objašnjenjima, na primer deca sa audio teškoćama zahtevaće transkripte sa stanaka i sl. Takođe, deo dece sa smetnjama u razvoju zavise od svojih staratelja ili negovatelja koji možda nisu direktno učestvovali u nekom od projekata. Sa druge strane darovita deca najčešće imaju izraženu radoznalost tako da je kod njih zahtev sa dodatnim informacijama izraženiji.

U budućim istraživanjima potrebno je produbiti temu vezanu za decu sa posebnim potrebama kako bi se detektovale koje dete spada u koju grupu. Ova gruba podela bi pomogla samo u dobijanju obrisa zakonitosti dinamike grupa dece sa posebnim potrebama. Svrha budućeg istraživanja bi trebalo da bude otkrivanje skrivenih mehanizama koje vode ka većem stepenu afirmacije dece sa posebnim potrebama. Da je ova tema aktuelna može se videti iz primera da se sve više napora ulaže u inkluzivnu nastavu i formiranju posebnih odeljenja za darovitu decu.

Reference

Bizer, K., Führ, M., Sustainable Behavioral Governance: Responsive Regulation for Innovation in Beckenbach, F., Kahlenborn, W. (ed.) New Perspectives for Environmental Policies through Behavioral Economics, Springer, Berlin, 2016.

Bonnett, M., `Education for Sustainable Development: a coherent philosophy for environmental education?`, Cambridge Journal of Education, Vol. 29, No. 3, pp. 313 – 324, 2013.

Carrillo-Hermosilla J., González, P. Könnölä, T., Eco-Innovation: when Sustainability and Competitiveness Shake Hands, Palgrave MacMillan, Hampshire, 2009.

Desha, C., Hagroves, K., *Higher Education and Sustainable Development: A model for curriculum renewal*, Routledge, London, 2014.

Environment Ambassadors for Sustainable Development *Program initiatives*, [Online], Available: http://www.ambassadors-env.com/en/program/programming-initiative/ , Accessed 19 Jun 2017, 2017.

Falkowski, B. T., Martinez-Bautista, I., Diemont, W.,A.,S., How valuable could traditional ecological knowledge educationbe for a resource-limited future?: An emergy evaluationin two Mexican villages, Ecological Modelling, 300, 2015

Flégl, M., Tichá, I., Kvasničková Stanislavská, L., K., Innovation of Doctoral Studies At The Fem Culs Prague, Journal on Efficiency and Responsibility in Education and Science, Vol. 6, No 4, 2013.

Krnel, D., Naglič, S., `Environmental literacy comparison between eco-schools and ordinary schools in Slovenia`, Science Education International, Vol.20, No.1/2, December, pp. 5-24, 2009.

Krozer, Y., *Theory and Practices on Innovating for Sustainable Development*, Springer, London, 2016.

Perales-Palacios, J. E., Burgos-Peredo, O., Gutiérrez-Pérez, J., The eco-schools program: A critical assessment of strengths and weaknesses, Perfiles Educativos, vol. XXXVI, núm. 145, 2014

Riley, P. *Attachment Theory and the Teacher–Student Relationship: A practical guide for teachers, teacher educators and school leaders*, Routledge, London, 2011.

Rolston, H. A., New Environmental Ethics: The Next Millennium for Life on Earth, Routledge, New York, 2012.

Shopova, T., Digital Literacy of Students and its Improvement at the University, Journal on Efficiency and Responsibility in Education and Science, Vol. 7, No. 2, 2014.

Teng, P. S. P. Linking Education to Socially-Relevant Bio entrepreneurship for Sustainable Development' in Kim, M. and Diong, H., C. (ed.) Biology Education for Social and Sustainable Development, Rotterdam: Sense Publisher, 2012.

UNESCO (2014). *Education for sustainable development* (ESD), [Online], Available:http://www.unesco.org/new/en/education/themes/leading-the-international-agenda/education-for-sustainable-development/, Accessed 19February 2016

Examination of steel tank floors by MFL (magnetic flux leakage) method

Ispitivanje poda čeličnih rezervoara metodom MFL (magnetic flux leakage) metoda promene magnetnog toka

Željko Krivačević, Dejan Grgić, Saša Stojanović

PI Transnafta, Pančevo, Serbia

JP Transnafta, Pančevo, Srbija

Izvod

Ispitivanje bez razaranja poda čeličnih rezervoara, metodom MFL (magnetic flux leakage) metoda promene magnetnog toka, sprovodi se kao metoda pogodna za otkrivanje i detekciju oštećenja od korozije kako sa gornje a naročito sa donje strane čelićnih limova poda rezervoara.

Uvod

Ispitivanje čeličnih limova poda rezervoara metodom MFL na skladištu derivata nafte, sproveden je kao jedna od metoda ispitivanja bez razaranja (IBR) tokom februara / marta 2015. godine. Ispitivanje je sprovedeno korišćenjem magnetne MFL metode koja se od 2000. godine dokazala kao jedina koja može detektovati oštećenja od korozije, odnosno oštećenja limova poda rezervoara koja nastaju sa “donje“ strane čeličnog lima (izmedju čeličnog lima i temelja rezervoara). Kao metoda pogodna za detekciju oštećenja od korozije prihvaćena je u celom svetu i Evropi koja u svojim dokumentima koja se bave sprečavanjem zagadjenja životne sredine (BREF document “Best Available Techniques (BAT) reference documents, the so-called BREFs”) spominje MFL ispitivanje kao metodu koja može biti vrlo korisna za otkrivanje oštećenja od korozije limova poda rezervoara.

Ispitivanje metodom MFL

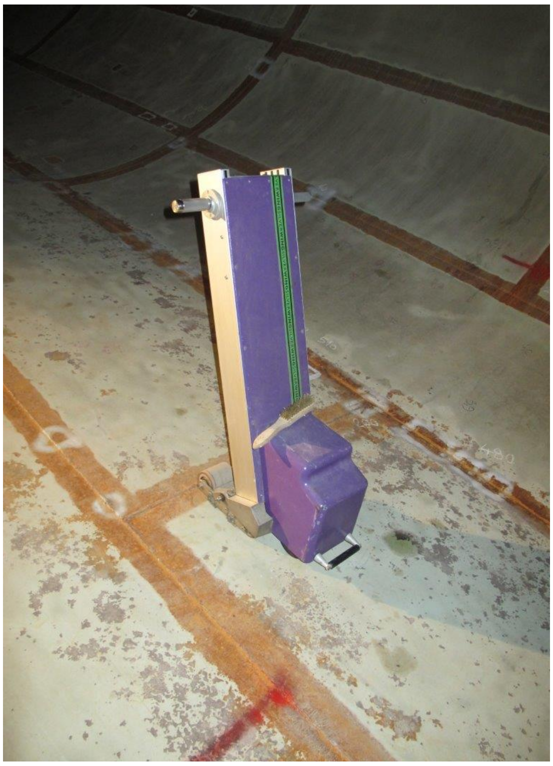
Korišćen je samohodni MFL 2000 uredjaj (slika dole) za ispitivanje promenom magnetnog toka. Pokreće se elektromotorom koji je ugradjen u kućište uredjaja zajedno sa magnetnim mostom (magneti + sonde), bazom (elektronski modul) i akumulatorima za pokretanje. Brzina skeniranja je konstantna i nema uticaja na rezultate ispitivanja. Na bazi postoji 36 malih LED dioda (1 za svaku sondu na magnetnom mostu) koje promenom boje iz zelene u crveno (ostanu da svetle dok se ne resetuje uredjaj) i označavaju koja je sonda detektovala grešku. Osim toga uredjaj ima i auto-stop funkciju koja se može isključiti, a služi da elektronika automatski zaustavi uredjaj nakon detektovanja greške. Uredjaj ima dva područja rada koja zavise od debljine čeličnog lima koji se ispituje i to:

- Ispitivanje čeličnih limova debljine ≤ 8 mm
- Ispitivanje čeličnih limova debljine > 8 mm

Uredjaj MFL 2000, kalibrisan je na čeličnom limu za kalibraciju indetične debljine lima debljini lima poda rezervoara koji se ispituje (4 mm) a sadrži četiri veštački proizvedene rupice od korozije kako sledi:

1. Cilindrična rupica od 120° koja prodire do 20% debljine lima od donje površine.
2. Cilindrična rupica od 120° koja prodire do 40% debljine lima od donje površine.
3. Cilindrična rupica od 120° koja prodire do 60% debljine lima od donje površine.
4. Cilindrična rupica od 120° koja prodire do 80% debljine lima od donje površine.

MFL 2000 je korišćen samo na čeličnim limovima poda rezervoara gde se i očekivalo najviše oštećenja tokom veka eksploatacije. Ispitivanje je sprovedeno red po red, a svaka sučeono zavarena čelična ploča (dimenzija 6000 mm x 1300 mm) u redu, naizmenično je skenirana. Tokom ispitivanja čeličnih limova poda rezervoara, zabeležena su samo oštećenja koja su iznosila preko 40 % gubitka nazivne debljine čeličnog lima (nazivna debljina čeličnog lima 4 mm).
Materijal čelika, odnosno čeličnih limova je kvaliteta SRPS C.B0.500: Č.0361, odnosno prema evropskim normama EN 10025: S235 JRG2. a sve table poda su medjusobno sučeono zavarene.



Slika 1. MFL 2000

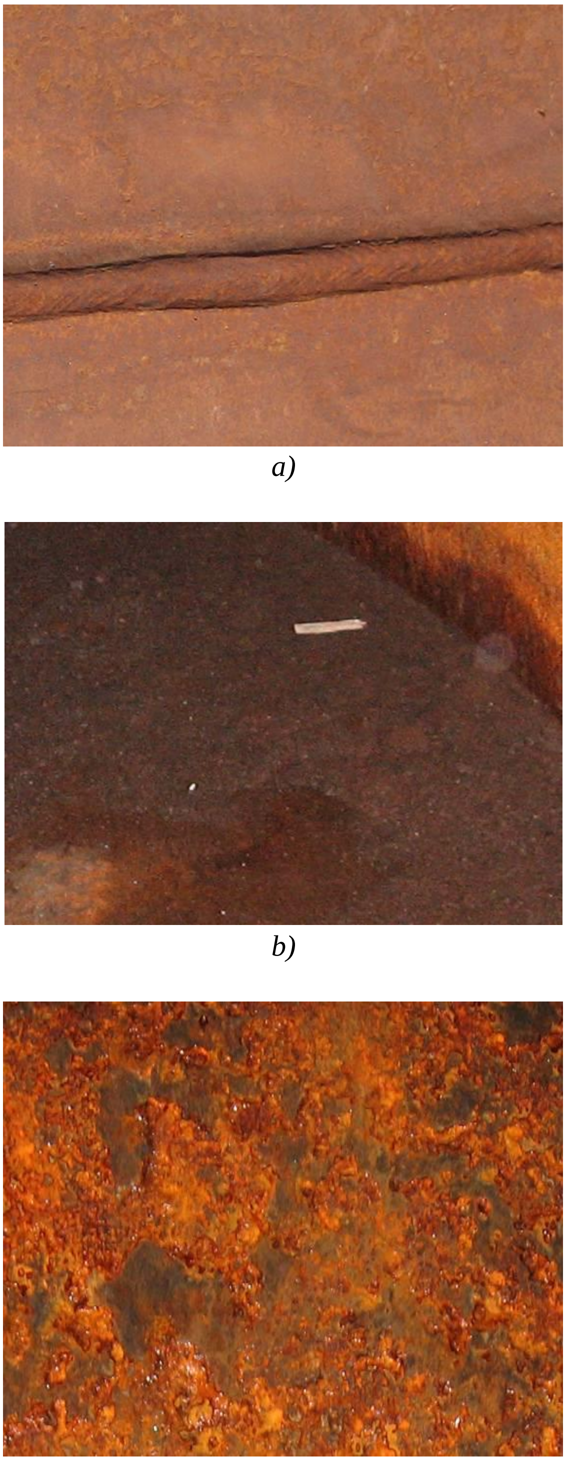
Ultrazvučna provera kalibracije sistema

Na samom početku sprovodjenja ispitivanja – na prvim detektovanim oštećenjima, izvršena je ultrazvučna kontrola veličine oštećenja sa kojom je provereno da li MFL uredjaj pouzdano detektuje oštećenja. Kod provere kalibracije MFL 2000 korišćen je ultrazvučni “Phased array” uredjaj “Olympus” i ravna sonda sa 64 kanala. Prilikom provere kalibracije MFL sistema, utvrdjeno je da MFL sistem pouzdano detektuje samo oštećenja koja su veća od kalibrisanih 40 % nominalne debljine čeličnog lima.

Potrebna čistoća površine čeličnog lima

Za potrebe vizuelnog pregleda i detaljnih ispitivanja bez razaranja (IBR) medju kojima je i metoda MFL, prethodili su radovi čišćenja, odmašćivanja gde je trebalo do stepena “gas free” a zatim peskarenja unutrašnjosti čeličnih rezervora, tj čeličnih limova sa kvalitetom peskarenja Sa1, prema ISO-8501-1 kao i peskarenje zavarenih spojeva čeličnih limova u širini 100 mm sa svake strane zavarenog spoja kvalitetom peskarenja Sa2,5 prema ISO-8501-1. Nakon završnog otprašivanja, čišćenje i odnošenja peska od peskarenja, rezervoari su bili spremni za ispitivanje.

Priprema površina za ispitivanje je uslov dobrim rezultatima jer usled velike hrapavosti površine (zbog korozije) može doći do pojave lažnih grešaka a isto tako lokacije sa stvarnim oštećenjima mogu postati nevidljive usled velikog šuma (slike dole).


a)

b)

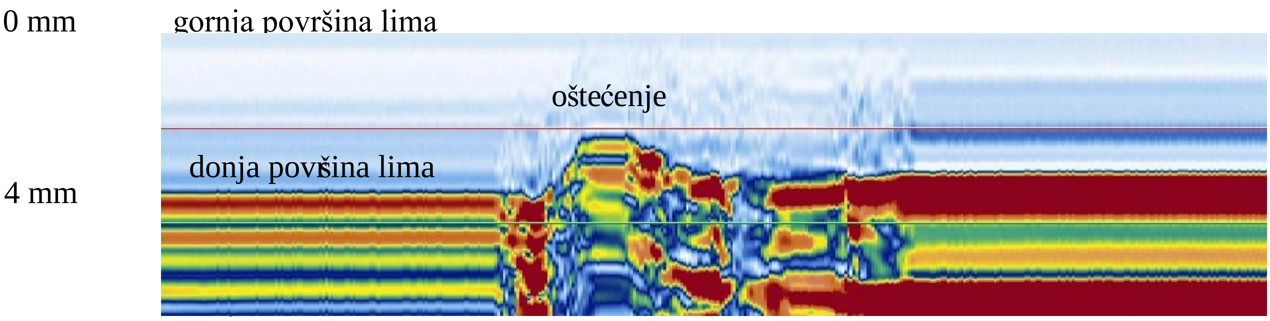
c)

Slika 2. a) Prihvatljiv i b) i c) neprihvatljiv rezultat

Rezultati

Ispitivanje čeličnih limova poda rezervoara MFL metodom sprovedeno je samo na ravnim delovima poda rezervoara a ukupna površina ispitivanja iznosila je oko 2.400 m^2 .
Za kriterijume prihvatljivosti grešaka osnovnog materijala primenjivani su važeći standardi (standardi ISO 5817, EN 970 i/ili EN 17637, EN 1593 i drugi).
Nakon sprovedenih MFL ispitivanja ravnog dela poda svih rezervoara i analize svih rezultata utvrdjena su znatna oštećenja na limovima:
634 nalaza sa stanjenjem osnovnog materijala poda od 40 % do 60 % ;
74 nalaza sa stanjenjem osnovnog materijala poda od 60 % do 80 % ;
7 nalaza sa stanjenjem osnovnog materijala poda sa više od 80 %;

Slika 3. Prikaz oštećenja koje je počelo sa "donje" strane lima koje je nemoguće detektovati ultrazvučnim merenjem debljine lima a vizuelnom metodom se otkrije kad izbije na površinu (nastane rupa)



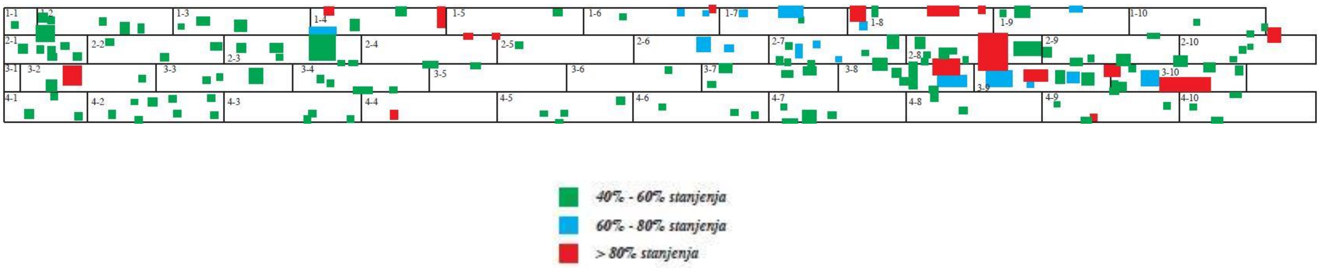
Slika 4. ltrazvučni prikaz lokacije sa oštećenjem sa "donje" strane lima (ultrazvučna provera sprovedena nakon detektovanja lokacije MFL metodom)

Sve lokacije na kojima su detektovana oštećenja limova poda rezervoara sa stanjenjem većim od 40% nominalne debljine čeličnog lima poda rezervoara, obeležena su belom bojom na samom podu rezervoara te su izmerene koordinate lokacije "zakrpe" kao i njene veličine što je dokumentovano skicom i pripadajućom tablicom sa svim izmerenim podacima za svaki rezervoar posebno.

Slika 5. Obeležavanje mesta za sanaciju nakon završenog MFL ispitivanja

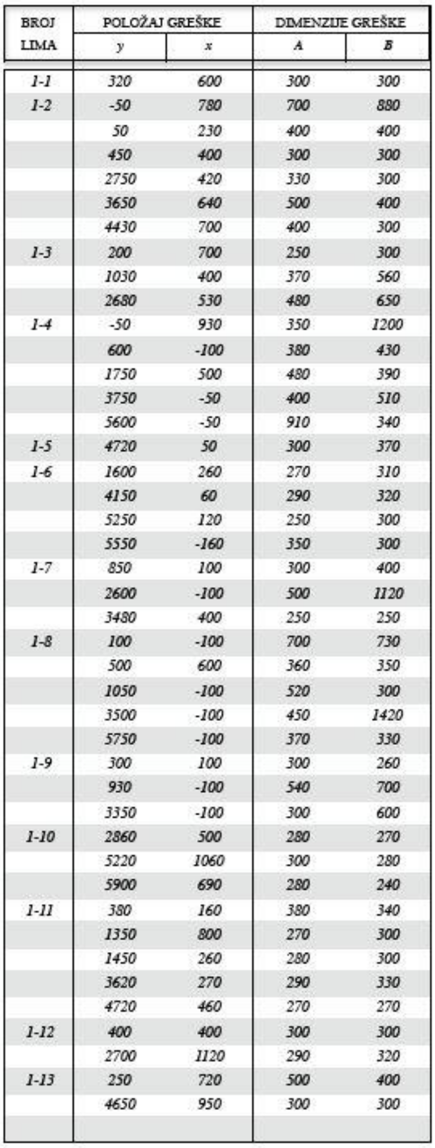
Slika 6. Deo pozicija mesta za sanaciju čeličnih limova poda rezervoara nakon završenog MFL ispitivanja

Ukupno stanje za svaku pojedinu ispitanu tablu čeličnog lima poda rezervoara nalazi se prikazano i grafičkim prikazom svih lokacija oštećenja i tabelarnim prikazom koordinata svake lokacije sa veličinama potrebnih "zakrpa". Svi kriterijumi popravaka trebaju da se baziraju na ukupnom stanju čeličnog poda rezervora prikazanom u rezultatima.

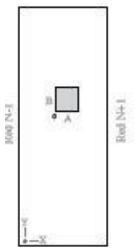


Slika 7. Grafički prikaz oštećenja tabli čeličnog poda rezervoara. Različite boje označavaju različiti % stanjenja čeličnog lima poda rezervora

Tabela 1. Tabelarni prikaz koordinata oštećenja svake lokacije sa dimenzijama potrebnih "zakrpa"



BROJ LIMA	POLOŽAJ GREŠKE		DIMENZIJE GREŠKE	
	y	x	A	B
1-1	320	600	300	300
1-2	-50	780	700	880
	50	230	400	400
	450	400	300	300
	2750	420	330	300
	3650	640	500	400
	4430	700	400	300
1-3	200	700	250	300
	1030	400	370	560
	2680	530	480	650
1-4	-50	930	350	1200
	600	-100	380	430
	1750	500	480	390
	3750	-50	400	510
	5600	-50	910	340
1-5	4720	50	300	370
1-6	1600	260	270	310
	4150	60	290	320
	5250	120	250	300
	5550	-160	350	300
1-7	850	100	300	400
	2600	-100	500	1120
	3480	400	250	250
1-8	100	-100	700	730
	500	600	360	350
	1050	-100	520	300
	3500	-100	450	1420
	5750	-100	370	330
1-9	300	100	300	260
	930	-100	540	700
	3350	-100	300	600
1-10	2860	500	280	270
	5220	1060	300	280
	5900	690	280	240
1-11	380	160	380	340
	1350	800	270	300
	1450	260	280	300
	3620	270	290	330
	4720	460	270	270
1-12	400	400	300	300
	2700	1120	290	320
1-13	250	720	500	400
	4650	950	300	300



Slika 8. Koordinate svakog oštećenja

Zaključak

Može se zaključiti da više od 80 % oštećenja nastaje na donjoj strani lima (izmedju lima i betona odnosno temelja rezervoara) koje nije moguće detektovati vizuelnom metodom ili metodom ultrazvučnog merenja debljine čeličnog lima jer te metode nisu adekvatne za detektovanje takvih vrsta oštečenja.

POSTERSKA SAOPŠTENJA

POSTER PRESENTATIONS

Enhancement of ultrafiltration of oily wastewaters by application of twisted tapes

Unapređenje ultrafiltracije zauljenih otpadnih voda primenom uvrnutih traka

Svetlana Popović[1], Milica Karadžić[1], Nataša Lukić[1], Predrag Kojić[1], Jiři Cakl[2], Matthias Wessling[3]

[1]University of Novi Sad, Faculty of Technology Novi Sad, Novi Sad, Serbia

[2]University of Pardubice, Faculty of Chemical Technology, Institute of Environmental and Chemical Engineering, Pardubice, Czech Republic

[3]RWTH University of Aachen, Faculty of Chemical-Process Engineering, Aachen, Germany

[1]Univerzitet u Novom Sadu, Tehnološki fakultet Novi Sad, Novi Sad, Republika Srbija

[2]Univerzitet u Pardubicama, Hemijsko-tehnološki fakultet, Institut za hemijsko inženjerstvo i zaštitu životne sredine, Pardubice, Republika Češka

[3]RVTH Univerzitet u Ahenu, Fakultet za hemijsko-procesno inženjerstvo, Aachen, Germany

Abstract

In this work, the influence of the geometry of twisted tape as turbulence promoter, on the permeation flux alleviation in ultrafiltration process for oily wastewater treatment have been investigated. A model system of metal working oil-in-water emulsion was filtered on ceramic ultrafiltration membrane having a cut-off of 100 kDa. Twisted tapes in two aspect ratios 1.5 and 2.5 were studied. The aspect ratio is the main geometrical characteristic as a ratio of a length of a helical element to its diameter used for the comparison of various types of promoters. Both tapes proved to be very efficient yielding very high fluxes compared to the conventional operation without a promoter. Flux improvements above 150% and 200% were obtained for twisted tape 2,5 and 1,5, respectively. Ultrafiltration enhanced by application of twisted tapes is more efficient than conventional because it requires lower energy for achieving the same flux as in conventional operation.

Key Words: *fouling minimisation, turbulence promoters, wastewater treatment, ultrafiltration.*

Izvod

U ovom radu ispitivan je uticaj geometrije uvrnute trake kao promotora turbulencije na unapređenje fluksa u procesu ultrafiltracije zauljene otpadne vode. Model sistem ulje-u-vodi emulzije koja se koristi u industriji za obradu metala je filtriran na ultrafiltracionoj keramičkoj membrani dimenzije 100 kDa. Testirane su uvrnute trake u dve karakteristične dimenzije 1,5 i 2,5, kako bi se smanjilo prljanje membrane. Karakteristična dimenzija predstavlja odnos dužine zavoja i prečnika uvrnute trake i koristi se za poređenje promotora različite geometrije i dimenzija. Primenom obe trake postignuti su zanačajno veći fluksevi permeata u poređenju sa konvencionalnim radom bez promotora. Moguće je postići unapređenje fluksa iznad 150% i 200% za uvrnuttu traku 2,5 i 1,5 respektivno. Ultrafiltracija unapređena primenom uvrnutih traka je znatno efikasnija od konvencionalne jer je za postizanje istog fluksa potrebno uložiti manju energiju nego kod konvencionalne ultrafiltracije.

Ključne reči: *smanjenje prljanja, promotori turbulencije, tretman otpadnih voda, ultrafiltracija.*

1. Introduction

Cutting oil emulsions in water are used in metal-working industry to prevent rust on machine parts and cutters, reduce friction and keep the temperature constant. Considering a large amount of used cutting oil emulsions they have to be treated before they are disposed of [1]. One of the promising methods of separating oil from water is the membrane ultrafiltration due to its efficiency, low energy consumption and low impact on the environment. A drawback of the pressure driven membrane process is the occurrence of the concentration polarization (CP) and/or fouling [2]. These phenomena cause a decrease of permeation flux across the membrane and lowering of process efficiency. The CP is especially pronounced in ultra- and micro-filtration of organic feeds. It appears in a very thin mass transfer boundary layer which can be disturbed by changing hydrodynamic conditions of the feed flow. Setting of the turbulent flow regime improves mass transfer and intensifies the process.

The conventional way of alleviation of permeation flux in membrane processes is an increase of cross flow velocity. That causes an increasing shear rate in the vicinity of the membrane surface and minimizing concentration polarization and fouling of the membrane. The alternative and simple technique of increasing shear rate is the insertion of static turbulence promoters (TP) in a membrane channel [3]. Static turbulence promoter uses only the energy of moving fluid to increase turbulence which is beneficial for disrupting boundary layer and increasing process capacity. They do not only increase shear rate but induce alternative flow paths which additionally disrupt boundary layer and minimise fouling [4, 5].

The objective of this paper is to present the method for the intensification of ultrafiltration of oil-in-water emulsion wastewater typically used in metal working industry. The intensification method is based on the alleviation of turbulence in the membrane channel by the insertion of twisted tape (TT), as motionless turbulence promoter, in it. The influence of the geometry of twisted tape on the boundary layer disruption and fouling minimization was investigated.

2. Materials and methods

The laboratory scale microfiltration/ultrafiltration setup made of stainless steel was used in experiments. The feed was pumped to the membrane module by the multistage centrifugal pump (CM1-9, Grundfos, Germany). The transmembrane pressure was monitored by digital pressure gauges (0-10 bar accuracy ±1%) while the flow was measured using a rotameter. The temperature was kept constant and monitored by a digital thermometer (accuracy ±0.5oC). Transmembrane pressure across the module and flow were adjusted using the bypass valve and the main flow valve. Permeate was collected in the container placed on the digital balance (EW 1500-2M, KERN, Germany) and continuously weighted while the data were transferred to a PC.

A single channel ceramic membrane (Altech, Germany) was chosen for ultrafiltration. As turbulence promoters, twisted tapes (TT) made of the Veroclear polymeric material by using rapid prototyping 3D printer (Objet Eden260, Stratasys, USA) were used. The distinct between the tapes is in their aspect ratio as a ratio of a length of a helical element to its diameter (Fig. 1). Characteristics of the membrane and TTs are given in Table 1.

A model system of the oil-in-water emulsion was used as a feed. The semisynthetic oil Paramo Ero 1070 (Paramo, Czech Republic) was used for making the emulsion in the concentration of 2.0%w/w. The average droplet size in the emulsion was 93.7±14.2 nm, measured using a Malvern Nano ZS analyzer at 20°C (Malvern Instruments Ltd., Worcestershire, United Kingdom).

Filtration was operated maintain the constant concentration of the feed by recycling both retentate and permeate continuously, for both modes of operation without and with twisted tapes, under the various cross-flow rates and low transmembrane pressure (TMP) of 50 kPa.

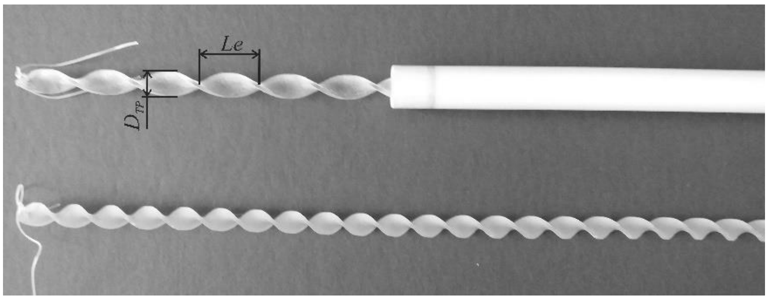


Fig. 1. Twisted tapes.

Table 1. Characteristics of membrane and TTs.

Membrane		Twisted tape		
Length (mm)	250.0		TT2.5	TT1.5
OD (mm)	10.0	D_{TP} (mm)	5.5	5.5
ID (mm)	6.0	L_{TP} (mm)	230.0	230.0
Cut-off (kDa)	100	δ_{TP} (mm)	1.0	1.0
Material	ZrO_2	Le (mm)	13.75	8.25
A_{ac} (cm^2)	47.2	$O_{TP}{}^*$	2.5	1.5

**aspect ratio O_{TP} = Le/D_{TP}, e – helical element*

2.1. Equations

The efficiency of a twisted tape was evaluated over two references: a flux improvement (FI) and specific energy consumption (E). The former represents a relative comparison of fluxes obtained with and without a twisted tape application:

$$FI = \frac{J_{TT} - J_{NTP}}{J_{NTP}} \cdot 100\ (\%) \tag{1}$$

The specific energy consumption (E) is by definition the hydraulic power dissipated (HDP) per unit volume of permeate. The HDP depends on the pressure loss (ΔP) along the membrane module and the applied cross flow rate (Q), so the specific energy consumption is calculated as:

$$E = \frac{Q\Delta P}{J_p A_{ac}} \tag{2}$$

3. Results and discussion

3.1. Influence of cross-flow velocity in NTP operation

Fig. 2 shows the time dependency of fluxes for oil-in-water ultrafiltration operated without twisted tapes (NTP) under the various cross flow rates. The curves of permeate flux have the shape typical for the occurrence of strong concentration polarization layer with the sharp flux decline in the first few minutes followed by the slow deposition of oil droplets. After about 15 min of ultrafiltration, the flux achieves a steady state value. It can be observed that the highest the cross-flow rate the highest the permeation fluxes.

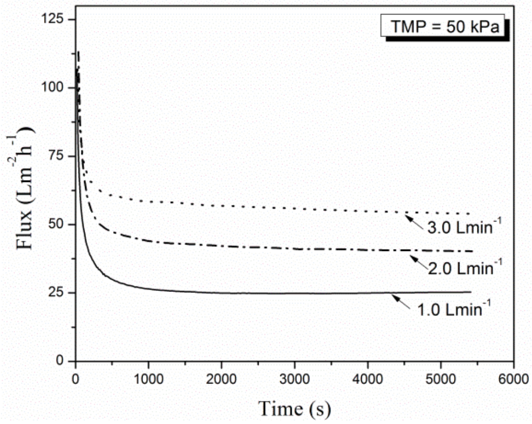


Fig. 2. Influence of cross-flow velocity on flux in operation without turbulence promoter (NTP).

This indicates that the main fouling mechanism is a surface fouling which can be minimized by alleviating turbulence in the membrane channel. The turbulence can be simply increased by increasing a cross-flow velocity in the membrane channel. This mechanism of fouling minimization is based on simply acceleration of fluid what prevents oil droplets to concentrate nearby the membrane surface.

3.2. Influence of twisted tape

Fig. 3 shows the time dependency of the fluxes obtained for both, the operation with twisted tapes and NTP operation, under the cross-flow rate of 1.0 Lmin^{-1}. The TT permeate fluxes are remarkably higher compared to those achieved in the NTP operation. The fluxes are enlarged three to four folds, depending on the aspect ratio and cross-flow rate. The lowest the aspect ratio of twisted tape, the highest the permeation fluxes.

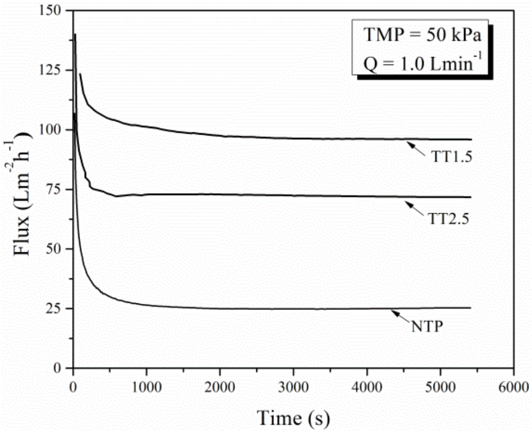


Fig. 3. Influence of twisted tape on flux at cross-flow rate 1.0 Lmin-1 and TMP 50 kPa.

The curves of permeate flux maintain the trend typical for the occurrence of CP layer with the sharp flux decline in the first few minutes. The achieved steady state fluxes are higher than for NTP operation under the same conditions. So TTs reduce CP and reversible surface fouling of the membrane significantly. The mechanism of intensification is based on the acceleration of the fluid and on the appearance of secondary flows and helical shape of flow streamlines which have mutual action in lifting the emulsion droplets from the membrane surface and minimizing fouling.

Fig. 4 shows the effect of cross-flow rate on the ultrafiltration with inserted TT of aspect ratio 1.5. The flux increases with an increase of the cross-flow rate. Mutual action of increased cross-flow rate and secondary flows formed due to the insertion of TT minimizes CP and surface fouling so improves mass transfer and thereby, increases process capacity.

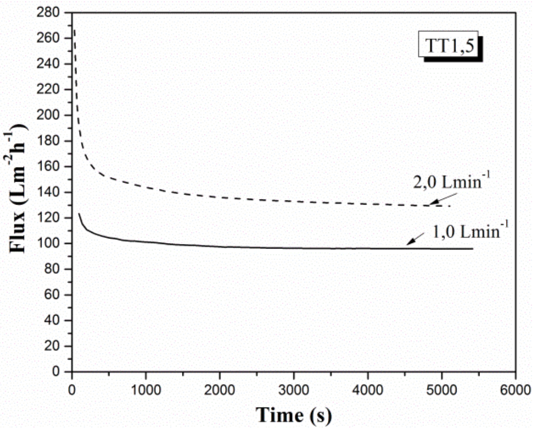


Fig. 4. Influence of cross-flow rate in TT operation at TMP 50 kPa.

Since both, the increase of cross-flow rate and presence of the twisted tape in the membrane channel induce pressure loss along the membrane, it is necessary to evaluate energy consumption.

3.3. Energy consumption

Fig. 5 shows comparison of energy consumptions versus obtained fluxes for the NTP and TT`s operation. It can be observed that remarkably higher fluxes were obtained with TTs for the same energy input. The specific energy consumption is higher for NTP operation due to much lower fluxes. Twisted tapes yielded very high fluxes despite to the increased pressure drop so the overall energy consumption was reduced. Flux improvements above 130% and 200% can be obtained for TT2.5 and TT1.5, respectively. The flux improvement increases with a decrease of the TT`s aspect ratio and decreases with an increase of cross-flow rate.

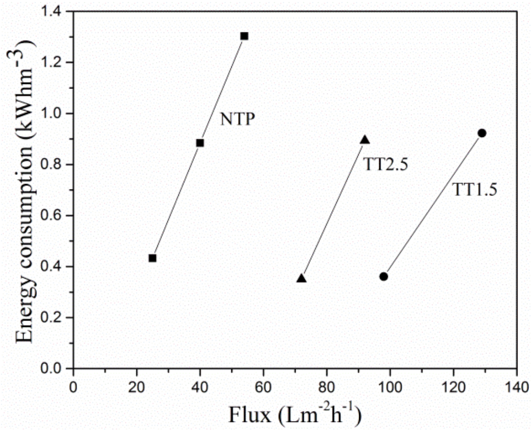


Fig.5. Energy consumption versus flux.

Despite to the enlarged pressure drop when TTs are applied, the efficiency of ultrafiltration is significantly improved taking into account both flux improvement and energy consumption.

4. Conclusion

The twisted tapes as turbulence promoters improve the mass transfer in ultrafiltration of oily wastewater by minimizing concentration polarization and fouling. By means of TTs, the permeate fluxes are remarkably increased. As TTs are low-pressure loss turbulence promoters so energy savings are obtained for the industrially desirable fluxes beyond 100 $Lm^{-2}h^{-1}$.

Acknowledgment

This work was financially supported by the Ministry of Education, Science and Technological Development of the Republic of Serbia, grant number 172025, and, by the Ministry of Education, Youth and Sports of the Czech Republic, Project CZ.1.07/2.3.00/30.0021 ‘‘Strengthening of Research and Development Teams at the University of Pardubice‘‘.

5. References

1. Milić, J.K., et al., "Recent developments in membrane treatment of spent cutting-oils: A review", *Industrial and Engineering Chemistry Research*, 2013. Vol. 52, No. 23, pp. 7603-7616.
2. Cakl, J., et al., "Effects of backflushing conditions on permeate flux in membrane crossflow microfiltration of oil emulsion", *Desalination*, 2000. Vol. 127, No. 2, pp. 189-198.
3. Krstic, D.M., et al., "Energy-saving potential of cross-flow ultrafiltration with inserted static mixer: Application to an oil-in-water emulsion", *Separation and Purification Technology*, 2007. Vol. 57, No. 1, pp. 134-139.
4. Popović, S., et al., "Intensification of microfiltration using a blade-type turbulence promoter", *Journal of Membrane Science*, 2013. Vol. 425-426, No. 0, pp. 113-120.
5. Popović, S., et al., "Uticaj promotora u obliku uvrnute trake na smanjenje prljanja membrane tokom mikrofiltracije mleka", *Hemijska industrija*, 2011. Vol. 65, No. 3, pp. 233-239.

Mass transfer in an external-loop airlift reactor: non-newtonian fluids

Nataša Lj. Lukić[1], Predrag S. Kojić[1], Svetlana S. Popović[1], Dragan Lj. Petrović[1]

[1]University of Novi Sad, Faculty of Technology, Department of Chemical Engineering, Novi Sad, Serbia

Abstract

The effects of effective viscosity, gas sparger type and superficial gas velocity on the volumetric mass transfer coefficient in an external-loop airlift reactor were investigated in this paper. The results showed that when single orifice was used, volumetric mass transfer coefficient values were up to 5 times lower in non-Newtonian fluids regardless of employed superficial gas velocity. On the other hand, when sinter plate was used an increase in volumetric mass transfer coefficient was observed at lower gas velocities. At higher superficial gas velocities, values of the volumetric mass transfer velocity are in agreement, regardless of employed sparger type.

1. Introduction

Airlift reactors are gas-liquid or gas-liquid-solid pneumatic contacting devices that are characterized by simple construction without moving parts, low energy demands, low shear rates and good mixing. Because of this they are widely employed in biochemical and pharmaceutical industry. There are two basic classes of airlift reactors: internal-loop and external-loop airlift reactors. Their productivity is highly affected by gas-liquid mass transfer and, hence, numerous research studies concerning mass transfer characteristics of airlift reactors can be found in the literature. In comparison to internal-loop, external-loop airlift reactors achieve higher liquid velocities which leads to lower mass transfer rates [1].

Mass transfer in non-Newtonian fluids, such as carboxymethylcellulose (CMC) solutions, has been extensively investigated in external-loop airlift reactors (EL-ALRs) [2-4]. The increase in viscosity mainly leads to a decrease in specific interfacial area (a) due to the appearance of large spherical-cap bubbles. Besides, a decrease in mass transfer coefficient (k_L) occurs due to lower diffusivity in viscous fluids [5]. As a result, values of the volumetric mass transfer coefficient (k_La) are significantly lower compared to the values obtained in water. However, some authors reported an increase in specific interfacial area at lower viscosities and, therefore, higher values of k_La [4]. Obviously, the influence of viscosity on mass transfer in EL-ALR is dependant on many other factors, such as superficial gas velocities, sparger type and reactor geometry.

The subject of this paper was to investigate synergistic effect of viscosity and sparger type on the volumetric mass transfer coefficient in external-loop airlift reactor. The volumetric mass transfer coefficient was examined in water and various carboxymethylcellulose solutions using single orifice or sinter plate as a sparger.

2. Materials and methods

All experiments were carried out at 20±1°C and atmospheric pressure in a 36.6 dm^3 external-loop airlift reactor made of stainless steel and Plexiglas. The schematic diagram of the experimental apparatus with geometrical characteristics is presented in Fig. 1.

The liquid height in the separator assured complete deaeration of gas bubbles and hence no bubbles were entrained in the downcomer. A single orifice (4 mm i.d.) or sinter plate (38 mm in diameter, average pore size 115 µm) was used as a gas (air) sparger. Mass flow controller (Bronkhorst High

Tech F 201AV) was applied to control and measure gas flow rate. Based on the cross-sectional area of the riser, superficial gas velocities (U_G) were in the range 0.0096-0.1194 m/s.

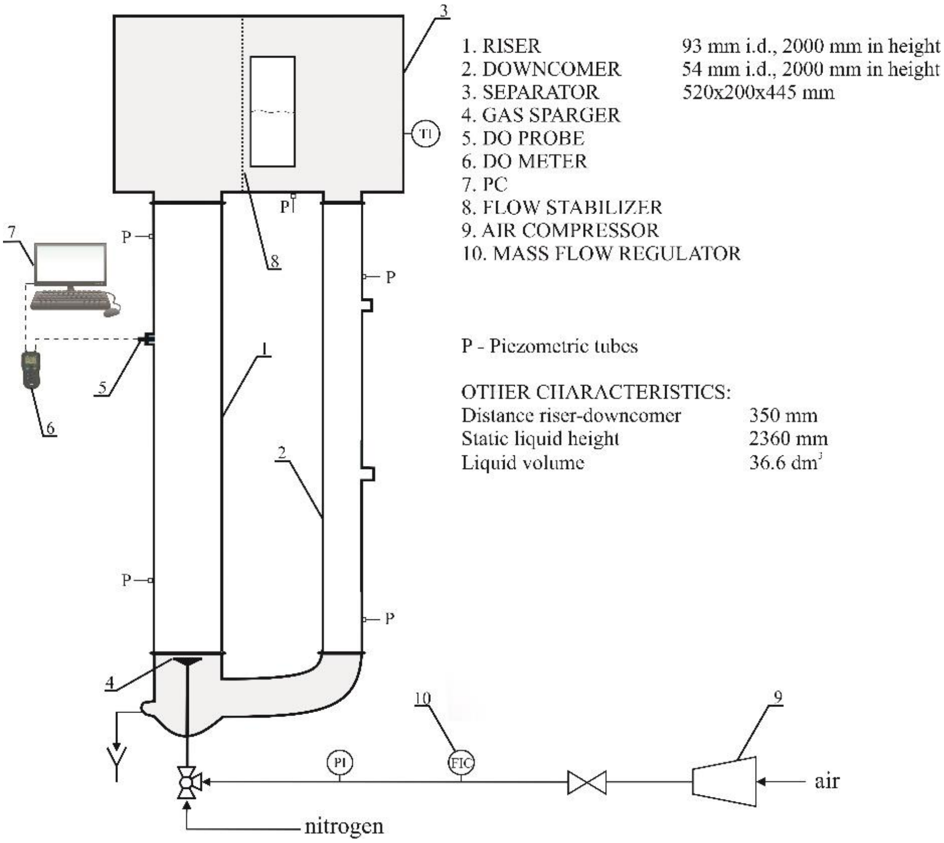


Fig. 1. Experimental setup

Tap water and aqueous solutions of carboxymethylcellulose (CEKOL 10000, CP Kelco, Aanekoski, Finland) were used as liquid phases. All liquid phases employed in this paper along with their properties are summarized in Table 1. Rheological properties, including flow consistency index, *K*, and flow behavior index, *n*, were determined with a controlled-stress rheometer HAAKE Rheostress RS600 (Thermo Electron Corporation, Karlsruhe, Germany) at a constant temperature of 20±0.05°C by employing cone-and-plate geometry C60/1Ti (diameter=60 mm and angle=1°).

Table 1. Properties of liquid phases used at 20°C

Liquid phase	Concentration [wt.%]	ρ [kg/m^3]	K [Pa·s^n]	N [-]
tap water	-	999	0.0010	1.0
CMC-1	0.1	1001	0.0104	0.845
CMC-2	0.2	1000	0.0402	0.751
CMC-3	0.3	1002	0.1004	0.684
CMC-4	0.4	1002	0.2342	0.620

The volumetric mass transfer coefficient was obtained by the dynamic oxygenation method [6]. The change in dissolved oxygen concentration with time was measured with luminescent dissolved oxygen probes (Hach Lange, Germany, model IntelliCAL LDO) and recorded on a multimeter

(Hach Lange, Germany, model HQ40d). Assuming an ideally mixed liquid and a first-order response of the probe, k_La was calculated by combining the following equations:

$$\frac{C^*-C_L}{C^*-C_{L0}} = \frac{1}{K_P-k_La_L}\left(K_P \mathrm{e}^{-k_La_Lt} - k_La_L\mathrm{e}^{-K_Pt}\right) \tag{1}$$

$$k_La_L = \frac{k_La}{1-\varepsilon_{GR}} \tag{2}$$

Methods for riser gas holdup (ε_{GR}) measurement are described in detail elsewhere [7].
The effective viscosity of pseudoplastic CMC solutions was determined by:

$$\mu_{eff} = K\gamma^{n-1} \tag{3}$$

By applying the methodology proposed by Cerri et al. [8] average shear rate (γ) was estimated as:

$$\gamma = \left(1.469 {U_G}^{-0.065} K^{0.369}\right)^{1/(n-1)} \tag{4}$$

3. Results and discussion

The influence of effective viscosity (μ_{eff}) and superficial gas velocity (U_G) on the volumetric mass transfer coefficient obtained with single orifice and sinter plate is shown in Figures 2 and 3, respectively. As can be seen from Figure 2, the addition of carboxymethylcellulose instantly led to a decrease in k_La values when single orifice was used. The higher the effective viscosity of CMC solution, the higher the decrease in k_La values. In the most viscous CMC solutions k_La values were about 5 times lower than k_La values obtained in water. This decrease in volumetric mass transfer coefficient is expected since with the increase in viscosity a considerable decrease in specific gas-liquid interfacial area (a) occurs. Additionally, mass transfer coefficient (k) also decreases because of the decrease in diffusivity with the increase in viscosity. It can be also seen from Figure 2 that, as expected, k_La values increased with the increase in superficial gas velocity.

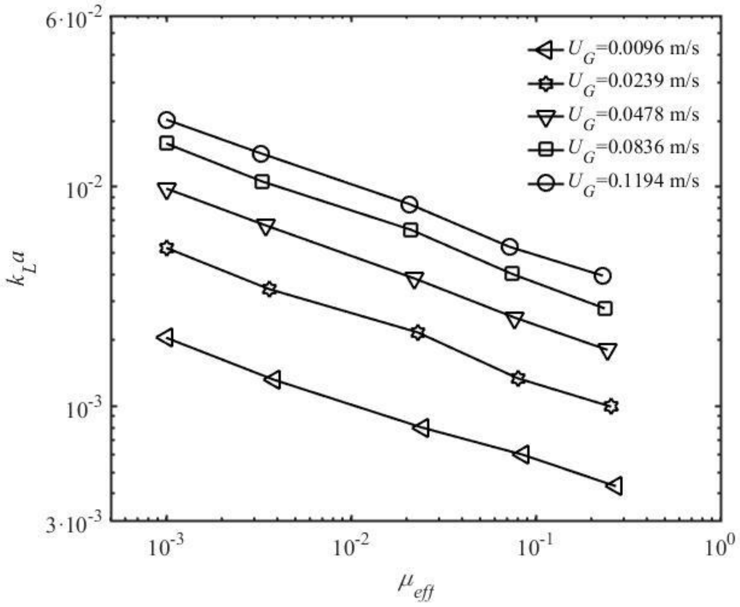


Fig. 2. The effect of effective viscosity on the volumetric mass transfer coefficient (single orifice)

As can be seen from Fig. 3, when sinter plate was used the k_La values initially increased with the increase in effective viscosity of CMC solutions at the lowest superficial gas velocity. Bubbles formed on sinter plate are more stable with lower Sauter mean diameter in comparison to bubbles formed on single orifice. Because of this, higher values of k_La were achieved with sinter plate.

Nevertheless, in highly viscous CMC solutions k_La values started to decrease with further increase in effective viscosity.

Comparing the results shown in Figures 2 and 3 it can be observed that strong influence of sparger type is present only at lower gas velocities, as noticed by other authors [9]. The volumetric mass transfer coefficient values were up to 550% higher with sinter plate in comparison to the values obtained with single orifice. At higher gas inputs, no differences in the k_La values obtained with single orifice and sinter plate were observed.

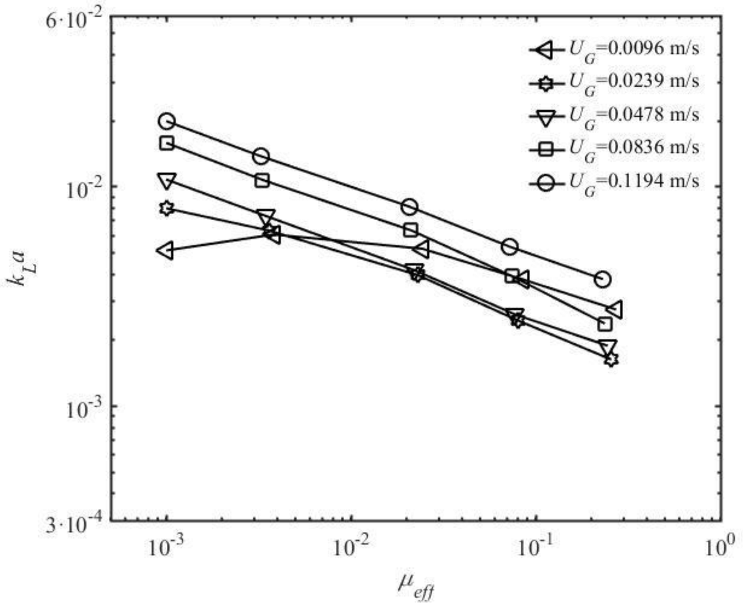


Fig. 3. The effect of effective viscosity on the volumetric mass transfer coefficient (sinter plate)

4. Conclusion

In this paper, the influence of both the effective viscosity (various carboxymethylcellulose solutions) and sparger type (single orifice and sinter plate) on the volumetric mass transfer coefficient in external-loop airlift reactor was investigated. The results showed that in carboxymethylcellulose solutions, the volumetric mass transfer coefficient significantly decreased at higher superficial gas velocities, regardless of used sparger type. Similar behaviour was noticed at lower gas inputs when single orifice was used as a sparger. On the contrary, when sinter plate was used, volumetric mass transfer coefficient increased with the increase in viscosity at lower gas inputs.

Acknowledgment

This research was financially supported by the Ministry of Education, Science and Technological Development of the Republic of Serbia (Project no. 172025).

5. References

1. Chisti, M.Y., Moo-Young, M., Airlift reactors: characteristics, applications and design considerations, *Chem. Eng. Commun.*, 1987. Vol. 60, No. 1-6, pp. 195-242.
2. Popovic, M.K., Robinson, C.W., Mass transfer studies of external-loop airlifts and a bubble column, *AlChE J.*, 1989. Vol. 35, No. 3, pp. 393-405.
3. Al-Masry, W.A., Dukkan, A.R., Hydrodynamics and Mass-Transfer Studies in a Pilot-Plant Airlift Reactor: Non-Newtonian Systems, *Ind. Eng. Chem. Res.*, 1998. Vol. 37, No. 1, pp. 41-48.

4. Wu, Q., Wang, X., Wang, T., Han, M., Sha, Z., Wang, J., Effect of liquid viscosity on hydrodynamics and bubble behaviour of an external-loop airlift reactor, *Can. J. Chem. Eng.*, 2013. Vol. 91, No. 12, pp. 1957-1963.
5. Kilonzo, P.M., Margaritis, A., The effects of non-Newtonian fermentation broth viscosity and small bubble segregation on oxygen mass transfer in gas-lift bioreactors: a critical review, *Biochem. Eng. J.*, 2004. Vol. 17, No. 1, pp. 27-40.
6. Merchuk, J.C., Yona, S., Siegel, M.H., Zvi, A.B., On the first-order approximation to the response of dissolved oxygen electrodes for dynamic K_La estimation, *Biotechnol. Bioeng.*, 1990. Vol. 35, No. 11, pp. 1161-1163.
7. Lukić, N.L., Šijački, I.M., Kojić, P.S., Popović, S.S., Tekić, M.N., Petrović, D.L., Enhanced hydrodynamics in a novel external-loop airlift reactor with self-agitated impellers, *J. Taiwan Inst. Chem. E.*, 2016. Vol. 68, No., pp. 40-50.
8. Cerri, M.O., Futiwaki, L., Jesus, C.D.F., Cruz, A.J.G., Badino, A.C., Average shear rate for non-Newtonian fluids in a concentric-tube airlift bioreactor, *Biochem. Eng. J.*, 2008. Vol. 39, No. 1, pp. 51-57.
9. Chaumat, H., Billet-Duquenne, A.M., Augier, F., Mathieu, C., Delmas, H., Mass transfer in bubble column for industrial conditions-effects of organic medium, gas and liquid flow rates and column design, *Chem. Eng. Sci.*, 2005. Vol. 60, No. 22, pp. 5930-5936.

Electrochemical formation of magnesium oxide/hydroxide structures

Elektrohemijsko formiranje različitih oblika magnezijum oksida/hidroksida

Vesna S. Cvetković[1], Nataša M. Vukićević[1], Nebojša D. Nikolić[1], Goran Branković[2], Jovan N. Jovićević[1]

[1]ICTM – Department of Electrochemistry, University of Belgrade, Njegoševa 12, Belgrade, Serbia

[2]Institute for Multidisciplinary Research, University of Belgrade, Kneza Višeslava 1a, Belgrade, Serbia

Izvod

Nanokristalni magnezijum oksidi i hidroksidi privlače posebnu pažnju zbog svoje velike specifične površine kao i specifičnih optičkih, termalnih, električnih i hemijskih karakteristika. Magnezijum oksidi i hidroksidi imaju široku primenu u katalizi, medicini, remedijaciji toksičnog otpada, kao superprovodni i kompozitni materijali u vasioskoj tehnici. Sastav i površinska morfologija ovih oksida i hidroksida je od primarne važnosti u njihovoj primeni, a poseban značaj pridaje se načinu sinteze i parametrima procesa formiranja njihovih nanokristalnih struktura.

U ovom radu predstavljen je novi metod sinteze magnezijum oksida/hidroksida zasnovan na procesima elektrohemijskog taloženja na radnoj elektrodi od staklastog ugljenika iz rastopa magnezijum nitrata heksahidrata. U eksperimentalnom radu korišćene su elektrohemijske metode linearne cikličke voltametrije i hronoamperometrije. Površina elektroda i morfologija dobijenih taloga su analizirane skenirajućom elektronskom mikroskopijom (SEM), energetskom disperzivnom spektroskopijom (EDS) i difrakcijom X-zraka (XRD). Talozi dobijeni potenciostatskim pulsevima su nanoveličina a njihova struktura nalik mačjim brkovima, iglama, spužvi ili saću. Ovi oblici rezultat su difuzione kontrole koja kontroliše elektrohemijsko taloženje magnezijum oksida i hidroksida i uticaja simultanog razvijanja vodonika i procesa elektrotaloženja. Eksperimentalni rezultati su pokazali da morfologija tako formiranog taloga značajno zavisi od primenjenog potencijala.

Abstract

Nanocrystalline magnesium oxides and hydroxides are attracting comprehensive attention due to their high surface area and their specific optical, thermal, electrical and chemical characteristics. Magnesium oxides and hydroxides have been widely used in catalysis, medicine, toxic waste remediation, for the superconducting and spaceflight composite materials. The composition and surface morphology of the oxides and hydroxides is of prime importance in their application and the special significance is paid to the synthesis and processing parameters of the resulting nanocrystaline structures.

A novel method based on electrodeposition processes of magnesium oxide/hydroxide synthesis is presented. It includes electrochemical deposition onto vitreous carbon from magnesium nitrate hexahydrate melt. Electrochemical techniques used in experiments were linear sweep voltammetry and potential step. Electrode surface and the morphology of the deposits synthetized were characterized by scanning electron microscopy (SEM), energy dispersive spectroscopy (EDS) and X-ray diffraction (XRD) analysis. Potential steps applied produced a number of nanosized shapes including whiskers, needles, spongy-like, and honeycomb-like forms. They are a result of diffusion control governing magnesium oxide and hydroxide deposition and influence of the simultaneous hydrogen evolution with the electrodeposition process. Experimental results showed that the morphology of the nanostructures obtained strongly depends on the potential applied.

Methods for treatment of waste waters from galvanizing plants

M. Stefănuţ[1], A. Căta[1], D. Roşu[1], M. Dobrescu[1], I.M.C. Ienaşcu[1,2]

[1]National Institute of Research and Development for Electrochemistry and Condensed Matter,

Dr. Aurel Păunescu Podeanu 144, 300569, Timişoara, Romania, mariana.stefanut@gmail.com

[2]"Vasile Goldiş" Western University of Arad, Faculty of Pharmacy, 86 Liviu Rebreanu, 310045,

Arad, Romania

Abstract

NTPA-002/2002 is the Romanian standard which impose limits of pollutants concentration in waste waters. Waste waters from galvanizing plants can have at drainage to sewage: max. 1 mg/L zinc, max. 1 mg/L total chromium and max. 5 mg/L iron. The aim of work is to eliminate the large quantity of zinc from washing and final waters in a galvanizing plant. The concentrations of waste varied between 120-400 mg/L Zn. In order to eliminate the metals (zinc, iron and chromium), some commercial flocculants, sedimentation and precipitation agents in various ratios were used. Finally, based on the difference of electrochemical potential between aluminum and zinc, a column with aluminum spiral rings or waste from processed aluminum profiles filling was tested for lowering the Zn concentration under 1 mg/L. The metals concentration was monitored by atomic absorption spectroscopy (AAS) using a novAA 400 G apparatus (Analytik Jena) equipped with a graphite furnace and provided with WinAAS 3.17.0 soft for evaluation, control and results display.

Introduction

The quantities of zinc in waste water from galvanizing plants heavily dependent on customers demand and the number of laps of employees. Romanian standard NTPA-002/2002 [1] imposes the pollutants limits in waste waters at discharge into natural receivers. There are many possibilities for eliminate the heavy metals from wastewaters [2,3]. The actual technologies have used some commercial substances in various ratios, flocculants and sedimentation and precipitation agents. They manifested activity in binding and speed up the coagulation/precipitation phenomena of zinc and other heavy metals from wastewaters with high metal concentrations. This work proposes to add a new step in Zn elimination: the using a column with aluminum filling. Based on the difference of electrochemical potential between aluminum and zinc, Zn^{2+} catch $2e^-$ and become Zn^0 and Al^0 loose $3e^-$ and become Al^{3+}. A column with aluminum spiral rings or other waste from processed aluminum profiles was introduced in process.

Materials and methods

The wastewaters were achieved as samples from a small galvanizing plant. The substances Enthol FHM B 714 (flocculant based on organic polymers) and Enthol Antiplex (agent for metal-complex decomposition) were purchased from Enthone Corporation and TMT 15 (organosulphide compound) was purchased from Elton Corporation S.A.-Romania. The pH influence between values 7-9 was studied. The waters were treated under magnetic stirring with the mentioned compounds. After the classical treatment, the waters were passing through a column with different aluminum filling using various flows: 1, 2 and 4 mL/min. Dimension of column was 80x3 cm (approx. 145 g filling). The metals concentration was monitored by atomic absorption spectroscopy (AAS) using a novAA 400 G apparatus, Analytik Jena-Germany, equipped with a graphite furnace and provided with WinAAS 3.17.0 soft for evaluation, control and results display. Calibration curves for each metal were previously traced using AAS standard solutions (Analytik Jena, Germany). Especially, the zinc concentration was followed.

Results and Discussion

Enthol FHM B 714 0.1% and Enthol Antiplex 0.1% and TMT 0.8% solutions were used. The experiments were made only with flocculant agent or with flocculant and sedimentation agents or with precipitant agent. Preliminary tests are showed that at pH=7 and pH=7.5 no semnificative results are obtained. At pH=8, pH=8.5 and pH=9 more interesting values for metals elimination were achieved in waste waters treatment (figures 1 and 2, Table 1). Initial concentration of zinc in waste was between 121.5 - 313.1 mg/L.

Figure 1 Aspect of samples after treatment with flocculant agent

Figure 2 Aspect of samples after treatment with flocculant and sedimentant agents

After classical tratment and after the water filtration, wastewaters with concentration between 27-34 mg/L (pH=9.0) were passed through a column with a flow of 1, 2 and 4 mL/min. (figure 3). It was tested two types of filling of waste aluminum from cables (a) and from industry of aluminum profiles fabrication (b) (figure 4). Each type of filling was washed twice with acetone and one times with ethanol in order to eliminate the all organic residues.

Table 1 Zinc concentration as a function of pH during classical treatment with comercial agents

No.	pH	Zn concentration in waste water, mg/L		
		Flocculant 0.2%	Flocculant 0.2% and sedimentant 0.1%	Precipitant TMT 15 0.8%
1.	7.0	84.70	-	-
2.	7.5	83.65	-	-
3.	8.0	26.86	27.60	-
4.	8.5	23.83	26.51	26.05
5.	9.0	21.79	21.00	26.96

Figure 3 Laboratory column

a) type 1 *b) type 2*

Figure 4 Aluminum filling of column

The best results were obtained at a flow of 1 mL/min., for one passing through the column, but we can not be obtained the concentration of Zn less than 4.5-5.9 mg/L (Table 2). The iron concentrations do not suffer signifiant changes.

Table 2 Variation of metals concentration

No.	Column						
	Conditions	Type 1 filling			Type 2 filling		
		Zn, mg/L	Al, mg/L	Fe, mg/L	Zn, mg/L	Al, mg/L	Fe, mg/L
1.	Initial	33.9	1.79	4.43	28.59	0.35	4.31
2.	Final	5.91	3.62	4.31	4.47	1.58	4.25

The calculation of species for metals in wastewater was useful for the corect choose of pH for work. Stabilities constants for *i* steps of MLi complex formation was expressed as:

$$\beta_i = \frac{[ML_i]}{[M]\cdot[L]^i} \tag{1}$$

Logarithms with the opposite sign of the constants βi were called total stability constants indices:

$$p\beta i = - \log \beta i \tag{2}$$

So, pβi (i = 1 ÷ 4) for complexes of Zn^{2+} and Al^{3+} with OH^- ions were presented in Table 3.

Table 3 Total stability constants indices

Complex	**pβ_1**	**pβ_2**	**pβ_3**	**pβ_4**
$[Zn(OH)_i]^{2-i}$	-4,4	-11,3	-13,14	-14,66
$[Al(OH)_i]^{3-i}$	-8,99	-19,3	-26,8	-32,7

The calculated chemical species in aqueous medium based on complexation equilibria constants were presented in figures 5 and 6.

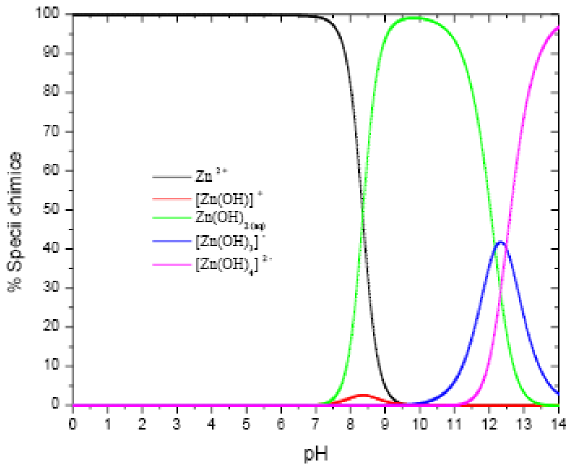


Figure 5 Calculated distribution of the chemical species of zinc (II) in water as a function of pH

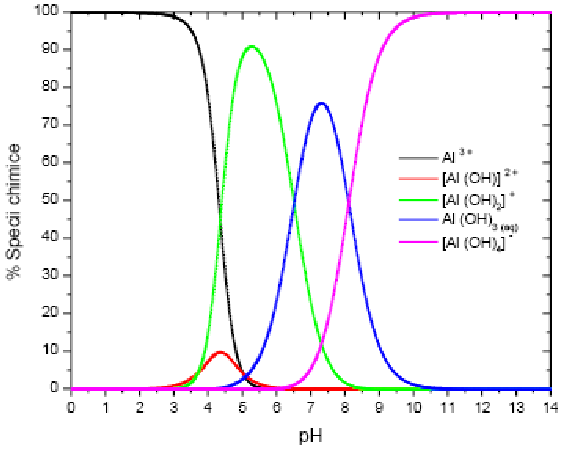
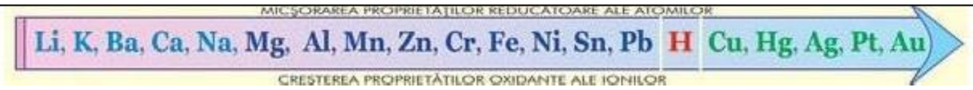


Figure 6 Calculated distribution of the chemical species of aluminum (III) in water as a function of pH

The results of calculation suggested the choice of a working pH between 8.5-9.

Conclusion

This work proposed the introduction of a new step in classical process of wastewaters treatment: a column with aluminum filling, in order to lowering the zinc concentration under 1 mg/L. Based on the difference of electrochemical potential between aluminum and zinc, the zinc ions from solution were deposited on aluminum surface and the aluminum ions passed into solution (see the electrochemical potential series of metals).



Sometimes, the process is called “cementation”. Best results were obtained at 1 mL/min. flow. The increasing of aluminum concentration presents not any risk because the plants of wastewaters treatment will use further aluminum sulphate, sodium aluminate, polychlorides, etc., as coagulants/flocculants in wastes treatment. We were studied also a theoretical model in order to analyze the kind and the concentration of soluble complexes in wastewaters at different values of pH. This work will be continued because the final zinc concentration was 4.5-5 mg/L and this value is not conforming to the demand of standard NTPA-002/2002.

References

1. Romanian STAS NTPA-002/2002.
2. Martin, W.F., Lippitti, J.M., Webb, P.J., Hazardous Waste Handbook for Health and Safety, 3rd Edition, Butterworth/Heinemann, Boston Oxford Auckland Johannesburg Melbourne New Delhi 2000, pp.21-34.
3. Cheremisinoff, N.P., Handbook of Water and Waste Water Treatment Technologies, Butterworth/Heinemann, Boston Oxford Auckland Johannesburg Melbourne New Delhi 2002, pp.37-122.

Ecological aspects of the geochemical composition of the soil and anthropogenic impact on the content of heavy metals

Ružica Micić, Biljana Dekić, Vidoslav Dekić, Strahinja Simonović, Dragana Sejmanović, Novica Ristić, Danijela Vukiocić

University of Pristina, Faculty of Science and Mathematics Kosovska Mitrovica, Serbia

Abstract

The state of the environment is the subject of research of many scientific studies from different fields and from different aspects, which approach this current problem. Natural and anthropogenic factors influence the content of pollutants in the environment, in the broadest sense. Kosovo and Metohija is known as the holy Serbian country, which represents the center of an old Serbian state with a large number of monasteries, and mining centers, as a significant part of medieval development. (1). Alongside the development of industry and traffic as the main sources of environmental pollution, the problem of its contamination, organic and inorganic contaminants has also grown. Also, Kosovo and Metohija is a contaminated area with the effects of post-war effects. Heavy metals, in addition to radionuclides, are the most toxic from the group of inorganic pollutants, are subject to analysis in many environmental samples, which enter the human food chain. In the human body, they cause numerous disorders and dysfunctions. The aim of this work is to determine the content of heavy metals in soil samples from the territory of Kosovo and Metohija, near major urban and industrial centers, using wet digestion, and modern ICP-OES analyzes. The content of toxic elements ranges: Pb (0.044-11.98 g / kg), As (0.007-0.33 g / kg), Cd (0.004-0.044 g / kg), and Cr (0.053-0.245 g/kg).

References

1. Blagojević, M., Medaković D., (2000). *History of the Serbian state.*
2. R. Mićić, S. Mitić, B. Arsić, M.Mitić, A.Jokić, D.Kostić, A.Pavlović, M. Čekerevac, Lj. Nikolić-Bujanović, Ž. Spalević, *Statistical characteristics of selected elements in vegetables from Kosovo, Environmentel Monitoring and Assessment, (2015) 187. (6)*

"Green" technology for obtaining biologically active compounds

Ioana M.C. Ienaşcu[1,2], Adina Căta[1], Mariana N. Ştefănuţ[1], Iuliana M. Popescu[3]

[1]National Institute of Research and Development for Electrochemistry and Condensed Matter, 144 Dr. A. P. Podeanu, 300569, Timişoara, Romania

[2]"Vasile Goldiş" Western University of Arad, Faculty of Pharmacy, Department of Pharmaceutical Sciences, 86 Liviu Rebreanu, 310045, Arad, Romania

[3]Banat's Agricultural Science University, Faculty of Agriculture, Department of Chemistry and Biochemistry, 119 Calea Aradului, 300645, Timişoara, Romania

Abstract

The goal of this work is to review some methods used for obtaining new potential biologically active derivatives, amides, esters, hydrazides and hydrazones. Along the traditional synthesis, a new technique set to revolutionize synthesis, which has recently moved to the forefront of chemical research, microwave-assisted organic synthesis, is presented. The advantages of microwave assisted synthesis, for instance, increasing the variety of this kind of drugs because the classical methods are time-consuming and expensive, counteraction the problematic properties of drugs, such as toxicity, side effects, are also outlined. Microwave-assisted organic chemistry pools together the environmental and economic benefits with the aim of developing eco-friendly processes.

1. INTRODUCTION

Worldwide, the pharmaceutical industry is strives to obtain some products, with high biological activity, a broad spectrum of action, minimal toxicity and side effects. Thus, finding new biologically active compounds has been a challenge for researchers, since the incidence of disease and the action spectrum of pathogens was constantly increasing. Despite progresses in technology, drug discovery remains an, "expensive, difficult, and inefficient process" with low proportion of new therapeutic discovery [1].

The most classes of current antibiotics, sulphonamides, penicillins, streptomycins, tetracyclines, macrolides, glycopeptides and cephalosporins, were developed around 1950 [2,3]. The improper and excessive consumption of antibiotics, resulted in the emergence of pathogenic strains with highly resistance to the majority of antibiotics available now on the market [4,5]. So, it is imperative to develop novel types of antimicrobials to defeat infections [6].

Salicylanilides showed strong antifungal and antibacterial activity [7], being active even against pathogens species such as methicillin-resistant *Staphylococcus aureus* and vancomycin-resistant *Enterococcus faecium* [8,9]. Salicylanilides also display antimycobacterial activity [10-12]. The presence of electron withdrawing groups on the salicylic ring and hydrophobic groups on the anilide nucleus are necessary for their activity [13]. The presence of phenolic hydroxyls plays an important role for the activity, being probably accountable for oxidative phosphorylation cleavage [14], but also adding irritative properties to the compounds.

Novel salicylanilide acetates were tested for their antifungal and antituberculotic activity. The compounds revealed superior activity compared to isoniazide against *Mycobacteria* isolates and enhanced antifungal activity compared to fluconazole [15].

Hydrazides constitute an important class of biologically active compounds with antibacterial and tuberculostatic activity [16]. Hydrazones showed, among antimicrobial activity, anticonvulsant, analgesic, antiinflammatory, antiplatelet, antitubercular and antitumoral properties [17-19]. Because of the blockage of –NH_2 group, hydrazones seems to exhibit lower toxicity compared to hydrazides

[20]. Salicylamidoacetic acid hydrazide exhibited superior antiinflammatory and analgesic activity than salicylamide itself and lower ulcerogenic activity [21]. Isonicotinic acid hydrazide and its hydrazones showed high activity against *M. tuberculosis* [22].

Because the development of chemical compounds with targeted biological properties is time-consuming and expensive, a major concern should be focussed to technologies that permit to quickly synthesized substances. Microwave-assisted organic synthesis represents an innovation for the development of new compounds due to the advantages obtained in comparison with conventional heating methods.

2. A COMPARISON BETWEEN CLASSICAL SYNTHESIS AND MICROWAVE-ASSISTED SYNTHESIS

2.1. SHORT OVERVIEW

Some methods which can be employed for synthesis of the desired compounds are: conventional heating synthesis and synthesis under microwave irradiation.

Starting with the first experiments in 1986, the microwave-assisted organic chemistry became an exciting field for research and development, the advantages and disadvantages of microwave techniques are well documented [23,24].

The performance of thermal chemical reactions that underlies microwave synthesis, compared to conventional heating synthesis, is due to the differences in means of energy transfer, being reflected in the methodologies, monitoring, types of equipment and vessels employed. The sample itself has substantial effects on microwave heating, the size, volume, nature, structure, physical and chemical properties can influence the reactions, the media and some safety issues [23,24].

The equipment that uses traditional heat transfer for organic reactions consists of oil bath, heating jackets, heating plates. Using this kind of heating source presents some disadvantages like slow heating, temperature gradient inside the sample that can lead to the decomposition of raw materials and final product. In case of microwave dielectric heating, the energy is introduced remotely and direct access by the energy source to the reaction vessel is obtained. The microwave radiation heats only the reactions mixture, passing through the walls of the vessel. Because the sample will be uniformly heated, fewer by-products will be obtained [23].

The microwave-assisted synthesis can be executed in the presence or in the absence of solvent.

For the first case, specific devices, providing resources for sample mixing, measurement and control of power, temperature and pressure are required. The advantages of this method are the reproducibility of the reactions, the ability to be conducted in the presence of solvents using lower pressures and the reactions speed. Solvents, like ethanol, are preferred, being accessible from renewable resources, readily purified and relatively environmental benign [24].

Important benefits also brings the microwave-assisted synthesis in the absence of solvent. Thus, the emissions and the necessity for redistillation are reduced due to the smaller amounts of solvents, necessary operations like extraction, distillation simplify the work-up, scale-up is possible, instead of mineral acids and oxidants ecofriendly solid supports can be used, the risks of overpressure and explosions are reduced. Generally, reactions are cleaner, faster and higher yielding than conventional synthesis, though, sometimes, in a microwave system, the reactions cannot be reproducible because the deficiency in mixing reactions and temperature measurement [23,24].

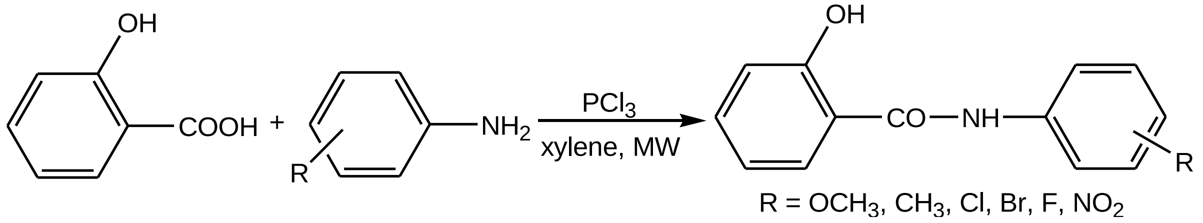
The microwave-assisted synthesis in the absence of solvent can be achieved using only neat reactants, reactants adsorbed onto solid supports, or reactants in the presence of phase transfer catalysts, for anionic reactions. In order to meet the green chemistry premises, the method using only neat reactants should be chosen when possible, because solvents are still necessary in “dry” media processes using solid supports, for loading the reagents onto the support and for elution of the products. When polar supports, alumina or silica gel, are used, extensive amounts of solvent may be needed. The reaction can occur as an interfacial procedure allowed by either a partial solubilisation of the solid in the liquid or by adsorption of the liquid on the solid surface. For example, in the absence of solvent or support, the reaction of amines with carboxylic acids takes place directly without any catalyst under microwave irradiation, only a slight excess of amine or acid being necessary [24].

2.2. WORKING METHODOLOGY FOR OBTAINING BIOLOGICALLY ACTIVE COMPOUNDS

Salicylanilides and their derivatives have been a topic of interest in medicinal chemistry and were proved to possess a wide range of biological activities including the antibacterial and antifungal ones [25,26]. These compounds were obtained by classical [12,21,27] and microwave-assisted synthesis [28-30], while compounds like esters, hydrazides, hydrazones, obtained by substitution of the phenolic hydrogen of o-hydroxy-N-phenyl-benzamide with various radicals: ethoxycarbonylalkyl, hydrazinocarbonylalkyl, benzylidene-hydrazinocarbonylalkyl, were synthesized using only traditional methods [21, 27, 31-36].

Amides were usually synthesized by the aminolysis reaction of carboxylic acid derivatives, esters, nitrile, isocyanide [28,29,37-41]. Amides can be also obtained through oxidative amidations of aldehydes with amines [42,43], rearrangement of ketones with trimethylsilyl azide in the presence of ferric chloride [44]. Direct amidation of carboxylic acid is limited in some measure due to the reduced reactivity of carboxylic acids, so, activating them is necessary for a smooth reaction [45,46]. These classical methods present some disadvantages: high cost of reagents, long reaction time, difficult operation, moderate yields. The direct amidation of carboxylic acids could be improved using microwave-assisted synthesis [30,47].

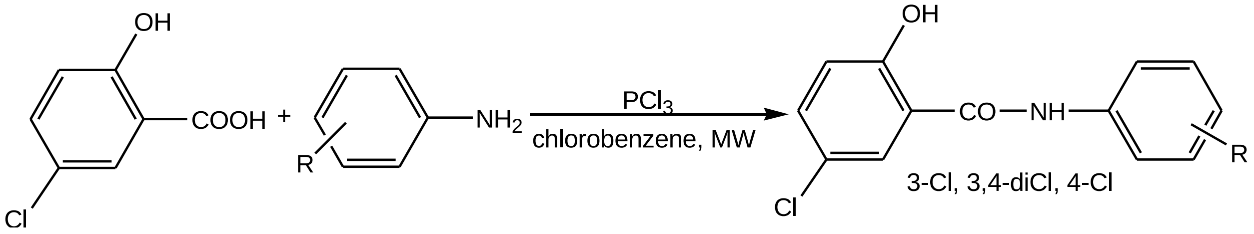
For instance, a very efficient procedure for obtaining aromatic amides was described, in which the direct reaction between salicyclic acid and aromatic amines, in xylene and in the presence of phosphorous trichloride, under microwave irradiation was followed (Scheme 1).



Scheme 1. Direct reaction between salicyclic acid and aromatic amines under microwave irradiation.

The best results, reaction times between 32-55 min, yields between 73-98%, were obtained working under 300 W and at a 40% molar ratio of PCl_3 [48].

Some 5-chlorosalycilanilides were routinely prepared by the reaction of 5-chlorosalicylic acid with the appropriate aniline in chlorobenzene with PCl_3 (Scheme 2).

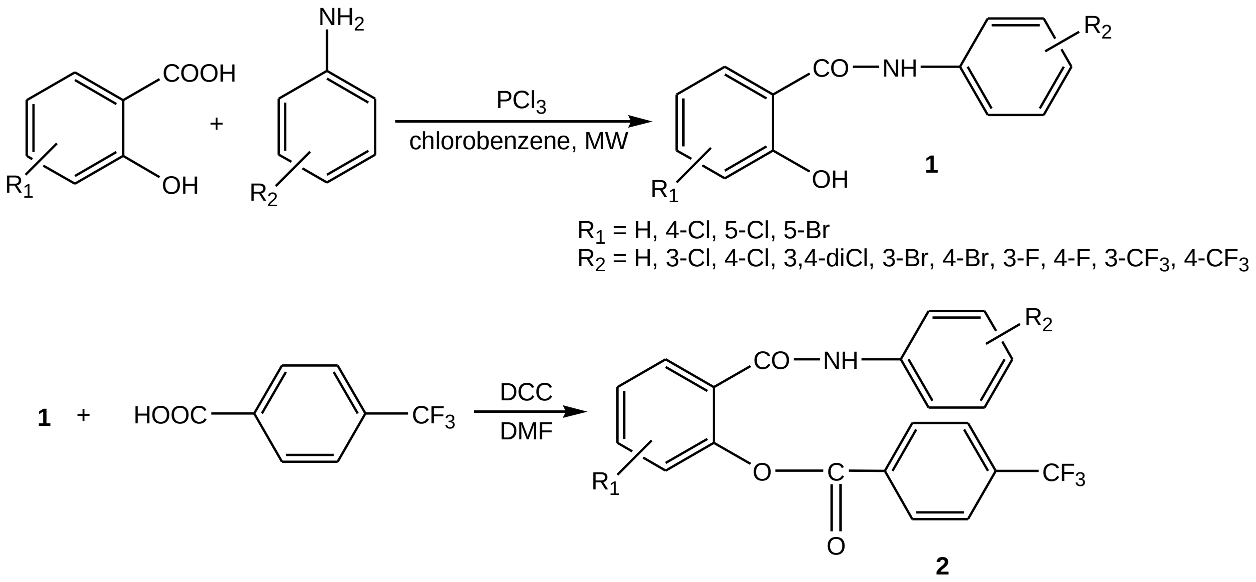


Scheme 2. Reaction between 5-chlorosalicyclic acid and aromatic amines under microwave irradiation.

By using microwave irradiation, the reaction time was shortened from several hours to minutes [49].

2-[2-(*N*-phenylcarbamoyl)phenoxy]alkanoic acids ethyl esters were obtained using solvents like dimethylformamide, ethanol and ethyl methyl ketone. Ethanol and ethyl methyl ketone proved to be the suitable rection media, where just the ester was obtained as a main product. Using dimethylformamide, a cyclic compound and the acid was obtained [27]. A new group of prodrugs with high activity, improved solubility and low toxicity was achieved by DCI-mediated condensation of salicylanilides with N-protected amino acids [50].

Salicylanilides were obtained by the reaction of appropriate salicylic acids and anilines in the presence of PCl_3 in chlorobenzene under microwave irradiation. Then they were esterified by 4-(trifluoromethyl)benzoic acid via N,N′-dicyclohexylcarbodiimide (DCC) coupling in dry N,N-dimethylformamide (Scheme 3).



R_1 = H, 4-Cl, 5-Cl, 5-Br
R_2 = H, 3-Cl, 4-Cl, 3,4-diCl, 3-Br, 4-Br, 3-F, 4-F, 3-CF_3, 4-CF_3

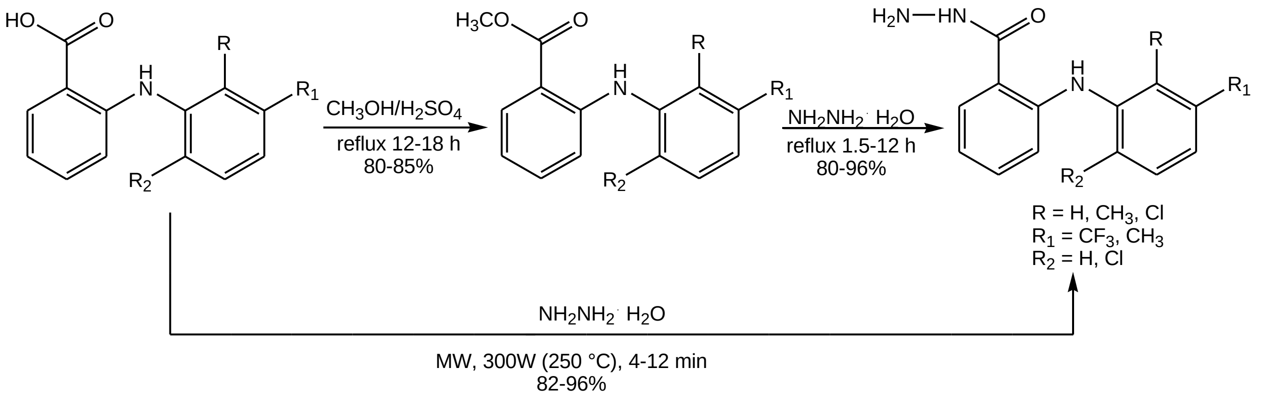
Scheme 3. Synthesis of salicylanilide 4-(trifluoromethyl)benzoates.

The salicylanilides were obtained in good yields ranged between 75–90%, meanwhile the esters yields were between 49–86% [51].

Hydrazides are generally synthesized by the hydrazinolysis of esters with hydrazine hydrate [21]. The reaction regularly takes place at room temperature, sometimes being necessary the heating of the reaction mixture on steam bath for 5 min to several days. Sometimes, the reaction initiates with difficulty after heating for days or even under pressure in a sealed tube, when partial decarboxylation may also happen [52]. Using conventional heating synthesis, the obtaining of dihydrazides, as by-product, is always possible.

A solvent-free microwave methodology has been experienced for the synthesis of some hydrazides. Hydrazinolysis of some esters, such as methyl salicylate, methyl nicotinate, ethyl phthalate, ethyl 3-hydroxynaphthoate was achieved by classical and solvent-free microwave irradiation synthesis. High yield and short reaction time point to the benefits of solvent free microwave method over the conventional one [53].

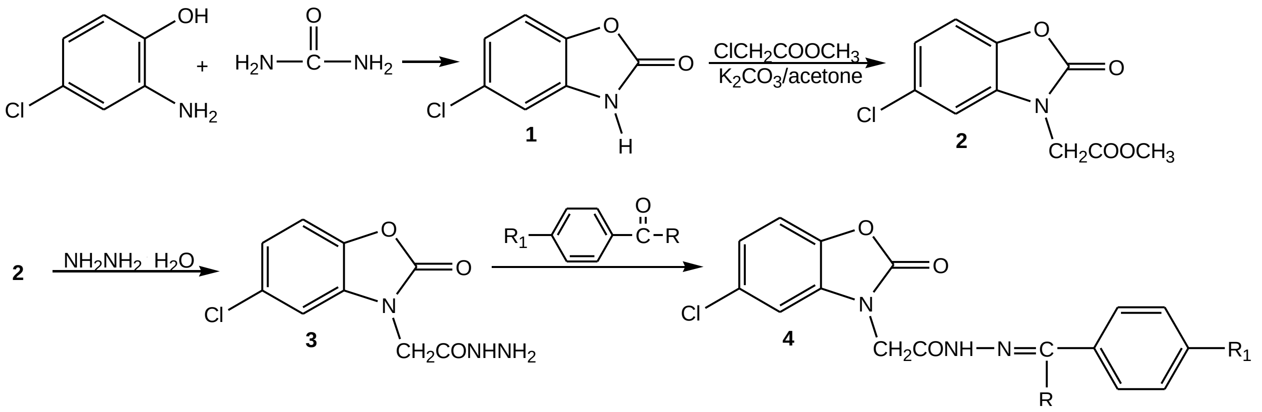
Using an efficient method based on one-step reaction under microwave irradiation and solvent-free conditions, fenamic acid hydrazides were obtained (Scheme 4). Beside the two-step conventional heating method, the process was simpler, the reaction time was shorter and the yields almost quantitative [54].



Scheme 4. Synthesis of fenamic hydrazides.

Because of the presence of an azometine -NHN=CH- proton, the hydrazones represent a significant class of compounds for the development of new drugs. Generally, the hydrazones are obtained using the reaction between substituted hydrazides and aldehydes or ketones in solvents such as ethanol, methanol, tetrahydrofuran, butanol, glacial acetic acid [55].

Several 5-chloro-2(3H)-benzoxazolinone-3-acetyl-2-(p-substituted benzal-hydrazone (**3**) and 5-chloro-2(3H)-benzoxazolinone-3-acetyl-2-(p-substituted acetophenone)-hydrazone (**4**) derivatives (Scheme 5) were obtained in reaction between 5-chloro-2(3H)-benzoxazolinone-3-acetyl hydrazide and benzaldehyde/acetophenone in ethanol, under microwave irradiation (400 W, 76-78 °C, 15 min) [56].



Scheme 5. Synthesis of benzal/acetophenone-hydrazones.

Some new quinoxalin-2(1H)-one-3-hydrazone compounds, were obtained using the condensation of 3-hydrazinoquinoxalin-2(1H)-one with an appropriate ketone under microwave irradiation. These novel hydrazones were obtained with higher yield and short reaction time compared to conventional heating method [57].

3. CONCLUSIONS

In the current context, researchers are continuously challenged to consider eco-friendly and sustainable approaches for the generation of desired target molecules.

Many researches have proven the advantages of the microwave dielectric heating in organic synthesis compared to the conventional heating: increased convenience, higher yields, greater selectivity, less catalyst, employment of green solvents, reduced reaction time.

This green chemistry tool seems to be also suitable for obtaining biologically active derivatives like anilides, esters, hydrazides and hydrazones.

Thus, in order to achieve a positive environmental and economic impact, microwave-assisted organic chemistry should be, whenever possible, the first choice for chemists interested to develop novel bioactive compounds.

4. REFERENCES

1. Anson, B.D., Ma, J., He, J.-Q., Identifying Cardiotoxic Compounds, *Genet. Eng. Biotechn. N.* 2009, 29 (9), 34–35.
2. Spellberg, B., Powers, J.H., Brass, E.P., Miller, L.G., Edwards, Jr. J.E., Trends in antimicrobial drug development: implications for the future, *Clin. Infect. Dis*. 2004, 38, 1279–1286.
3. Chopra, I., Hesse, L., O'Neill, A.J., Exploiting current understanding of antibiotic action for discovery of new drugs, *J. Appl. Microbiol.* 2002, 92, 4S–15S.
4. Alanis, A.J., Resistance to antibiotics: are we in the postantibioticera?, *Arch. Med. Res.* 2005, 36, 697–705.
5. Norrby, S.R., Nord, C.E., Finch, R., Lack of development of new antimicrobial drugs: a potential serious threat to public health, *Lancet. Infect. Dis.* 2005, 5, 115–119.
6. DiMasi, J.A., Hansen, R.W., Grabowski, H.G., The price of innovation: new estimates of drug development costs, *J. Health. Econ.* 2003, 22, 151–185.
7. Vinsova, J., Imramovsky, A., Salicylanilides: Still a topical potential antibacterially active group, *Ces. Slov. Farm.* 2004, 53, 294–299.
8. Hiramatsu, K., Hanaki, H., Ino, T., Yabuta, K., Oguri, T., Tenover, F.C., Methicillin-resistant *Staphylococcus aureus* clinical strain with reduced vancomycin susceptibility**,** *J. Antimicrob. Chemother.* 1997, 40, 135–136.
9. Chu, D.T.W., Plattner, J.J., Katz, L., New directions in antibacterial research, *J. Med. Chem.* 1996, 39, 3853–3874.
10. Waisser, K., Bures, O., Holy, P., Kunes, J., Oswald, R., Jiraskova, L., Pour, M., Klimesova, V., Kubicova, L., Kaustova, J., Relationship between the structure and antimycobacterial activity of substituted salicylanilides, *J. Arch. Pharm.* 2003, 336, 53–71.
11. Kunes, J., Balsanek, V., Pour, M., Waisser, K., Kaustova, J., On the relationship between the substitution pattern of thiobenzanilides and their antimycobacterial activity, *Il Farmaco* 2002, 57, 777–782.
12. Waisser, K., Hladuvkova, J., Kunes, J., Kubicova, L., Klimesova, V., Karajannis, P., Kaustova, J., Synthesis and antimycobacterial activity of salicylanilides substituted in position 5, *J. Chem. Pap.-Chem. Zvesti* 2001, 55, 121–129.
13. Macielag, M.J., Demers, J.P., Fraga-Spano, S.A., Hlasta, D. J., Johnson, S.C., Kanojia, R.M., Eussell, R.K., Sui, Z., Widner-Wells, M.A., Werblood, H., Folen, B.D., Goldschmidt, R.M., Loeloff, M.J., Webb, G.C., Barrett, J.F., Substituted salicylanilides as inhibitors of two-component regulatory systems in bacteria, *J. Med. Chem.* 1998, 41, 2939–2945.
14. Terada, H., Goto, S., Yamamoto, K., Takeuchi, I., Hamada, Y., Miyake, K., Structural requirements of salicylanilides for uncoupling activity in mitochondria: quantitative analysis of structure-uncoupling relationships, *Biochim. Biophys. Acta* 1988, 936, 504–512.
15. Vinsova, J., Imramovsky, A., Buchta, V., Ceckova, M., Dolezal, M., Staud, F., Jampilek, J., Kaustova, J., Salicylanilide Acetates: Synthesis and Antibacterial Evaluation, *Molecules* 2007, 12, 1-12.
16. Sharma, R.N., Sharma, K.P, Dikshit, S.N., Synthesis, characterization and biological activities of some new acid hydrazones derived from 2-[(N-benzoyl)2,5-dichloroanilido]acetohydrazide, *Int. J. Chem. Tech. Res.* 2011, 3, 381-390.
17. Rollas, S., Gülerman, N., Erdeniz, H., Synthesis and antimicrobial activity of some new hydrazones of 4-fluorobenzoic acid hydrazide and 3-acetyl-2,5-disubstituted-1,3,4-oxadiazolines, *Farmaco.* 2002, 57, 171-174.
18. Küçükgüzel, Ş.G., Rollas, S., Küçükgüzel, İ., Kiraz, M., Synthesis and antimycobacterial activity of some coupling products from 4-aminobenzoic acid hydrazones, *Eur. J. Med. Chem.* 1999, 34, 1093-1100.

19. Küçükgüzel, Ş.G., Oruç E.E., Rollas S., Şahin, F., Özbek, A., Synthesis, characterization and biological activity of novel 4-thiazolidinones, 1,3,4-oxadiazoles and some related compounds, *Eur. J. Med. Chem.* 2002, 37, 197-206.
20. Buu-Hoi, P.H., Xuong, D., Nam, H., Binon, F., Royer, R., Tuberculostatic hydrazides and their derivatives, *J. Chem. Soc*. 1953, 1358-1364.
21. Fahmy, H.H., El-Eraky, W., Synthesis and evaluation of the analgesic and antiinflammatory activities of O-substituted salicylamides, *Arch. Pharm. Res.* 2001, 24 171-179.
22. Sah, P.P.T., Peoples, S.A., Isonicotinyl hydrazones as antitubercular agents and derivatives for idendification of aldehydes and ketones, *J. Am. Pharm. Assoc*. 1954, 43, 513-524.
23. Lidstrom, P., Tierney, J., Wathey, B., Westman, J., Microwave assisted organic synthesis – a review, *Tetrahedron* 2001, 57, 9225-9283.
24. Strauss, C.R., Varma, R.S, Microwaves in Green and Sustainable Chemistry, *Top. Curr. Chem.* 2006, 199-231
25. Vinsova, J., Imramovsky, A., Salicylanilides: still a topical potential antibacterially active group, *Ces. Slov. Farm.* 2004, 53, 294-299.
26. Ienaşcu, I., Lupea, A.X., Hădărugă, D., Hădărugă, N., Popescu, I., The antimicrobial activity and quantitative structure-biological activity relationships evaluation of some novel 2-hydroxybenzamide derivatives, *Rev. Chim.* 2008, 59(2), 247-250.
27. Kwiecien, H., Synthesis and properties of new 2-alkyl-1,4-benzoxazepine derivatives. Part I. Synthesis and cyclization of 2-phenoxyalkanoic acid derivatives, *Polish. J. Chem.* 1996, 70, 733-741.
28. Iranpoor, N., Zeynizadeh, B., Microwavepromoted trifluoroacetylation of amines with $TiO(CF_3CO_2)_2$, *J. Chem. Res.* 1999, 124–125.
29. Rannard, S.P., Davis, N.J., The selective reaction of primary amines with carbonyl imidazole–containing compounds: Selective amide and carbamate synthesis, *Org. Lett.* 2000, 2, 2117–2120.
30. Perreux, L., Loupy, A., Volatron, F., Solvent-free preparation of amides from acids and primary amines under microwave irradiation, *Tetrahedron* 2002, 58, 2155–2162.
31. Lupea, A.X., Popescu, I., Tarabasanu, C., Ienaşcu, I., Badea, V., “The synthesis and characterisation of some ortho-substituted phenoxyalkanoic acids and their derivatives”, *J. Serb. Chem. Soc.* 71(12), 1247–1261, 2006.
32. Lupea, A.X., Popescu, I., Tarabasanu, C., Ienascu, I., Padure, M., Synthesis of new 2-[2-(4-chloro-phenylcarbamoyl)-phenoxy]alkanoic acids derivatives, *Rev. Roum. Chem.* 51(6), 517-521, 2006.
33. Ienaşcu, I., Lupea, A.X., Popescu, I., Tomas, Ş., Zamfir, A.D., Synthesis and characterization of some new 2-hydroxy-N-(3-trifluoromethyl-phenyl)-benzamide derivatives, *Rev. Chim.* 59(1) 56-59, 2008.
34. Ienaşcu, I., Lupea, A.X., Popescu, I., Moşoarcă, C., Zamfir, A.D., Synthesis and characterization of some new 2-hydroxy-N-(2-trifluoromethyl-phenyl)-benzamide derivatives, *Rev. Roum. Chem.* 53(4), 273-276, 2008.
35. Ienaşcu, I.M.C., Lupea, A.X. Popescu, I.M., Pădure, M.A., Zamfir, A.D., The synthesis and characterization of some novel 5-chloro-2-(substituted alkoxy)-N-phenylbenzamide derivatives, *J. Serb. Chem. Soc.* 74 (8–9), 847–855, 2009.
36. Ienaşcu, I.M.C., Padure, M.A., Lupea, A.X., Balcu, I., Popescu, I.M., Synthesis and Characterization of Some New Salicylamide Derivatives with Potential Biological Activity, *Rev. Chim.* 61(4) 368-371, 2010.
37. Biagi, G., Giorgi, I., Livi, O., Nardi, A., Calderone, V., Martelli, A., Martinotti, E., Salerni, O.L., Synthesis and biological activity of novel substituted benzanilides as potassium channel activators, *V. Eur. J. Med. Chem*. 2004, 39, 491–498.
38. Wamser, C.C., Yates, J.A., Kinetics and mechanisms for the two-phase reaction between aqueous aniline and benzoyl chloride in chloroform, with and without pyridine catalysis, *J. Org. Chem.* 1989, 54, 150–154.
39. Varma, R.S., Naicker, K.P., Solvent-free synthesis of amides from non-enolizable esters and amines using microwave irradiation, *Tetrahedron Lett.* 1999, 40, 6177–6180.
40. Hans, J.J., Driver, R.W., Burke, S.D., Direct transacylation of 2,2,2-trihaloethyl esters with amines and alcohols using phosphorus(III) reagents for reductive fragmentation and in situ activation, *J. Org. Chem.* 2000, 65, 2114–2121.

41. Veitch, G.E., Bridgwood, K.L., Ley, S.V., Magnesium nitride as a convenient source of ammonia: Preparation of primary amides, *Org. Lett.* 2008, 10, 3623–3625.
42. Gao, J., Wang, G.W., Direct oxidative amidation of aldehydes with anilines under mechanical milling conditions, *J. Org. Chem.* 2008, 73, 2955–2958.
43. Ekoue-Kovi, K., Wolf, C., Metal-free one-pot oxidative amination of aldehydes to amides, *Org. Lett.* 2007, 9, 3429–3432.
44. Yadav, J.S., Subba Reddy, B.V., Subba Reddy, U.V., Praneeth, K., Azido-Schmidt reaction for the formation of amides, imides, and lactams from ketones in the presence of $FeCl_3$, *Tetrahedron Lett.* 2008, 49, 4742–4745.
45. Burnell-Curty, C., Roskamp, E.J., The conversion of carboxylic acids to amides via tin(II) reagents, *Tetrahedron Lett.* 1993, 34, 5193–5196.
46. Basel, Y., Hassner, A., Activation of carboxylic acids as their active esters by means of tert-butyl 3-(3,4-dihydrobenzotriazine-4-on)yl carbonate, *Tetrahedron Lett.* 2002, 43, 2529–2533.
47. Vasquez-Tato, M.P., Microwave-mediated synthesis of amide, *Synlett.* 1993, 506.
48. Lu, C.-R. Zhao, B., Jiang, Y.-P., Ding, H., Yang, S., One-pot synthesis of salicylanilides by direct amide bond formation from salicyclic acid under microwave irradiation, *Synth. Commun.* 2011, 41(9), 1257-1266.
49. Ferriz J. M., Vavrova K., Kunc F., Imramovsky A., Stolarikova J., Vavrikova E., Vinšova J., Salicylanilide carbamates: Antitubercular agents active against multidrug-resistant Mycobacterium tuberculosis strains, *Bioorg. Med. Chem.* 18 (2010) 1054–1061.
50. Imramovsky, A., Vinsova, J., Monreal Ferriz, J., Kunes, J., Pour, M., Dolezal, M., Salicylanilide esterification: unexpected formation of novel seven-membered rings, *Tetrahedron Letters*, 2006, 47, 5007–5011.
51. Krátký, M., Vinšová, J., Antifungal Activity of Salicylanilides and Their Esters with 4-(Trifluoromethyl)benzoic Acid, *Molecules* 2012, 17, 9426-9442.
52. Bruice, T.C., Benkovic, S.J., The Compensation in Δ*H*[UNK] and Δ*S*[UNK] accompanying the conversion of lower order nucleophilic displacement reactions to higher order catalytic processes. The temperature dependence of the hydrazinolysis and imidazole-catalyzed hydrolysis of substituted phenyl acetates, *J. Am. Chem. Soc*, 1964, 86, 418.
53. Jain, A.K., Gupta, P.K., Ganesan, K., Pande A., Malhotra R.C., Rapid solvent-free synthesis of aromatic hydrazides under microwave irradiation, *Defence Sci. J.* 2007, 57, 267-270.
54. Aboul-Fadl, T., Abdel-Aziz, H.A., Kadi, A., Bari, A., Ahmad P., Al-Samani, T., Ng, S.W., Microwave-Assisted One-Step Synthesis of Fenamic Acid Hydrazides from the Corresponding Acids, *Molecules* 2011, 16, 3544−3551.
55. Rollas, S., Küçükgüzel, Ş.G., Biological Activities of Hydrazone Derivatives, *Molecules* 2007, 12, 1910-1939.
56. Önkol, T., Gökçe, M., Tosun, A. U., Polat, S., Serin, M.S., Tezcan, S. Microwave synthesis and antimicrobial evaluation of 5-chloro-2(3h)-benzoxazolinone-3-acetyl-2-(p-substituted benzal) hydrazone and 5-chloro-2(3h)-benzoxazolinone-3-acetyl-2-(p-substituted acetophenone)hydrazone derivatives *Turk. J. Pharm. Sci.* 2008, 5 155-166.
57. Ajani, O.O., Obafemi, C.A., Ikpo, C.O., Ajanaku, K.O., Ogunniran, K.O., Oladele Olusola James, O.O., Comparative study of microwave assisted and conventional synthesis of novel 2-quinoxalinone-3-hydrazone derivatives and its spectroscopic properties, *Int. J. Phys. Sci.* 2009, 4, 156-164.

Thermal Stability of Anthocyanin-based Extract from Red Onion Skin

Adina Căta[1], Mariana N. Ştefănuţ[1], Ioana M.C. Ienaşcu[1,2]

[1]National Institute of Research and Development for Electrochemistry and Condensed Matter, Dr. Aurel Păunescu Podeanu 144, 300569, Timişoara, Romania

[2]"Vasile Goldiş" University of Arad, Faculty of Medicine, Pharmacy and Dentistry,Liviu Rebreanu 86, 310045, Arad, Romania

Abstract

The effect of thermal processing and storage on anthocyanin stability from red onion (Allium cepa L.) was investigated in this study. Anthocyanins extraction was carried out with acidified methanol in ultrasonic conditions. The degradation of anthocyanin pigments from onion skin extract was followed during heating at 90℃ for 5 hours and during storage in darkness at 25°C for 30 days. Anthocyanins content was quantified by using a pH differential method. Also, during the stability tests, the total phenolics content and antioxidant activity were determined. Total phenolic content was assessed by the Folin-Ciocalteau assay, and the antioxidant activities were determined by the DPPH, ABTS and FRAP assays. During heating at 90℃, the extract shows a good stability. During storage at room temperature, the extract suffers a 47% decrease in anthocyanin content. Evaluation of total phenolics and antioxidant activities during heating at 90℃ shows an increasing trend, while a minor decrease was observed for samples stored at room temperature.

Introduction

Onions (*Allium cepa* L.) are one of the oldest and most frequently cultivated vegetables worldwide. Onions contain high levels of flavonoids which are responsible for a great part of the health benefits of these vegetable, flavonols and anthocyanins being the main subclasses present. The latter are concentraded mainly in the outher shell of red onions [1,2]. Anthocyanins are polyphenolic water soluble pigments widely spread in many fruits and vegetables. Easy incorporation in aqueous media and their attractive orange, red, purple, and blue colours gives them a high potential for use as alternative to artificial colorants in food products. Furthermore, anthocyanins possess a significant antioxidant effect which gives them a potential role in prevention of various diseases associated with oxidative stress such as cancer [3], diabetes [4] or cardiovascular diseases [5].

The main drawback in using anthocyanins as food colorants is their low stability. Anthocyanins are readily oxidized due to their antioxidant properties and therefore susceptible to degradation reactions during extraction, purification, processing or storage which may have a profound impact on color quality or nutritional properties. Various factors such as pH, temperature, enzymes, light, oxygen, solvents, or the presence of other compounds [6] limit the practical applicability of these pigments. Thermal treatment is one of the methods used to preserve and extend the shelf life of foods but it is also a significant factor that affects the anthocyanins stability. Traditional thermal processing of foods involves heating to temperatures in the range 50 to 150ºC, depending upon pH of the product and desired shelf life [7]. From some investigations on red onion anthocyanin extracts, an increase of temperature above 45–50°C depending on pH of the obtained extract may produce anthocyanin decomposition [8].

The aim of this study is to investigate the stability of anthocyanin extract from red onion skin during thermal treatment at 90°C and storage at room temperature. The extraction of the pigments was carried out with acidified methanol in ultrasonic conditions. The changes in monomeric anthocyanin content, total phenolics content and antioxidant activity were followed during stability tests.

Experimental

Materials

Folin-Ciocalteu reagent, 1,1-diphenyl-dipicrylhydrazyl (DPPH), gallic acid and 6-hidroxy-2,5,7,8-tetramethylchromane-2-carboxylic acid 97 % (Trolox) and methanol (HPLC grade) were purchased from Sigma-Aldrich, Germany. Iron (III) chloride, 2,4,6-tris(2-pyridyl-1,3,5-triazine (TPTZ) and 2,2'-azino-bis(3-ethylbenzthiazoline-6-sulphonic acid) (ABTS) were purchased from Sigma, Germany. Hydrochloric acid was obtained from Merck, Germany. Red onions were purchased from a local market (Timisoara, Romania). For the experimental tests, the outer dry layers were manually separated from the bulb and then were ground in an electric blender.

Anthocyanin extraction

Extraction of anthocyanins was performed by the following procedure: in a sealed container, the onion skin and the solvent (acidified methanol with 0.1% HCl) at solid to solvent ratio 1:4 (w/v) were placed in the ultrasonic bath. The operating parameters were: frequency 59kHz, power 270 W, temperature 25 ± 3°C and ultrasonic time 30 minutes. After extraction, the solid was removed by vacuum filtration. The obtained extract was concentrated by evaporation under vacuum using a rotary evaporator (Laborota 4000 Efficient, Heidolph, Germany) at 30°C to prevent anthocyanin degradation.

Stability tests

Thermal stability of the anthocyanin extract was studied at room temperature for 30 days of storage as well as at 90°C for 5 hours. For accelerated degradation tests (90°C), aliquots of 1 mL extract were introduced in hermetically sealed glass tubes to avoid evaporation and placed in a drying chamber with digital adjustment of temperature. At regular intervals (30, 60, 120, 180, 240 and 300 minutes), the tubes were removed from the drying chamber and rapidly cooled into an ice-water bath to stop thermal degradation. The samples were stored at -20°C until analyzes. For the evaluation of the thermal stability were determined: the anthocyanin content, the total content of phenolic compounds and the antioxidant activity.

Determination of anthocyanin content

Total monomeric anthocyanins content was quantified by a pH differential method developed by Giusti and Wrolstad [9] using two buffer solutions: potassium chloride buffer 0.025 M (pH 1.0) and sodium acetate buffer 0.4 M (pH 4.5). The absorbance was measured simultaneously at 522 nm (λ_{max}) and 700 nm after 15 minutes of incubation at room temperature using a Jasco V 530 UV-Vis spectrophotometer. The following equation was used for calculating the monomeric anthocyanin pigment concentration:

$$C(mg/l) = \frac{A \times MW \times DF \times 1000}{\varepsilon \times l} \qquad (1)$$

where: $A=(A_{\lambda max}-A_{700})_{pH\ 1.0}-(A_{\lambda max}-A_{700})_{pH\ 4.5}$, *MW* is the molecular weight, *DF* is the dilution factor, ε is the molar absorbance and *l* is the pathlength (1 cm). The total monomeric anthocyanins content was expressed as cyanidin-3-glucoside equivalents (MW=449.2 and ε=26900). All samples were analyzed in triplicate.

Determination of total phenolics

The amount of total phenolics was quantified according to the Folin-Ciocalteu method [10]. Briefly, 20 μL of each extract, 15 mL dd water and 1 mL Folin-Ciocalteu reagent were added to a 20 mL volumetric flask. The contents were mixed and incubated for 5 min at room temperature. Then, 3 mL of 20% (w/v) sodium carbonate solution was added, followed by the addition of dd water to volume and mixing. After incubation for 2 hours at room temperature, the absorbance at 765 nm was measured. Gallic acid (50 – 550 mg/L) was used as reference compound for calibration curve. Total phenolics content was expressed as mg gallic acid equivalents per litter of fruit extract (mg GAE/L). All samples were analyzed in triplicate.

Antioxidant activity

Determination of antioxidant activity was performed using three methods: DPPH [11], ABTS [12] and FRAP [13]. The antioxidant reference compound used was Trolox. The calibration curves were obtained using standard solutions in the range 0.2-1.0 mmol/L Trolox. For the evaluation of antioxidant activities, each sample was diluted 1: 500 (v/v) for the DPPH and ABTS assays and 1: 1000 (v/v) for FRAP assay. The absorbance of the samples was measured at 515 nm for DPPH assay, 734 nm for ABTS assay and 593 nm against for FRAP assay using a Jasco V 530 UV-Vis spectrophotometer. Each sample was analyzed in triplicate.

Results and discussion

Total monomeric anthocyanin contents from onion skin extract during thermal treatment at 90°C were determined at regular time intervals. The experimental results are shown in Fig. 1. There was a decreasing trend in the anthocyanin content but the decrease in concentration was not very pronounced. From an initial monomeric anthocyanin content of 1384±19 mg/L, the loss of pigments after 5 hours of thermal treatment was only 19.6%. The anthocyanins occurring in red onions are mainly cyanidin glucosides acylated with malonic acid or nonacylated [14], therefore the presence of acylated anthocyanins could be an explanation for the absence of a more drastic reduction in anthocyanin concentration. It has already been shown that anthocyanins with acylating substituents are more stable during processing and storage than other natural pigments [15].
The effect of thermal treatment on total phenolics content of onion extract can be observed in Fig. 2.

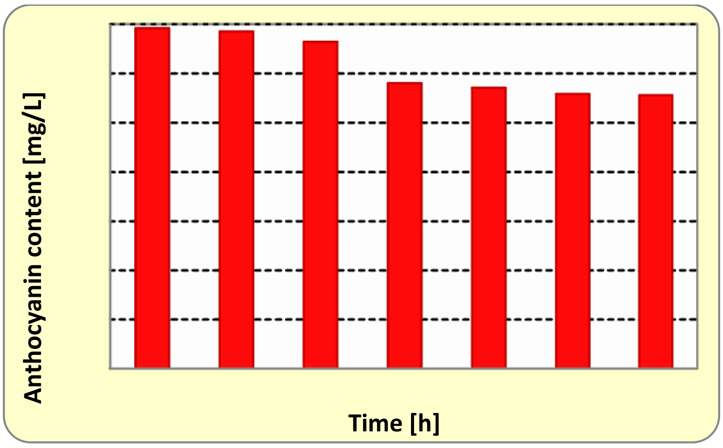


Fig. 1. Variation of anthocyanin content in red onion extract during thermal treatment at 90°C

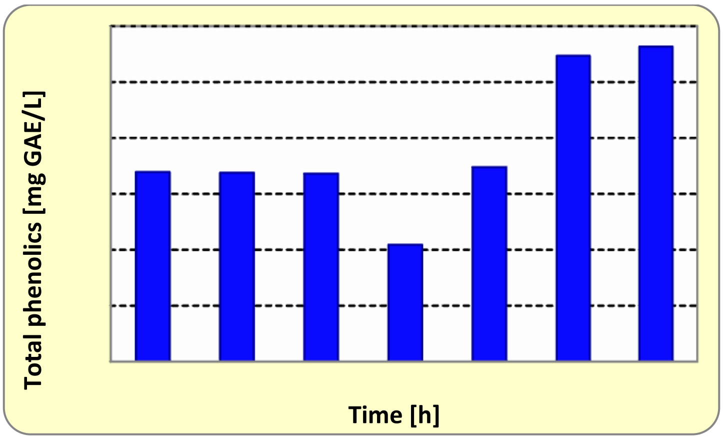


Fig. 2. Variation of total phenolics content in red onion extract during thermal treatment at 90°C

There is a decrease in the phenolic compounds content up to 2 hours of thermal treatment from 25391±74 to 24091±53 mg GAE/L, then a strong increase towards the end of the thermal treatment, the phenolics content reaching 27634±102 mg GAE/L. This increase in phenolics concentration could indicate the formation of some degradation products of phenolic nature.

To prove the effect of heat treatment on onion extract, the antioxidant capacities were also evaluated by using DPPH, ABTS and FRAP assays. Fig. 3 shows the antioxidant activities expressed in mmol/L Trolox Eq. for samples degraded at 90°C.

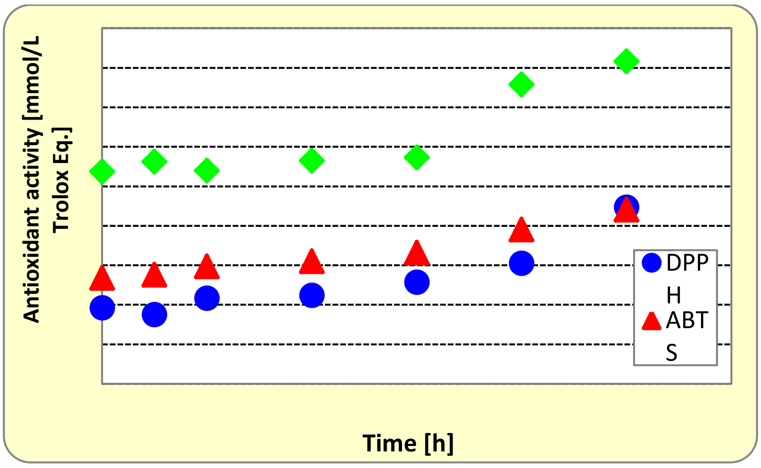


Fig. 3. Variation of antioxidant activity in red onion extract during thermal treatment at 90°C

Overall, the values obtained for antioxidant activities by DPPH and ABTS assays are relatively close, while the results obtained by FRAP assay are higher. Good correlations between the values determined by the three methods were obtained (Fig. 4), especially between ABTS and DPPH (R^2 = 0.9397). Although the values obtained by the three classical methods are different, however it can be observed the same general tendency of increasing the antioxidant activities. This may be due to the formation of some degradation products, such as acids or other phenolic compounds, which may have antioxidant properties.

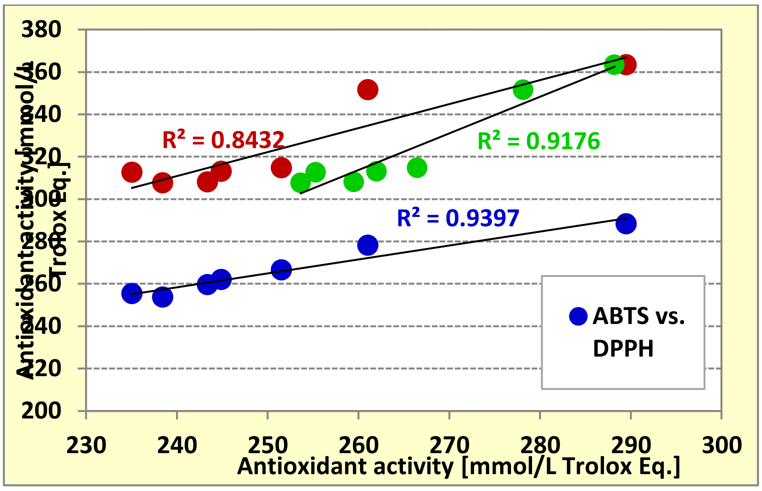


Fig. 4. Correlation between antioxidant activities assessed by DPPH, FRAP, and ABTS methods

To study the stability of the anthocyanin extract at ambient temperature, the same analyzes applied for accelerated degradation at 90°C were performed. The changes in anthocyanin content were monitored for one month (Fig. 5).

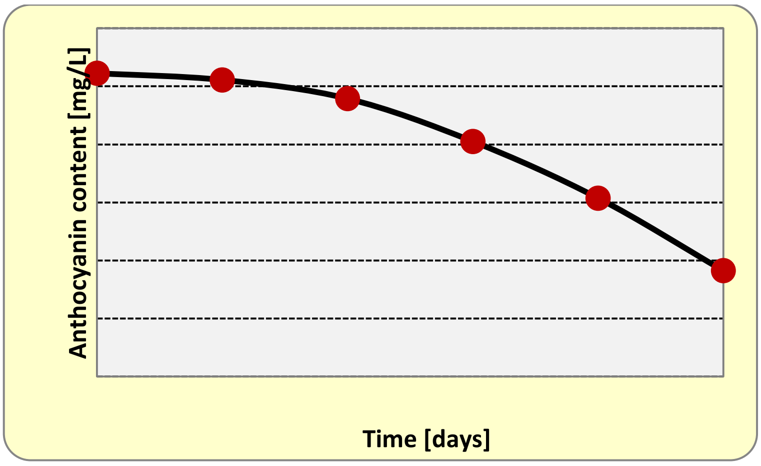


Fig. 5. Variation of anthocyanin content in red onion extract during storage at room temperature

It is observed a continuous decrease of it, after one month reaching a 47% decrease in the concentration of anthocyanins in the extract. Antioxidant activity shows a slight decreasing trend during storage at room temperature.

Conclusions

A concentrated anthocyanin extract from red onion dry skins was prepared and its stability at room temperature and at elevated temperature (90°C) was studied. During degradation, the samples were analyzed in terms of monomeric anthocyanin content, total phenolics content and antioxidant activity. At room temperature anthocyanins degradation occurs slowly, after 30 days of storage the loss in anthocyanins content was 47%. In the case of accelerated degradation tests at 90°C, after 5 hours of thermal treatment applied to onion skin extract, only 20% decrease in the anthocyanin content was found. The content of phenolic compounds and antioxidant activity showed a tendency to increase after 2 hours of thermal treatment due to the formation of some degradation products of phenolic nature possessing antioxidant potential. Although the dry skin of red onions is non-edible, this accumulates high levels of anthocyanins which showed a fairly good stability to heat treatment thus demonstrating a good potential for their use as natural food colorants.

Acknowledgments

This work is part of the project PN 16-14 03 06 / 2016 “Innovative solutions for the stabilization of natural extracts based on anthocyanins”, carried out under NUCLEU Program funded by National Authority for Scientific Research (Romania).

References

1. Pérez-Gregorio, R. M, García-Falcón, M. S., Simal-Gándara, J., Rodrigues, A. S., Almeida, D. P. F., Identification and quantification of flavonoids in traditional cultivars of red and white onions at harvest, *J. Food Compost. Anal.* 2010, 23, 592–598.
2. Corzo-Martínez, M., Villamiel, M., An overview on bioactivity of onion. In: *Onion consumption and health*, Ed. C.B. Aguirre et al., Nova Science Publishers, 2012, pp. 1-48.
3. Wang, L. S., Stoner, G. D., Anthocyanins and their role in cancer prevention, *Cancer Lett.* 2008, 269, 281-290.
4. Guo, H., Ling, W., The update of anthocyanins on obesity and type 2 diabetes: Experimental evidence and clinical perspectives, *Rev. Endocr. Metab. Disord.* 2015, 16, 1-13.
5. Wallace, T. C., Anthocyanins in cardiovascular disease, *Adv. Nutr.* 2011, 2, 1-7.
6. Castañeda-Ovando, A., Pacheco-Hernández, M., Páez-Hernández, M. E., Rodríguez, J. A., Galán-Vidal, C. A., Chemical studies of anthocyanins: A review, *Food Chem.* 2009, 113, 859-871.
7. Patras, A., Brunton, N. P., O’donnell, C., Tiwari, B. K., Effect of thermal processing on anthocyanin stability in foods; mechanisms and kinetics of degradation, *Trends Food Sci. Technol.* 2010, 21, 3-11.
8. Oancea, S., Drăghici, O., pH and thermal stability of anthocyanin-based optimised extracts of Romanian red onion cultivars, *Czech J. Food Sci.* 2013, 31, 283-291.
9. Giusti, M. M., Wrolstad, R. E., Unit F1.2. Anthocyanins. Characterization and Measurement of Anthocyanins by UV-Visible Spectroscopy, *Current Protocols in Food Analytical Chemistry*, John Wiley & Sons, Inc., 2001, pp. F1.2.1-F1.2.13.
10. Waterhouse, A. L., Unit I1.1. Polyphenolics. Determination of Total Phenolics, *Current Protocols in Food Analytical Chemistry*, John Wiley & Sons, Inc., 2002, pp. I1.1.1-I1.1.8.
11. Brand-Williams, W., Cuvelier, M. E., Berset, C., Use of a free radical to evaluate antioxidant activity, *LWT - Food Sci. Technol.* 1995, 28, 25-30.
12. Ozgen, M., Reese, R. N., Tulio Jr, A. Z., Scheerens, J. C., Miller, R., Modified 2,2-azino-bis-3-ethylbenzothiazoline-6-sulfonic acid (ABTS) method to measure antioxidant capacity of selected small fruits and comparison to ferric reducing antioxidant power (FRAP) and 2,2’-diphenyl-1-picrylhydrazyl (DPPH) methods, *J. Agric. Food Chem.* 2006, 54, 1151-1157.
13. Benzie, I. F. F., Strain, J. J., The ferric reducing ability of plasma (FRAP) as a measure of “Antioxidant power”: The FRAP assay, *Anal. Biochem.* 1996, 239, 70-76.
14. Slimestad, R., Fossen, T., Vagen, I. M., Onions: a source of unique dietary flavonoids, *J. Agric. Food Chem.* 2007, 55, 10067–10080.
15. Bąkowska-Barczak, A., Acylated anthocyanins as stable, natural food colorants – a review, *Pol. J. Food Nutr. Sci.* 2005, 14/55, 107-116.

Selection of wastewater treatment technology of the capital of podgorica in the new plant

Izbor tehnologije prečišćavanja otpadnih voda glavnog grada podgorica u novom postrojenju

Darko Vuksanović[1], Petar Živković[2], Vladan Vučelić[3]

[1]University of Montenegro, Faculty of Metallurgy and Technology, Podgorica, Montenegro,

[2]Medix d.o.o. Podgorica, Montenegro,

[3]Vodovod i kanalizacija d.o.o. Podgorica, Montenegro

[1]Univerzitet Crne Gore-Metalurško-tehnološki fakultet Podgorica,

[2]Medix d.o.o. Podgorica,

[3]Vodovod i kanalizacija d.o.o. Podgorica

Abstract

Podgorica The capital of Montenegro has 210,000 inhabitants. There is a well-resolved issue of water supply with quality drinking water. It is very important to mention that in 1978, Podgorica had built a wastewater treatment plant. The capacity of the built plant is 55,000 ES, which is inadequate to process already connected 119,000 ES. The capacity of the new planned plant is for 235,000 ES in 2040.

The future plant will be built at a new location in the industrial zone of "KAP" (Aluminum plant Podgorica). The new plant will be a unique system in which three plants will be built for purification of waste water, a treatment plant for the sludge in order to obtain biogas, that is, electricity and hot water, and a plant for the incineration of the sludge residue in the fluidizing layer.

It is planned that the purified water - effluent that flows into the recipient-Morača River is A1 class. It is water that can be used for bathing and watering agricultural products. Taking into account that this is a sensitive area, in this way, Skadar Lake will be protected from the impact of municipal wastewater. Eliminating odors is foreseen for all three plants. It is also planned the destruction of pathogenic bacteria by UV rays.

The aim of this work is to demonstrate that the optimum available technology is selected for the new plant, which will provide the maximum protection of the recipient-river Morača, the Skadar Lake as a national park and the land of the Zeta Plain.

Key words: *waste water, purification, plant*

Izvod

Podgorica Glavni grad Crne Gore ima 210.000 stanovnika. Ima dobro riješeno pitanje vodosnabdijevanja kvalitetnom vodom za piće. Veoma je važno napomenuti, da je Podgorica još 1978 godine izgradila postrojenje za prečišćavanje otpadnih voda. Kapacitet izgrađenog postrojenja iznosi 55.000 ES, koji je nedovoljan da obradi već priključenih 119.000 ES. Kapacitet novog planiranog postrojenja je za 235.000 ES u 2040. godini.

Buduće postrojenje će biti izgrađeno na novoj lokaciji u industrijskoj zoni KAP-a. Novo postrojenje će predstavljati jedinstveni sistem u kojem će biti izgrađena tri postrojenja, za prečišćavanje otpadnih komunalnih voda, postrojenje za tretman mulja u cilju dobijanja biogasa, *odnosno električne energije i tople vode i postrojenje za insineraciju ostatka mulja u fluidizirajućem sloju.*

Projektovano je, da prečišćena voda – effluent koja se upušta u recipijent rijeku Moraču bude A1 klase. To je voda koja se može koristiti za kupanje i zalivanje poljoprivrednih proizvoda. Uzimajući u obzir da se radi o senzitivnom području, na ovaj način će Skadarsko jezero biti zaštićeno od uticaja komunalnih otpadnih voda. Eliminacija mirisa je predviđena za sva tri postrojenja. Planirano je uništavanje patogenih bakterija UV zracima.

Cilj ovog rada je da se pokaže da je za novo postrojenje odabrana optimalna dostupna tenologija koja će obezbijediti maksimalnu zaštitu recipijenta-rijeku Moraču, Skadarsko jezero kao nacionalni park i zemljište Zetske ravnice.

Ključne riječi: *otpadne komunalne vode, prečišćavanje, postrojenje*

Uvod

Postojeće postrojenje za prečišćavanje otpadnih voda (PPOV) Glavnog grada Podgorice izgrađeno je 1978 godine. Kapacitet postojećeg postrojenja je za 55.000 ES, a sadašnji protok komunalnih otpadnih voda i teret zagađenja od približno 119.000 ES. Sakupljanje i odvođenje komunalnih otpadnih vodavrši se u postojećoj kanalizacionoj mreži i odvodi se u postrojenje, koje ima 100% preopterećenje. Postojeća tehnologija na starom postrojenju ne obezbeđuje kvalitet prečišćene vode-efluenta A1 klase, nekvalitetno riješeno pitanje odlaganja i obrade kanalizacionog mulja, uklanjanje neprijatnih mirisa, uslovljavaju hitno rješevanje ovog važnog ekološkog problema u Podgorici. Zbog ograničenog kapaciteta postojećeg postrojenja, od ukupno sakupljene i dovedene količine komunalne otpadne vode na postrojenju se potpuno obrađuje 50 % komunalnih otpadnih voda. Ostala količina se dovodi na primarno mehaničko prečišćavanje, zatim kolektorom ispušta u recipijent-rijeku Moraču. Ispuštanje samo djelimično obrađene komunalne otpadne vode kao neprečišćenog efluenata značajno utiče na kvalitet rijeke Morače, tako da poslije kolektora za ispuštanje obrađenih voda, vode Morače odgovaraju kvalitetu A2 i A3 klase. Svi navedeni faktori su izuzetno važni razlozi za potrebom izgradnje novog postrojenja odgovarajućeg kapaciteta i prihvatljive tehnologije prečišćavanja.

Takođe, važan razlog izgradnje novog postrojenja je i taj, što se postojeće postrojenje i odlaganje izdvojenog mulja nalaze u široj gradskoj zoni Podgorice i okruženo je stambenim objektima i velikim komercijalnim marketima koji nijesu kompatibilni sa navedenim industrijskim postrojenjem.

Prije donošenja konačne odluke o izgradnji novog postrojenja urađene su tri Studije od strane poznatih firmi koje se bave projektovanjem postrojenja PPOV-a a to su : "SOGREAH" – Francuska, Institut za vode WYG – London, FICHTNER – Njemačka. Sve tri Studije su pokazale da se u Podgorici hitno mora izgraditi odgovarajuće postrojenje za prečišćavanje komunalnih otpadnih voda, da predložena lokacija za nova postrojenja u potpunosti zadovoljava kriterijume, a koji se moraju ispuniti da bi se na toj lokaciji izgradilo postrojenje za PPOV. Investitor insistira da novo postrojenje mora da ispuni sledeće uslove:

-da se izgradnjom savremenog postrojenja za prečišćavanje otpadnih voda obezbjeđuje potrebna efikasnost prečišćavanja, da kvalitet efluenta bude A1 klase, u cilju adekvatne zaštite rijeke Morače, vodoizvorišta Boljesestre, Skadarskog jezera i zemljišta Zetske ravnice,

-da se u skladu sa projektovanim kapacitetom za 235.000 ES izvrši proširenje kanalizacione mreže, čime će se omogućiti uklanjanje neispravnih sanitarnih objekata, prevashodno zbog korišćenja septičkih jama,

-da se planiranim proširenjem kanalizacione mreže i priključenje do 2040. godine od 116.000 ES će se automatski poboljšati stanje u svim zonama u Podgorici koje nijesu pokrivene kanalizacionom mrežom,

- da se kanalizacioni mulj tretmanom prevede u biogas, električnu energiju i toplu vodu,
- da se uklone neprijatni mirisi iz svih proizvodnih pogona i uklone sve patogene bakterije iz efluenta,

Parametri za projektovanje PPOV u Podgorici

Parametri projektovanja za dimenzionisanje budućeg PPOV Podgorica, koji su zasnovani na potrebnim kriterijumima projektovanja prikazani su u tabeli 1.

Tabela 1. Parametri projektovanja za dimenzionisanje novog PPOV Podgorica

Parametar	Jedinica	2016.	2020.	2030.	2040.
Ekvivalentni stanovnik	**ES**	**119.800**	**135.400**	**187.700**	**235.200**
Protok otpadnih voda pri suvom vremenu	m^3/d	31.970	31.140	38.830	46.340
Protok otpadnih voda pri vlažnom vremenu	m^3/d	45.070	46.200	56.180	57.450
Teret zagađenja					
BPK_5	kg/d	7.189	8.122	11.263	14.109
HPK	kg/d	14.379	16.244	22.526	28.219
SS	kg/d	8.388	9.475	13.140	16.461
Koncentracija					
BPK_5	mg/l	225	261	290	304
HPK	mg/l	450	522	580	609
SS	mg/l	262	304	338	355

Proizvodnja kanalizacionog mulja se procjenjuje sa 10.100 t/god., za projektovani kapacitet PPOV od 135.000 ES, za fazu 0 do 2020. godine. Za fazu 1 do 2030. godine, projektovani kapacitet PPOV je 187.700 ES, pri čemu je godišnja količina mulja proračunata na 13.800 t/god. Za fazu 2 do 2040. godine, projektovani kapacitet PPOV je 235.000 ES, pri čemu je godišnja količina mulja proračunata na 17.000 t/god.

Odabrana lokacija za novo PPOV nalazi se približno 3 km južno od Podgorice, na lijevoj obali rijeke Morače i u neposrednoj blizini Kombinata aluminijuma Podgorica (KAP-a).

Slika 1. Odabrana lokacija za novo PPOV

Predloženo idejno rješenje za PPOV-a Podgorica

Na osnovu Studijom urađenog rješenja od firme FICHTNER - Njemačka uzeti su koraci procesa koji odgovaraju zahtjevima Investitora ViK-a Podgorica, da kvalitet prečišćene vode –efluenta bude A1 klase, da se eliminišu neprijatni mirisi, da se izvrši potpuni tretman mulja u cilju dobijanja biogasa, električne energije i tople vode. Projekat je uzeo u obzir minimalni protok voda rijeke Morače kao recipijenta u periodu jun-oktobar. Investitor je zahtijevao da Projektant Studije vodi računa da koncentracije N (azota) i P (fosfora) u efluentu budu da zadovoljavaju kvalitet za senzitivna područja.

Odabrano tehnološko rješenje predviđa:

A. Primarno prečišćavanje komunalnih otpadnih voda
B. Sekundarno prečišćavanje komunalnih otpadnih voda
C. Tercijarno prečišćavanje komunalnih otpadnih voda
D. Napredno prečićavanje komunalnih otpadnih voda (uklanjanje patogenih bakterija)
E. Obrada kanalizacionog mulja (proizvodnja biogasa, električne energije i tople vode)
F. Odvodnjavanje mulja (zgušnjavanje i smanjenje zapremine)

Na osnovu dvofazne ocjene opcija procesa i varijanti, za razmatranje su određene sledeće tehnologije procesa:

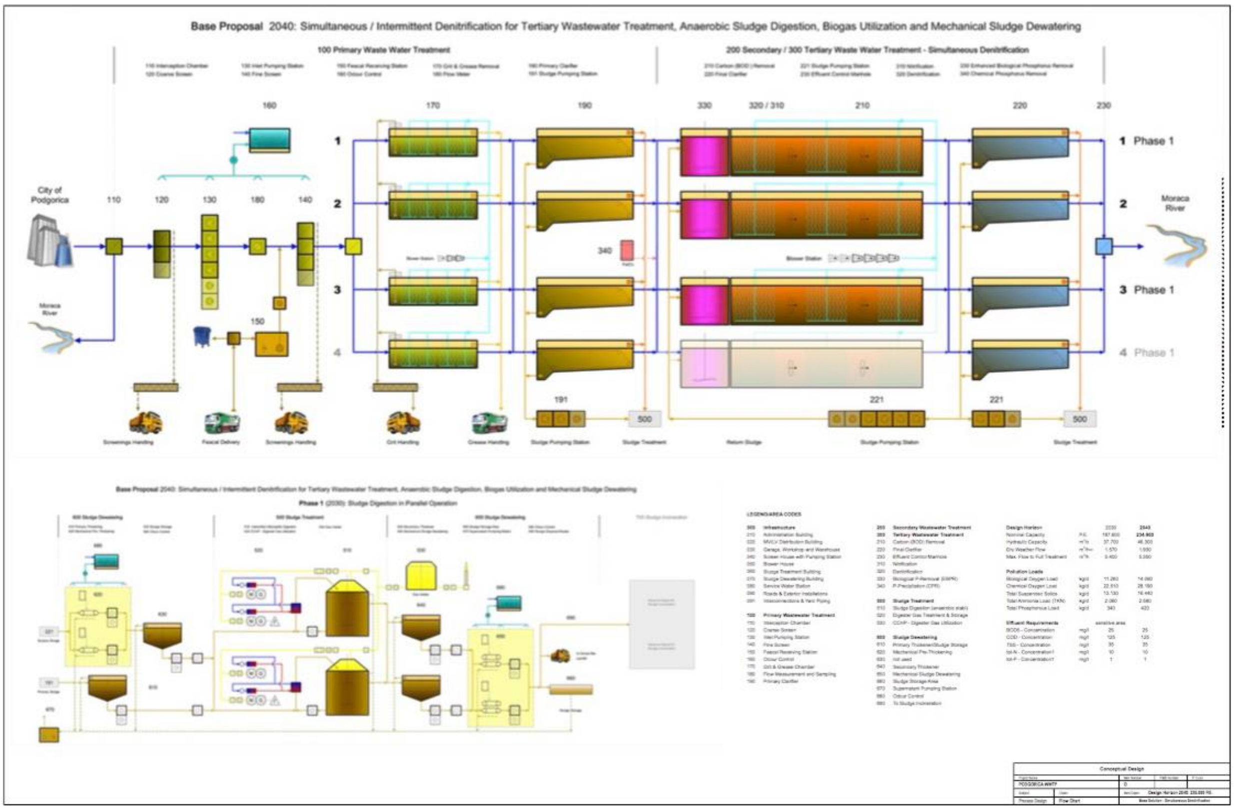
- Osnovno rješenje: Istovremena ili povremena denitrifikacija (potpuno miješanje) sa EBPR (Bio-P)+CPR, sa anaerobnom digestijom i odvodnjavanjem mulja, ponovnom upotrebom gasa iz digestora radi rekuperacije energije.
- Alternativno rješenje: Proces A^2/O (klipno proticanje sa prethodno primijenjenom denitrifikacijom) sa EBPR (Bio-P)+CPR, sa anaerobnom digestijom i odvodnjavanjem mulja, ponovnom upotrebom gasa iz digestora radi rekuperacije energije.

Pregled usvojenih opcija procesa prikazan je u tabeli 2.

Tabela 2. Predložena tehnologija za prečišćavanje otpadnih voda i preradu mulja

Korak tretmana	Osnovno rješenje	Alternativno rješenje
Prečišćavanje otpadnih voda (CAS za tercijarno prečišćavanje, BNR sa EBPR+CPR)	Istovremena ili povremena denitrifikacija (potpuno miješanje)	Bioreaktor sa klipnim proticanjem (nitrifikacija) sa prethodno primijenjenom denitrifikacijom (i Bio-P za EBPR)
Prerada mulja	Anaerobna mezofilna digestija mulja	
Prečišćavanje i ponovna upotreba gasa	Skladištenje gasa iz digestora i prečišćavanje uz rekuperaciju energije putem CCHP (CHP+proizvodnja rashladne energije)	
Odvodnjavanje mulja	Ugušćivanje i odvodnjavanje mulja	
Tretman neprijatnih mirisa	Bio-filter za pogone za mehanički tretman i odvodnjavanje mulja	

Simultana denitrifikacija sa EBPR (Bio-P)+CPR, uz odvojenu digestiju mulja i odvodnjavanje sa ponovnom upotrebom gasa iz digestora za rekuperaciju energije kao varijanta konvencionalnog postupka sa aktivnim muljem (CAS), odabrana je kao osnovno rješenje imajući u vidu jednostavniji i stabilniji proces biološkog prečišćavanja (u odnosu na A^2/O).



Slika 2. Preporučeni proces prečišćavanja komunalnih otpadnih voda u Podgorici sa idejnim rješenjem procesa prečišćavanja mulja

A1: Osnovni predlog

- Primarno prečišćavanje

- Sekundarno prečišćavanje

- Tercijarno prečišćavanje

Simultana denitrifikacija sa biološkim i hemijskim uklanjanjem P (fosfora)

Proces tretmana mulja sa paralelnim i serijskim radom digestora

Pogoni su povezani sa bio-filterima koji služe za uklanjanje i kontrolu mirisa kako bi se spriječilo i smanjilo ispuštanje neprijatnog mirisa u atmosferu.

Proces A^2/O (klipno proticanje sa prethodno primijenjenom dentrifikacijom) sa EBPR (Bio-P)+CPR, uz odvojenu digestiju i odvodnjavanje mulja sa ponovnim korišćenjem gasa iz digestora radi rekuperacije energije razmotren je kao varijanta i potencijalna modifikacija procesa za buduću nadgradnju PPOV-a.

Varijacija procesa alternativnog rješenja odnosi se na projekat bioreaktora za sekundarno i tercijarno prečišćavanje otpadne vode, koji obuhvata posebne odjeljke za prethodno primijenjenu denitrifikaciju i bazen sa klipnim proticanjem za nitrifikaciju. Sve ostale jedinice procesa ostaju nepromijenjene.

Pogoni za prečišćavanje otpadnih voda u novom PPOV Podgorica obuhvataju sledeće najvažnije korake procesa:

- mehaničko prečišćavanje otpadnih voda, uključujući crpnu stanicu,
- sekundarno prečišćavanje i
- tercijarno prečišćavanje otpadnih voda, uključujući transport mulja.

Pogoni su povezani sa biofilterima koji služe za uklanjanje i kontrolu mirisa kako bi se spriječilo i smanjilo ispuštanje neprijatnog mirisa u atmosferu.

Zaključak

Na osnovu analize navedenih alternativa prečišćavanja preporučuje se kao najizvodjivija tehnologija procesa za izvođenje PPOV Podgorica:

1. **Opcija A1**: simultana denitrifikacija sa odvojenom digestijom mulja
2. **Opcija A2**: prethodno primijenjena denitrifikacija (A^2/O) sa odvojenom digestijom mulja

Studijom predloženiprodužení konvencionalni proces prečišćavanja otpadnih voda i prerade mulja (A1) ima sledeće prednosti:

- Predstavlja opšte prihvaćenu tehonlogiju procesa sa bogatim iskustvom u čitavoj Evropi;
- Obezbeđuje kvalitet prečišćene vode –efluenta A1 klase, koja se može koristiti za kupanje i zalivanje poljoprivrednih proizvoda, koncentracija ukupnog azota TN je $\leq$10mg/l, ukupnog fosfora TP je $\leq$ 1 mg/l , a TSS $\leq$ 35 mg/l ;
- Obezbjeđuje povećanu zapreminu bioreaktora (oko 20%) i zaštitnog (bafer) kapaciteta (od oscilacija opterećenja) u poređenju sa A2;
- Ima smanjen broj operativnih i servisnih tačaka (bez pumpi za internu recirkulaciju);
- Ima ograničenu potrebu za instrumentima i jednostavnu kontrolu procesa (DO/Redox);
- Daje mogućnost budućih modifikacija procesa prečišćavanja otpadnih voda, tj. prenamjenu u A^2/O ili proces sa faznim napajanjem (step-feed-process) sa odgovarajućom rezervom kapaciteta za prečišćavanje;
- Daje mogućnost budućih modifikacija procesa prerade mulja, tj. prelazak sa paralelnog na serijski rad digestora sa odgovarajućom rezervom kapaciteta za prečišćavanje.

Izgradnja PPOV Podgorica imaće pozitivne uticaje na:

- Lokalne vodne resurse, rijeku Moraču, Nacionalni park Skadarsko jezero i životnu sredinu Zetske ravnice,
- Opšte zdravlje stanovništva (eliminacija bolesti vezanih za neprečišćene otpadne vode).

Literatura

1. Studija izvodljivosti za projekat prečišćavanja otpadnih voda u Podgorici, FASEP br. 552, Završni izvještaj, SOGREAH konsultanti,februar 2004. god.
2. Fond za infrastrukturne projekte na zapadnom Balkanu, TA-MON-05/07. Razvojni projekat za vode i otpadne vode u Podgorici. Pripremna studija za projekat. Završni izvještaj, WYG International,april 2011. god.
3. Studija izvodljivosti za izgradnju postrojenja za prečišćavanje otpadnih voda (PPOV) i proširenja kanalizacione mreže u Podgorici, FICHTNER WATER Frajburg Njemačka, januar 2017. godina.
4. Prethodna studija opravdanosti sa Generalnim projektom kanalizacionog sistema za upotrijebljene vode Podgorice. Finalna verzija, IK Consulting Engineers, Agencija za izgradnju i razvoj Podgorice, decembar 2008. god.
5. Preporuka elemenata za izbor optimalnog tehničko-tehnološkog procesa postrojenja za prečišćavanje komunalnih otpadnih voda (PPOV), postrojenja za tretman kanalizacionog mulja i postrojenja za zbrinjavanje obrađenog kanalizacionog mulja u Glavnom gradu-Podgorici,JP „Vodovod i kanalizacija” Podgorica,maj 2012.
6. Prostorno-urbanistički plan (PUP) Glavnog grada Podgorica do 2025. godine, Urbi Montenegro-Podgorica, Urbanistički institut Republike Slovenije-Ljubljana, WINsoft-Podgorica, Geateh-Ljubljana, februar 2014. god.
7. Stanje kvaliteta voda u Crnoj Gori 2014. godine, Zavod za hidrometeorologiju i seizmologiju, Odsjek za kvalitet voda, februar 2015. god.

Waste water purification system in the pharmaceutical industry

Sistem za prečišćavanje otpadnih voda u farmaceutskoj industriji

Refik Zejnilović[1], Dragan Radonjić[2], Darko Vuksanović[2], Jelena Šćepanović[2]
[1]University of Montenegro, Faculty of Pharmacy, Podgorica, Montenegro,
[2]University of Montenegro, Faculty of Metallurgy and Technology, Podgorica, Montenegro
[1]Farmaceutski fakultet Podgorica
[2]Metalurško-tehnološki fakultet Podgorica

Abstract

The main task of this paper is to show the status settlement waste water in terms of quality, both the same and the discharge. After considering the technical possibilities, as well as the rationalization of the wastewater treatment process, it was decided that the existing sewage systems will continue to drain the atmospheric waters, while for the sanitary-fecal and technological wastewater; a new drainage system will be designed. The sewage network will be directed towards a common plant for the pre-treatment of all wastewater, after which the wastewater will be discharged into the public sewage network of the city of Podgorica. In this sense it is necessary to separate them and form a separate sewerage network.

Key words: *Waste water, sewage*

Izvod

Osnovni zadatak u ovom radu je prikaz rješavanja statusa otpadnih voda, kako po kvalitetu, tako isto i po mjestu ispuštanja. Nakon razmatranja tehničkih mogućnosti, kao i racionalizacije procesa tretmana otpadnih voda usvojeno je rješenje da se postojećim kanalizacionim sistemima i dalje odvode atmosferske vode, dok će za sanitarno-fekalne i tehnološke otpadne vode biti isprojektovana nova odvodna kanalizacija. Kanalizaciona mreža će biti usmjerena ka zajedničkom postrojenju za predtretman svih otpadnih voda, poslije koga će otpadne vode biti ispuštene u javnu kanalizacionu mrežu grada Podgorice. U tom smislu je potrebno je izvršiti razdvajanje istih i formiranje separatne kanalizacione mreže.

Ključne riječi: *otpadne vode, kanalizacija*

Osnovni podaci o kvantitativno-kvalitativnim karakteristikama otpadnih voda

Ono što je potrebno posebno napomenuti su podaci o osnovnim karakteristikama otpadnih voda koje se produkuju u farmaceutskoj industriji. Ovi podaci su poslužili kao jedna od glavnih podloga pri izradi Glavnog projekta tretmana otpadnih voda koje nastaju u proizvodnim i administrativnim objektima. Fizičko-hemijske analize je radio Centar za ekotoksikološka ispitivanja Crne Gore iz Podgorice, za dvije lokacije i došao do osnovnih pokazatelja zagađenja otpadnih voda koje je neophodno redukovati prije njihovog ispuštanja u gradsku kanalizaciju.
Generalno se može konstatovati sljedeće:

- Količina otpadnih voda koje se produkuju u toku 24 sata za svaki pogon iznosi:
    - Pogon čvrstih formi, (jednosmjenski do dvosmjenski rad) $Q_1 = 20\ m^3/dan$
    - Pogon tečnih formi, (jednosmjenski do trosmjenski rad) $Q_2 = 100\ m^3/dan$

- Hemijsko opterećenje otpadnih voda je neravnomjerno i zavisi od procesa koji se odvijaju, prije svega u Pogonu tečnih formi koji ima dva proizvodna odjeljenja, odjeljenje za proizvodnju prostih i složenih infuzionih rastvora, i odjeljenje solucija gdje se proizvode kapi za oči i kapi za nos. Za proizvodnju se koristi voda kvaliteta WFI (water for injection). Rad se obavlja dvosmjenski, a po potrebi i trosmjenski.
- U Pogonu čvrstih formi proizvodnja se bazira na pripremi cefalosporina za oralnu upotrebu postupcima homogenizacije ili suve granulacije. U zasebnim proizvodnim odjeljenjima vrši se proces punjenja granula i kapsula kao i kompresovanje lijekova u formi tableta. U zavisnosti od obima proizvodnja se odvija jednosmjenski ili dvosmjenski.
- pH vrijednost otpadnih voda, u ekstremnim slučajevima se može kretati u granici od: pH = 6,0 – 10
- Uočljiva je i povremena pojava neugodnih mirisa posebno ako se zna da se objekat nalazi u blizini stambenog naselja.
- Temperatura otpadnih voda, takođe može biti povremeno ograničavajući faktor prilikom upuštanja istih u javnu kanalizacionu mrežu grada Podgorice, jer je maksimalno izmjerena trenutna vrijednost bila: t = 60°C.

Sa sigurnošću se može tvrditi da će odležavanjem i miješanjem prispjele otpadne vode u prihvatnom bazenu ista redukovati svoju temperaturu ispod zahtijevane vrijednosti od 40°C.

Pored gore navedenih parametara zagađenja u otpadnim vodama nisu registrovane neke druge ograničavajuće vrijednosti parametara za njihovo nesmetano ispuštanje u javnu kanalizacionu mrežu grada.

Uslovi za upuštanje otpadnih voda u gradsku kanalizaciju

Ispuštanje prečišćenih otpadnih voda mora biti u skladu sa Pravilnikom o kvalitetu i sanitarno-tehničkim uslovima za ispuštanje otpadnih voda u recipijent i javnu kanalizaciju, načinu i postupku ispitivanja kvaliteta otpadnih voda, minimalnom broju ispitivanja i sadržaju izvještaja o utvrđenom kvalitetu otpadnih voda („Sl. list CG“, 45/08, 9/10, 26/12, 52/12 i 59/13) koji definiše kvalitet otpadnih voda koje se mogu ispuštati u recipijent (tabela 1).

U tabeli 1 dati su parametri koji se odnose na maksimalno dozvoljene koncentracije u otpadnim vodama prije ispuštanja u recipijent.

Tabela 1. Maksimalno dopuštene koncentracije u otpadnim vodama prije ispuštanja u javnu kanalizaciju („Službeni list CG“ br. 45/08, 9/10, 26/12, 52/12 i 59/13)

Rednibroj	**Parametar**	**Jedinicamjere**	**Maksimalno dopuštena koncentracija**
1	pH		6-9
2	Temperatura	ºC	40
3	Miris		primijetan
4	Taložive materije	ml/lh	10
5	Ukupne suspendovane materije	mg/l	500
6	BPK$_5$	mgO$_2$/l	500
7	HPK ($K_2Cr_2O_7$)	mgO$_2$/l	700
8	Aluminijum	mg/l	4,0
9	Arsen	mg/l	0,2
10	Bakar	mg/l	1,0
11	Barijum	mg/l	5,0
12	Bor	mg/l	4,0

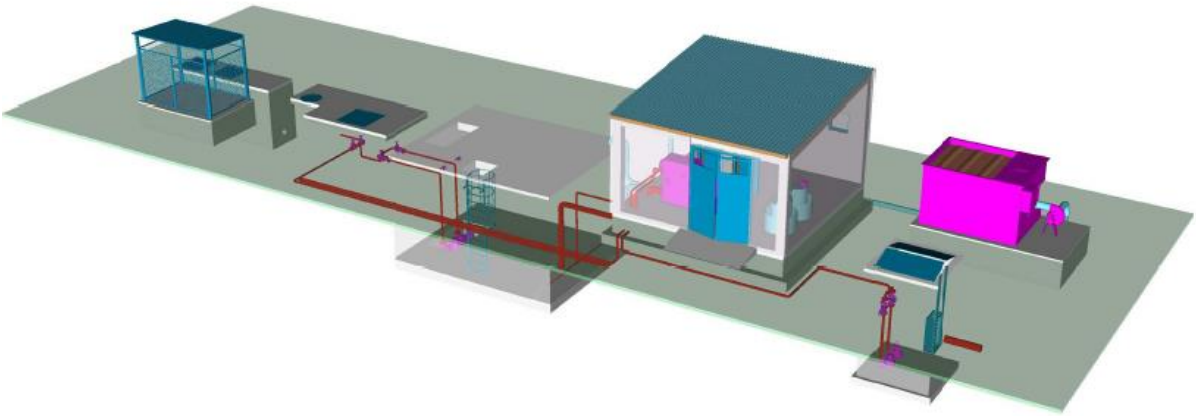
13	Cink	mg/l	2,0
14	Kobalt	mg/l	2,0
15	Kalaj	mg/l	2,0
16	Kadmijum	mg/l	0,1
17	Živa	mg/l	0,01
18	Ukupni hrom	mg/l	2,0
19	Hrom 6+	mg/l	0,2
20	Mangan	mg/l	4,0
21	Nikal	mg/l	2,0
22	Olovo	mg/l	2,0
23	Selen	mg/l	0,1
24	Srebro	mg/l	0,5
25	Gvožđe	mg/l	5,0
26	Vanadijum	mg/l	0,1
27	Ukupni fenoli	mg/l	0,5
28	Fluoridi	mg/l	5,0
29	Sulfiti	mg/l	10
30	Sulfidi	mg/l	1,0
31	Sulfati	mg/l	400
32	Ukupni fosfor	mgP/l	7
33	Aktivni hlor	mg/l	0,3
34	Nitriti (N)	mgN/l	30,0
35	Nitrati (N)	mgN/l	50,0
36	Mineralna ulja	mg/l	10,0
37	Ukupna ulja i masnoće	mg/l	50
38	Aldehidi	mg/l	2,0
39	Alkoholi	mg/l	10
40	Ukupni aromatični ugljovodonici	mg/l	0,4
41	Ukupni nitrirani ugljovodonici	mg/l	0,1
42	Ukupni halogeni ugljovodonici	mg/l	1,0
43	Ukupni organofosfatni pesticidi	mg/l	0,1
44	Ukupni organohlorni pesticidi	mg/l	0,05
45	Ukupne površinski aktivne supstance	mg/l	20,0
46	Ukupni deterdženti	mg/l	4,0
47	Radioaktivnost	Bq/l	1,0

Iz priložene Tabele 1 vidljivo je da su otpadne vode, u odnosu na kvalitet otpadnih voda koje je dozvoljeno ispuštati u gradsku kanalizacionu mrežu, relativno malo zagađene parametrima zagađenja koji se ne smiju ispuštati u nju izuzev povremeno povećane temperature, pH vrijednosti i neugodnih mirisa. Navedena zagađenja pretežno potiču iz pogona za HPV (hemijska priprema vode), gdje se vrši regeneracija jonoizmenjivačkih masa reakcionih i filterskih kolona u kojima se odvijaju procesi pripreme tehnološke vode za proizvodnju, kao i od pranja reakcionih posuda i radnih prostora.

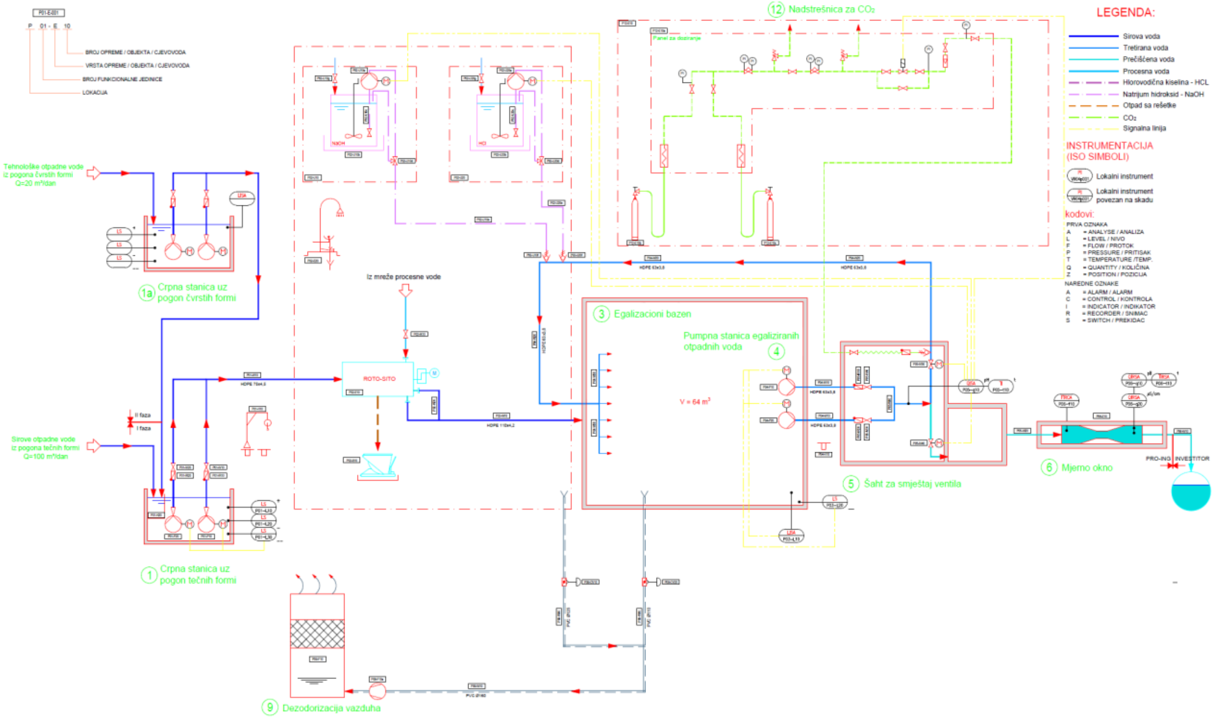
Usvojeni tehničko-tehnološki koncept tretmana otpadnih voda

Imajući u naprijed iznesene činjenice o kvalitetu i količini otpadnih voda, kao i uslovima za ispuštanje otpadnih voda u gradski kolektor, nastao je koncept tretmana miješanih otpadnih voda.

Nesmetano ispuštanje miješanih otpadnih voda je moguće nakon njihove egalizacije i retenzioniranja, međusobnog prinudnog miješanja, mjerenja, eventualne korekcije pH vrijednosti i kontinuiranog i kontrolisanog ispuštanja tako predtretiranih otpadnih voda, preko mjerno-kontrolnog šahta, u gradski kanalizacioni kolektor.



Slika 1. Tehnološka linija sistema za prečišćavanje otpadnih voda u farmaceutskoj industriji



Slika. 2 P&U dijagram

Na osnovu svih raspoloživih činjenica i uslova za upuštanje otpadnih voda u recipijent i gradsku kanalizacionu mrežu, sanitarno-fekalne i tehnološke otpadne vode oba Pogona međusobno će se spojiti i nakon cijeđenja, egalizacije i eventualne korekcije pH vrijednosti uz mjerenje protoka, temperature i pH vrijednosti ispuste u gradski kanalizacioni kolektor. Time bi se izbjegli rigorozni uslovi koji su propisani za upuštanje otpadnih voda u recipijent, rijeku Moraču, dok se upuštanjem ovih, predtretiranih otpadnih voda u gradski kolektor omogućava njihov dalji tretman na gradskom postrojenju za prečišćavanje sanitarno-fekalnih i industrijskih otpadnih voda grada Podgorice.

Osnovni koncept tretmana otpadnih voda se sastoji u tome da se atmosferske vode razdvoje od ostalih voda, potom da se iz Pogona čvrstih formi sanitarno-fekalne i tehnološke otpadne vode prepumpaju sa uronjenim centrifugalnim pumpama do crpnog bazena u kome se sakupljaju sanitarno-fekalne i tehnološke otpadne vode Pogona tečnih formi. Odatle se pomješane otpadne vode dalje prepumpavaju na uređaj za cijeđenje istih, tzv. roto sito, koje se nalazi u zatvorenom i ventiliranom prostoru. Pumpne stanice rade automatski, zavisno od intenziteta dotoka otpadnih voda u crpni bazen i nivoa tečnosti u njemu, što se reguliše pomoću plivajućih nivo prekidača. Usitnjen materijal se izdvaja na rotirajućem situ čiji je svijetli otvor između trapeziodnih sajli 1,0 mm, uz istovremeno pranje bubnja i gravitacioni odvod procijeđenih otpadnih voda u prihvatni egalizaciono-retenzioni bazen.

Ujednačavanje kvaliteta svih otpadnih voda koje dotiču u ovaj bazen se vrši istom pumpom sa kojom se vrši prepumpavanje egaliziranih otpadnih voda u gradsku kanalizaciju. Bazen je takođe snabdjeven sa ultrazvučnom nivo sondom, kojom se reguliše rad pumpne stanice za recirkulaciju i mješanje sadržaja egalizacionog bazena. Ukoliko se u toku miješanja i egalizacije izmjeri pH vrijednost sadržaja bazena veća od dozvoljene vrijednosti od: pH = 6 – 9, tada se automatski vrši doziranje kiselog ili alkalnog neutralizacionog sredstva uz recirkulaciju otpadnih voda u samom bazenu. Prihvaćene otpadne vode će se prepumpavati u gradski kolektor onda kada se u bazenu dostigne određena količina otpadnih voda uz automatsko uključenje jedne od dvije montirane potopljene centrifugalne pumpe. Uslov za mogućnost prepumpavanja ovih otpadnih voda u gradski kolektor je, pored količine voda u bazenu i postizanje zahtijevane pH vrijednosti, kao i dozvoljena temperatura, kada se otvara elektromotorni ventil (EMV) za ispuštanje otpadnih voda, a zatvara EMV za recirkulaciju istih u bazenu. Prije ispuštanja otpadnih voda u gradski kolektor otpadne vode prolaze kroz mjerač protoka gdje se mjeri trenutna i ukupna količina prepumpanih otpadnih voda, kao i pH vrijednost i temperatura. Ukoliko jedan od mjerenih parametara ne odgovara zadatim vrijednostima dozvoljenim za upuštanje u gradsku kanalizacionu mrežu, tada se zatvara elektromotorni ventil za ispuštanje istih u gradsku kanalizaciju Podgorice i voda se dalje miješa u egalizacionom bazenu, eventualno koriguje pH vrijednost kako bi se dovela u zahtijevane MDK vrijednosti.

Na osnovu poznatih fizičko-hemijskih analiza otpadnih voda uočeno je da iste povremeno imaju neprijatan miris i da bi se onemogućilo širenje tih mirisa u okolinu, bazen je pokriven i iz njega se vazduh prinudno izvlači plastičnim, radijalnim ventilatorom i odvodi u filter za prečišćavanje vazduha od neugodnih mirisa. Isti postupak prinudne ventilacije se vrši u tehničkoj zgradi, gdje se nalazi roto sito i posude za pripremu i doziranje neutralizacionih sredstava, rastvora HCl i NaOH.

Na osnovu stehiometrijskih odnosa u procesu neutralizacije potrošnja neutralizacionih stredstava je različita i za korekciju pH vrijednosti iz kisele ($pH \leq 5$) u blago kiselu, do neutralnu sredinu (pH =6,5-7) će se koristiti 1%-ni rastvor natrijum hidroksida (NaOH), dok će se za korekciju pH vrijednosti iz alkalne ($pH \geq 11$) u blago alkalnu, do neutralnu sredinu (pH = 7-8,5) koristiti 10%-ni rastvor hlorovodonične kiseline.

Principijelno proces neutralizacije se može prikazati sljedećim jednačinama:

$$H^+ + NaOH \rightarrow H_2O + Na^+$$

$$OH^- + HCl \rightarrow H_2O + Cl^-$$

$$\text{sumarno: } HCl + NaOH \rightarrow H_2O + NaCl$$

Potrošnja sredstva za neutralizaciju zavisi od izmjerene pH vrijednosti dotičućih otpadnih voda, što će se utvrditi na licu mjesta u toku eksploatacije postrojenja.

Predloženo rješenje garantuje ujednačavanje kvaliteta svih dotičućih količina otpadnih, uklanjanje čvrstih i vlaknastih materija mineralnog i organskog porijekla, kao i korekciju pH vrijednosti u zahtijevanim granicama. Retenzijom i miješanjem svih voda različitih temperatura u prihvatnom bazenu, postići će se egalizacija i dovođenje njihove zajedničke temperature na zahtijevanu vrijednost, a to je manje od 40°C. Ukoliko je temperatura pomiješanih otpadnih voda u egalizacionom bazenu veća od dozvoljene iste se neće prepumpati u gradsku kanalizaciju nego će se recirkulacijom miješati sve dok se ne postigne dozvoljena temperatura, manja od 40°C, kada će se nesmetano ispustiti u gradski kolektor.

Dio tehničke zgrade, kao i egalizaciono-retenzioni bazen će biti ventiliran, zbog mogućnosti povremene pojave neugodnih mirisa, koje sa sobom nose otpadne vode. Usisani vazduh će se usmjeravati ka uređaju za prečišćavanje vazduha od neugodnih mirisa, što je uslovljeno blizinom stambenog naselja i mogućnosti njegovog nekontrolisanog širenja.

Zaključak

Ovim predtretmanom biće zadovoljeni osnovni uslovi za nesmetano upuštanje svih otpadnih voda u gradsku kanalizacionu mrežu.

Nakon pumpne stanice otpadne vode dolaze na postrojenje koje se sastoji od:

- horizontalnog rotacionog sita, rotostrainera,
- egalizaciono-retenzionog bazena,
- sistema za miješanje i recirkulaciju prihvaćenih otpadnih voda,
- sistema za mjerenje i doziranje neutralizacionih sredstava,
- mjerno-kontrolnog šahta za mjerenje karakterističnih parametara zagađenja, protoka, pH i temperature.

Svi navedeni procesi: prepumpavanje, miješanje, eventualna korekcija pH vrijednosti otpadnih voda, kao i mjerenje tretiranih otpadnih voda prije ispuštanja u gradski kolektor, se vrše automatski, uz neophodnu kontrolu rukovaoca zaduženog za ovo postrojenje.

Literatura

1. Zakon o uređenju prostora i izgradnji objekata („Sl. list CG“, br. 51/08, 40/10, 34/11, 47/11, 35/13, 39/13, 33/14).
2. Zakon o životnoj sredini („Sl. list CG“, br. 52/16).
3. Zakon o vodama („Sl. list RCG“, br. 27/07, „Sl. list CG“, br. 73/10, 32/11, 47/11, 48/15, 52/16, 55/16, 2/17)
4. Zakon o procjeni uticaja na životnu sredinu („Sl. list RCG“, br. 80/05, „Sl. list CG“, br. 40/10, 73/10, 40/11, 27/13).
5. Uredba o klasifikaciji i kategorizaciji površinskih i podzemnih voda, („Sl. list CG“, br. 02/07).
6. Pravilnik o kvalitetu i sanitarno-tehničkim uslovima za ispuštanje otpadnih voda u recipijent i javnu kanalizaciju, načinu i postupku ispitivanja kvaliteta otpadnih voda, minimalnom broju ispitivanja i sadržaju izvještaja o utvrđenom kvalitetu otpadnih voda, Sl. list CG 45/08, 09/10, 26/12, 52/12 i 59/13).

Monitoring of the waste water treatment plant from the tunnel

Monitoring rada postrojenja za prečišćavanje otpadnih voda iz tunela

Jelena Šćepanović[1], Darko Vuksanović[1], Dragan Radonjić[1], Refik Zejnilović[2]

[1]University of Montenegro, Faculty of Metallurgy and Technology, Podgorica, Montenegro,

[2]University of Montenegro, Faculty of Pharmacy, Podgorica, Montenegro

[1]Metalurško-tehnološki fakultet Podgorica

[2]Farmaceutski fakultet Podgorica

Abstract

The main task of this paper is to show the state of waste water from the tunnel during construction on their penetration, in terms of quality, and by the discharge. After defining the technical solutions, as well as the monitoring of the quality of waste water from the tunnel after their purification, as a basic problem in the quality of the purified waste water, there is an increasing level of pH. Considering that tunneling works are carried out in individual parts with an increased quantity of wastewater, this can in practical terms be a serious problem if the quality of purified waste water does not meet the quality defined by the Regulation. Through the monitoring that is carried out periodically it is possible to define the potential impacts to the environment or natural recipient by wastewater. Defined impacts provide guidance on which way should be provided with the filtration of waste water from the tunnel, which may later be discharged into the recipient (water courses, or ground).

Key words: *Monitoring, waste water, pH value*

Izvod

Osnovni zadatak u ovom radu je prikaz stanja otpadnih voda iz tunela tokom izvođenja radova na njihovom probijanju, kako po kvalitetu, tako i po mjestu ispuštanja. Nakon definisanja tehničkih rješenja, kao i praćenja kvaliteta otpadnih voda iz tunela poslije njihovog prečišćavanja, kao osnovni problem u kvalitetu prečišćenih otpadnih voda javlja se povećani nivo pH. Obzirom da se radovi na probijanju tunela izvode u pojedinim djelovima sa povečanom količinom otpadnih voda, to u praktičnom smislu može da predstavlja ozbiljan problem ukoliko kvalitet prečišćene otpadne vode ne zadovoljava kvalitet definisan Pravilnikom. Putem monitoringa koji se provodi periodično moguće je definisati moguće uticaje na okolnu sredinu, odnosno prirodni recipijent od strane otpadnih voda. Definisani uticaji daju smjernice na koji način treba obezbijediti adekvatno prečišćavanje otpadnih voda iz tunela, koje se kasnije mogu ispuštati u recipijent (vodeni tokovi ili zemljište).

Ključne riječi: *monitoring, otpadne vode, pH vrijednost*

Osnovni podaci o otpadnim vodama iz tunela

Prilikom izvođenja radova na probijanju tunela, zavisno od lokacijskih karakteristika zone u kojoj se radovi izvode, iz tunela se javljaju otpadne vode. Količina ovih otpadnih voda zavisi od toga da li se radi o krečnjačkoj ili o flišnoj zoni. Prilikom izvođenja radova u krečnjačkoj zoni količina ovih voda je prisutna u neznatnoj količini i ne predstavlja značajniji problem. Međutim, izvođenjem radova u flišnoj zoni stvaraju se značajne količine otpadne vode koje se moraju izvesti iz tunela do mjesta gdje je neophodno njihovo prečišćavanje.

Na osnovu definisanja podataka o količinama otpadnih voda iz tunela na dnevnom nivou vrši se projektovanje tehničkog rješenja, odnosno kapaciteta postrojenja koje će moći da prihvati sve otpadne vode iz tunela i da ih kroz izgrađeni sistem za prečišćavanje dovede do stanja da se mogu ispuštiti u recipijent.

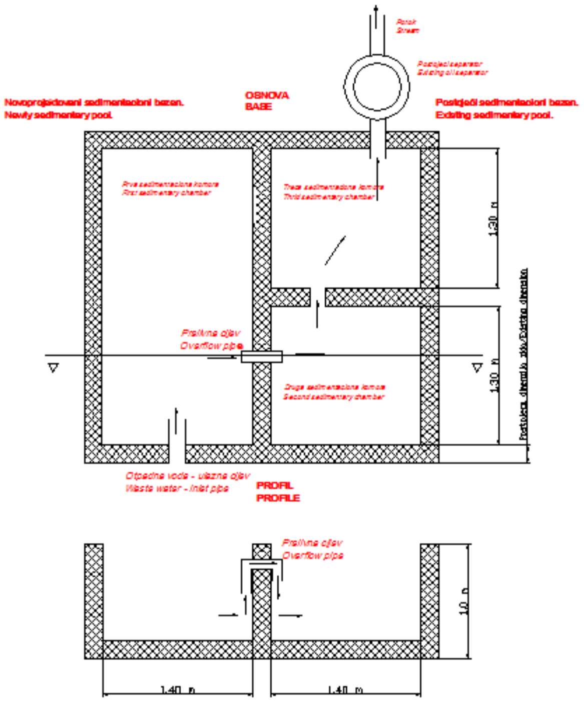
Otpadne vode iz tunela u značajnoj mjeri su bogate suspendovanim materijama, a u većini slučajeva je zbog korišćenja aditiva za beton, koji se primjenjuje tokom torkretiranja, povećan je i pH.

Pored gore navedenih parametara zagađenja u otpadnim vodama iz tunela nisu registrovane neke druge ograničavajuće vrijednosti parametara za njihovo nesmetano ispuštanje u recipijent.

Opis sistema za prečišćavanje otpadnih voda iz tunela

Sistemi za prečišćavanje otpadnih voda iz tunela na kojima su vršena ispitivanja stepena prečišćavanja sastoje se od prihvatnih cijevi koje otpadne vode iz tunela dovode do sistema, višekomornih taložnika i separatora ulja i masti. Jedan ovakav sistem prikazan je na slici 1, a njegov šematski prikaz dat je na slici 2.

Slika 1. Sistem za prečišćavanje otpadnih voda iz tunela



Slika 2. Šematski prikaz sistema za prečišćavanje otpadnih voda iz tunela

Sa slike 1 se vidi da je osim taložnih bazena projektovan i implementiran i bazen u koji se odlaže mulj iz taložnika. Ovo je značajno zbog lakšeg održavanja taložnika, jer je zbog kontiuniranog priliva otpadne vode iz tunela, taložnike neophodno čistiti skoro svakodnevno.

Uslovi za upuštanje otpadnih voda u recipijent

Ispuštanje prečišćenih otpadnih voda mora biti u skladu sa Pravilnikom o kvalitetu i sanitarno-tehničkim uslovima za ispuštanje otpadnih voda u recipijent i javnu kanalizaciju, načinu i postupku ispitivanja kvaliteta otpadnih voda, minimalnom broju ispitivanja i sadržaju izvještaja o utvrđenom kvalitetu otpadnih voda („Sl. list CG“, 45/08, 9/10, 26/12, 52/12 i 59/13) koji definiše kvalitet otpadnih voda koje se mogu ispuštati u recipijent (tabela 1).
U tabeli 1 dati su parametri koji se odnose na maksimalno dozvoljene koncentracije u otpadnim vodama prije ispuštanja u recipijent.

Tabela 1. Maksimalno dopuštene koncentracije u otpadnim vodama prije ispuštanja u recipijent („Službeni list CG“ br. 45/08, 9/10, 26/12, 52/12 i 59/13)

Redni broj	**Parametar**	**Jedinica mjere**	**Maksimalno dopuštena koncentracija (MDK)**
1	pH		6,5-8,5
2	Temperatura	ºC	30
3	Δt , ne više od	ºC	2
4	Boja	mg/l Pt skale	5
5	Miris		bez

6	Taložive materije	ml/lh	0,5
7	Ukupne suspendovane materije	mg/l	35
8	BPK_5	mgO_2/l	25
9	HPK	mgO_2/l	125
10	Ukupni organski ugljenik (TOC)	mgC/l	15
11	Aluminijum	mg/l	3,0
12	Arsen	mg/l	0,1
13	Bakar	mg/l	0,5
14	Barijum	mg/l	3,0
15	Bor	mg/l	2,0
16	Cink	mg/l	1,0
17	Kobalt	mg/l	1,0
18	Kalaj	mg/l	0,75
19	Kadmijum	mg/l	0,01
20	Živa	mg/l	0,005
21	Ukupni hrom	mg/l	1,25
22	Hrom 6+	mg/l	0,1
23	Mangan	mg/l	2,5
24	Nikal	mg/l	1,25
25	Olovo	mg/l	0,5
26	Selen	mg/l	0,03
27	Srebro	mg/l	0,15
28	Gvožđe	mg/l	2,0
29	Vanadijum	mg/l	0,05
30	Ukupni fenoli	mg/l	0,1
31	Fluoridi	mg/l	2,0
32	Sulfiti	mg/l	2,0
33	Sulfidi	mg/l	0,25
34	Sulfati	mg/l	20
35	Aktivni hlor	mg/l	0,05
36	Mineralna ulja	mg/l	2,0
37	Ukupna ulja i masnoće	mg/l	10
38	Aldehidi	mg/l	1,0
39	Alkoholi	mg/l	1,0
40	Ukupni aromatični ugljovodonici	mg/l	0,05
41	Ukupni nitrirani ugljovodonici	mg/l	0,025
42	Ukupni halogeni ugljovodonici	mg/l	0,25
43	Ukupni organofosfatni pesticidi	mg/l	0,025
44	Ukupni organohlorni pesticidi	mg/l	0,025
45	Ukupne površinski aktivne supstance	mg/l	4,0
46	Ukupni deterdženti	mg/l	0,5
47	Radioaktivnost	Bq/l	0,5

Rezultati monitoringa otpadnih voda iz tunela

Imajući u naprijed iznesene činjenice o kvalitetu i količini otpadnih voda, kao i uslovima za ispuštanje otpadnih voda u recipijent, vršena su ispitivanja kvaliteta otpadnih voda iz tunela poslije prolaska kroz implementirani sistem za prečišćavanje. Rezultati monitoringa dati su u tabeli 2.

Tabela 2. Rezultati monitoringa kvaliteta otpadnih voda iz tunela sa 5 lokacija

Parametar	Lokacija 1	Lokacija 2	Lokacija 3	Lokacija 4	Lokacija 5	MDK
pH	9,76	9,77	9,78	11,62	10,8	6,5-8,5
Ukupne suspendovane materije (mg/l)	2,2	1,0	1,0	5,8	99,6	35
BPK_5 (mg/l)	2,14	1,96	2,05	-	-	25
HPK ($K_2Cr_2O_7$) (mg/l)	60,0	28,0	44,0	-	-	125
TOC (ukupni organski ugljenik) (mg/l)	1,34	1,90	2,21	-	-	15

Iz tabele 2 se vidi de je tokom mjerenja kvaliteta otpadnih voda iz tunela nakon njihovog prolaska kroz sistem za prečišćavanje vrijednost pH iznad dozvoljenog nivoa. Takodje, kod preve 4 lokacije ukupne suspendovane materije su na dozvoljenom nivou, osim kod lokacije 5 gdje je vidljivo da je ova vrijednost znatno iznad dozvoljenih koncentracija

Dobijeni rezultati pokazuju da sistemi za prečišćavanje otpadnih voda iz tunela nijesu obuhvatili sistem za neutralizaciju povećanog nivoa pH, zbog čega se ove prečišćene otpadne vode prema datim vrijednostima iz Pravilnika ne bi smjele ispuštati u recipijent. Prema tome, neutralizacija pH do dozvoljenih granica predstavlja smjernicu za nadogradnju postojećeg sistema za prečišćavanje otpadnih voda iz tunela. Kada je u pitanju povećani sadržaj ukupnih suspendovanih materija na lokaciji 5, mjera zaštite je definisanje dužeg vremena taloženja čestica kroz povećanje zapremine i površine taložnog sistema.

Sve navedeno je usko povezano sa mogućim uticajima na kvalitet pojedinih segmenata životne sredine (zemljište i vode), koji su evidentni prilikom ispuštanja otpadnih voda na ovakav način.

U procesu korekcije pH vrijednosti iz alkalne ($pH \geq 11$) u blago alkalnu, do neutralnu sredinu ($pH = 7\text{-}8,5$) preporuka je koristiti 10%-ni rastvor hlorovodonične kiseline (HCl).

Hlorovodonična kiselina spada u jake kiseline. U kiselini je maseni udio hlorovodonika 34-36 %.

U vodi reakcija HCl je:

$$HCl + H_2O \rightarrow H_3O^+_{(aq)} + Cl^-_{(aq)}$$

Reakcija neutralizacije je:

$$H_3O^+_{(aq)} + OH^-_{(aq)} \rightarrow 2H_2O_{(l)}$$

Hloridni jon koji je hidratisan $Cl^-_{(aq)}$ kao anjon jake kiseline ne daje nikakvu reakciju i ne doprinosi promjeni pH vrijednosti rastvora, jer ne podliježe hidrolizi. Prema tome, HCl kiselina se može koristiti uspješno i bezbjedno za neutralizaciju. Hloridni jon nema ograničenja za ispuštanje u recipijent.

Zaključak

Na osnovu svega navednog i prezentiranih rezultata mjerenja kvaliteta otpadnih voda iz tunela može se zaključiti sledeće:
1. Otpadne vode na svih 5 lokacija pokazuju da je nivo pH iznad dozvoljenih granica. Ispuštanje otpadnih voda sa povećanom vrijednošću pH u recipijent negativno se odražava na kvalitet životne sredine, odnosno prevashodno na zemljište i vode.
2. Projektovani sistemi za prečišćavanje otpadnih voda iz tunela, uglavnom na svim prezentiranim lokacijama pokazuju zadovoljavajuće vrijednosti ukupnih suspendovanih materija, osim na lokaciji 5, što pokazuje da ovaj sistem nije projektovan na adekvatan način i da je potrebna njegova nadogradnja.
3. Na svim projektovanim sistemima za prečišćavanje otpadnih voda neophodno je izvršiti postavljanje dodatnog sistema za neutralizaciju pH u cilju potpune zaštite životne sredine.

Literatura

1. Zakon o uređenju prostora i izgradnji objekata („Sl. list CG“, br. 51/08, 40/10, 34/11, 47/11, 35/13, 39/13, 33/14).
2. Zakon o životnoj sredini („Sl. list CG“, br. 52/16).
3. Zakon o vodama („Sl. list RCG“, br. 27/07, „Sl. list CG“, br. 73/10, 32/11, 47/11, 48/15, 52/16, 55/16, 2/17)
4. Zakon o procjeni uticaja na životnu sredinu („Sl. list RCG“, br. 80/05, „Sl. list CG“, br. 40/10, 73/10, 40/11, 27/13).
5. Uredba o klasifikaciji i kategorizaciji površinskih i podzemnih voda, („Sl. list CG“, br. 02/07).
6. Pravilnik o kvalitetu i sanitarno-tehničkim uslovima za ispuštanje otpadnih voda u recipijent i javnu kanalizaciju, načinu i postupku ispitivanja kvaliteta otpadnih voda, minimalnom broju ispitivanja i sadržaju izvještaja o utvrđenom kvalitetu otpadnih voda, Sl. list CG 45/08, 09/10, 26/12, 52/12 i 59/13).

Polypyrrole as cathodic material in electrochemical cell with aqueous electrolyte

Elektrohemijska ćelija sa katodom na bazi polipirola i vodenim rastvorom elektrolita

Marija Janačković[1], Milica Gvozdenović[2], Braninir Grgur[2]

[1]University of Priština, Faculty of Technical Sciences, Kosovska Mitrovica, Serbia,

[2]University of Belgrade, Faculty of Technology and Metallurgy, Belgrade, Serbia

[1]Univerzitet u Prištini, Fakultet tehničkih nauka, Kosovska Mitrovica

[2]Univerzitet u Beogradu, Tehnološko-metalurški fakultet Beograd

Abstract

Polypyrrole cathode was formed on graphite electrode by electrochemical polymerization of pyrrole from electrolyte containing 0,1 mol dm^{-3} pyrrole and 1,0 mol dm^{-3} HCl at constant current density of 2 mA cm^{-2} during 1h. The estimated active mass of PPY was 14 mg. Galvanostatic charge/discharge (doping/dedoping) curves of PPY electrode in 2,0 mol dm^{-3} NH_4Cl and 1,1 mol dm^{-3} $ZnCl_2$ were recorded using different currents in order to obtain electrochemical characteristics. Electrochemical cell with PPY cathode, zinc anode and aqueous electrolyte composed of 2,0 mol dm^{-3} NH_4Cl and 1,1 mol dm^{-3} $ZnCl_2$ was formed and relevant electrical parameters were estimated from charge/discharge voltage curves. Based on the estimated values of electrical parameters such as: specific capacity, specific power and energy the Zn|PPY cell can be classified as "supercapttery".

Izvod

Katoda na bazi polipirola (PPY) formirana je galvanostatskom polimerizacijom pirola iz rastvora 0,1 mol dm^{-3} pirola i 1,0 mol dm^{-3} HCl, na grafitnoj elektrodi primenom gustine struje od 2 mA cm^{-2} u trajanju od 1 h. Procenjena je aktivna masa PPY koja je iznosila 14 mg. Elektrohemijska karakterizacija katode na bazi PPY izvršena je snimanjem galvanostatskih krivih punjenja i pražnjenja (dopovanja i dedopovanja) različitim strujama u vodenom elektrolitu sastava 2,0 mol dm^{-3} NH_4Cl i 1,1 mol dm^{-3} $ZnCl_2$, na osnovu čega je odeđena efikasnost iskorišćenja kapaciteta ove elektrode. Formirana je elektrohemijska ćelija sa vodenim elektrolitom sastava 2,0 mol dm^{-3} NH_4Cl i 1,1 mol dm^{-3} $ZnCl_2$ u kojoj je elektroda od PPY bila katoda, dok je anoda bila elektroda od cinka. Relevantni električni parametri ove ćelije određeni su na bazi snimanja napona punjenja/pražnjenja. Prema procenjenim vrednostima električnih parametara: specifične kapacitivnosti, specifične snage i specifične energije, ispitivana Zn|PPY ćelija sa vodenim rastvorom elektrolita odgovara kategoriji „superkapabaterija".

Economical meaning of corrosion: losses and damages

Ekonomsko značenje korozije: gubici i štete

Dragiša Obradović[1], Dragan Obradović[2]

[1]Faculty for Management, Belgrade, SDIT-HTM Požarevac, Serbia,

[2]School of agriculture, Požarevac, Serbia

[1]Fakultet za menadžment, Beograd, SDIT-HTM Požarevac

[2]Poljoprivredna škola, Požarevac

Abstract

Corrosion is a process of destruction of the surface of metallic materials under the influence of the surrounding environment, ie. reaction of metallic material with its environment, which causes a measurable change of the material and which leads to the corrosion damage. This reaction is in most cases the electrochemical nature, but can also occur due to the effects of chemical and fizfčkih process. Corrosion leads to irreversible loss of metal and causing massive damage because before the expiry of the normal working life become unusable many devices, plant, equipment, transport means and different constructions. By reducing the corrosion reduces the possibility of loss of various products, and thus achieves an increase in their cost. From these estimates clearly show that the corrosion is one of the important factors of the global crisis of materials and energy.

Keywords: *corrosion, a process category, testing, protection ...*

Izvod

Korozija je proces površinskog razaranja metalnih materijala pod dejstvom okolne sredine, tj. reakcija metalnog materijala sa svojom okolinom, koja prouzrokuje merljive promene materijala i koja dovodi do korozionog oštećenja. Ova reakcija je u većini slučajeva elektrohemijskog karaktera, a može da nastane i usled delovanja hemijskih i fizfčkih procesa. Korozija dovodi do nepovratnog gubitka metala i izaziva ogromne štete jer pre isteka uobičajenog radnog veka postaju neupotrebljivi mnogi uređaji, postrojenja, mašine, transportna sredstva i različite konstrukcije. Smanjenjem korozije smanjuje se mogućnost gubitaka različitih proizvoda, a time postiže povećanje njihove ekonomičnosti. Iz navedenih procena očigledno proizlazi da je korozija jedan od važnih faktora svetske krize materijala i energije.

Ključne reči: *korozija, proces, kategorija, testiranje, zaštita…*

1. Uvod

Sa velikim brojem svetske populacije koja živi u neposrednoj blizini vode i vlage, korozija metalnih materijala je neizbežan deo ljudskog iskustva. Dok oksidacija gvožđa (rđa) predstavlja najlakše identifikovan oblik korozije, ovaj proces oksidacije predstavlja samo deo materijalnih gubitaka. Danas je uticaj korozije na društvo i srodna degradacija materijala daleko postignut zahvaljujući povećanom složenošću i raznolikosti materijala, koji uključuju ne samo metalne materijale, već i keramiku, polimere i kompozite koji takođe podležu ekstremnim ekologijama. Iako su ostali problemi vezani za koroziju ostali, napredovanje tehnologije i potreba za globalnom održivošću donose sa sobom nove i nove korozijske probleme čiji negativni uticaji moraju biti minimizovani kroz odgovarajuću selekciju materijala, ublažavanje i praćenje i razvoj novih materijala. Uticaji korozije često opisuju u ekonomskom smislu. Finansijski gubici procijenjeni su u nekoliko studija koji su zaključili da degradacija materijala preuranjenih cena troši industrijske zemlje oko 3% svog bruto domaćeg proizvoda (BDP).

Korozijski procesi, s kojima se svakodnevno susrećemo i koji predstavljaju pretvaranje velikog broja korisnih metala u nekorisne spojeve, pa i štetne korozijske produkte, u suštini su spontani procesi između metala i komponenata okoline pri čemu metali prelaze u termodinamički stabilnije stanje. Čelik je materijal koji se najviše upotrebljava kod izrade raznih konstrukcija, pa je njegovo korozijom ponašanje i zaštitu od korozije potrebno dobro poznavati. Korozija smanjuje upotrebnu vrednost čelika, skraćuje vek trajanja konstrukcija, poskupljuje njihovo održavanje, uzrokuje gubitke u proizvodnji, zastoje u radu, havarije, nesreće i dr. Ekonomsko značenje korozije čelika je veliko i ono raste sa industrijalizacijom privrede. Stvarnu štetu nastalu zbog korozije na čeličnim konstrukcijama je teško izračunati jer osim direktnih šteta uključuje i indirektne koje su velike. Da bi došlo do pojave korozije ili procesa oštećivanja čelične konstrukcije, mora u posmatranom sistemu postojati hemijska, mehanička, biološka ili neka druga pokretačka sila. Ona je uzrok štetne pojave ili procesa, a njeno delovanje se opiru fizikalni i hemijski otpori. Korišćenjem raznih tehnologija antikorozivne zaštite, upravo se ti otpori povećavaju i usporavaju tok korozijskih procesa. Iz navedenog proizlazi veliki značaj pravovremene i kvalitetne zaštite od korozije, a istraživanja pokazuju da se četvrtina šteta od korozije može sprečiti primenom savremenih tehnologija zaštite. Najzastupljenija metoda zaštite čeličnih konstrukcija od korozije je primenom premaza. Tehnologija zaštite primenom premaza vrlo je zahtevna i značajan je činilac u osiguranju kvaliteta konstrukcija u celosti. Današnji trend su vodotopivi i vodorazredivi premazi, premazi sa visokom suvom materijom, praškasti premazi, te premazi koji otvrdnjavaju zračenjem. Njihov razvoj i sve veća primena posebno su intenzivirani zbog zakonskih odredbi koje ograničavaju emisiju isparljivih organskih rastvarača.

2. Tehnološki razvojni proces

U savremenim uslovima našeg privrednog i društvenog razvoja zaštita životne sredine i njeno dalje unapređivanje predstavljaju veoma značajno pitanje za koje je trajno zainteresovano celo naše društvo. Tehnološki proces, praćen razvojem proizvodnih snaga i uvećanjem ekonomskog potencijala zemlje, kao i razvoj društvenih odnosa, omogućavaju šire promene u pogledu materijalnog položaja i načina života čoveka. Ali, taj razvoj je istovremeno stvorio i neke probleme, određene opasnosti i rizike, veći stepen ugroženosti čoveka u radnoj i životnoj sredini. Pri tome se ne sme zaboraviti da čovek može održati svoje vitalne sposobnosti i opstati kao društveno biće jedino pod uslovom da reguliše i uskladi svoje odnose ne samo unutar svoje zajednice već i sa ostalim živim organizmima u svojoj sredini, što nesumnjivo nije ni lako ni jednostavno. Savremena nauka, tehnika i tehnologija, nisu i ne mogu biti činioci, koji bi sami po sebi ugrožavali životnu sredinu, već su to, u prvom redu, ponašanje čoveka i neodgovarajući društveni odnosi u kojima se odvijaju savremeni procesi razvoja ne samo u našoj zemlji već i u velikom delu sveta. Otuda je važno da se izmeni odnos čoveka prema životnoj sredini i njenim postojećim bogatstvima. Degradirajući čitave ekosisteme drastičnim eliminisanjem zakonomernosti prirodne ravnoteže, čovek uslovljava i neposrednu budućnost čovečanstva, a time i postojeće društvene odnose. Društveni odnosi i kulturni aspekti čovekovog ponašanja čine osnovu njegovog odnosa prema životnoj sredini mnogo složenijom i kvalitetno drugačijom u odnosu na sve druge vrste.

3. Ekonomski pogled na koroziju

Korozija štetno utiče na sirovine, proizvode ili poluproizvode. Štete na opremi koje izaziva korozija mogu se svrstati u dve glavne grupe direktne i indirektne štete. Direktni troškovi se vide u pogledu ranije zamene korodiranih delova ili zastoja zbog sprovođenja antikorozivne zaštite. Indirektni troškovi su troškovi koji se mogu videti u pogledu smanjenih kapaciteta ili smanjenom kvalitetom proizvoda pa tako i manjom profitabilnošću opreme koja je oštećena korozijom. Ako pogledamo zadnjih nekoliko godina možemo primetiti da se cene konstrukcijskih materijala, pogotovo onih postojanih (Pb, Cu, Zn, Sn) kreću prema gore zbog sve veće cene energenata koji su potrebni za preradu sirovina, ali i zbog sve manjih zaliha sirovina za proizvodnju. Istovremeno se povećava potražnja za konstrukcionim materijalima. Zbog svega toga zaštita od korozije postaje vrlo važna zbog produženja eksploatacije opreme i zaštite materijala, koji postaju skupi, od propadanja. Zaštita od korozije se počela ozbiljnije primenjivati sa povećanom eksploatacijom čelika i metalnih materijala. Veliki skok u razvoju antikorozivne zaštite desio se s primenom prvih parobroda i železnice. Drugi svetski rat doprinosi daljem razvoju antikorozivne zaštite. Jedna od grana industrije koja je u zadnjih nekoliko decenija doprinela razvoju je automobilska industrija. Kako vidimo veliki skokovi u razvoju antikorozivne zaštite dešavaju se pojavama industrija koje brzo napreduju, tako da danas na razvoj najviše utiče nuklearna tehnika, elektronika, automatizacija i svemirska tehnika. Primena u privredi i danas zaostaje za teoretskim znanjima, što je najviše zbog razloga brzog napretka tehnologije zaštite od korozije. Brojnim studijama je dokazano da se sa jednim dolarom uloženim u antikorozivnu zaštitu dobije od tri do šest dolara u pogledu duže trajnosti i veće pouzdanosti opreme.

4. Proces korozije

Elementi se retko nalaze u čistom metalnom stanju. Umesto toga, nalaze se u hemijskim kombinacijama sa jednim ili više ne-metalnih elemenata. Ove hemijske kombinacije poznate su kao rude. Gvožđe, bakar i cink ruda su tri najčešća ruda pronađena u zemaljskoj kori. Značajna energija se mora potrošiti kako bi se smanjila ruda na čist metal. Ova energija se može primeniti metalurškim ili hemijskim sredstvima i to se radi u procesu koji se naziva topljenje i prečišćavanje. Dodatna energija se takođe može koristiti u obliku hladnoće ili grejanja i livenje čistog metala u radni oblik. Korozija, koja se jednostavno može definisati kao rđa, tendencija je da se metali vrate u svoje prirodno, niže energetsko stanje rude.

Metalna korozija uključuje i oksidaciju ili izlaganje kiseoniku u okolini i elektrohemijskim procesima, što znači da se metalne ćelije formiraju na površini korozije, što u velikoj meri ubrzava transformaciju metala nazad u stanje rude i uključuje i hemijske reakcije i tok elektrona. Osnovni elektrohemijski proces koji pokreće koroziju metala je galvanska akcija, gde se struja stvara interno fizičkim i hemijskim reakcijama koje se javljaju među komponentama ćelije.

5. Procene gubitaka zbog korozije

Procene gubitka uzrokovanih uticajem korozije pokazuju da se u industrijskim zemljama troškovi kreću u rasponu od 3 do 5 odsto bruto domaćeg proizvoda godišnje. Rezultati studije koju je napravila Federalna uprava u Sjedinjenim Američkim Državama 1998. godine pokazala je da su godišnji troškovi nastali zbog uticaja korozije na federalnom nivou otprilike 276 milijardi dolara ili 3,1% BDP-a. Procene koje se najčešće vrše ne koriste podatke vezane uz indirektne štete zbog korozije niti podatke u kojima se ne može direktno odrediti cena poput nesreća. No svrha procena nije da bi se dobilo znanje o potrebnim sredstvima koja se moraju rezervisati za obnovu opreme i primenu antikorozivnih metoda, već da bi se pokazalo koliki je uticaj korozije na BDP, pokazalo se da sa pravilnim korišćenjem antikorozivnih metoda može da uštedi značajna sredstva . Zanimljiv je i podatak da se troškovi zbog uticaja korozije ne mogu potpuno smanjiti, ali se pravilnom upotrebom antikorozivnih mera može postići ušteda od 30%. Ako taj podatak iznesemo u egzaktnim podacima dobijamo da su Sjedinjene Američke Države mogle da uštedi 82,5 milijardi dolara u jednoj godini.

6. Kategorije korozije

Tradicionalno, korozija se klasifikuje u osam kategorija zasnovanih na morfologiji napada, kao i vrsti okruženja na kome je materijal izložen. Jedinstvena ili opšta korozija je najčešća vrsta korozije i primeri ove vrste korozije obiluju, uključujući koroziju čeličnih mostova, korozuju podzemnih cevovoda. Svako ko je napustio komad nezaštićenog čelika spolja je upoznat sa uniformnom korozijom. Na sreću, ujednačena korozija je predvidljiva i može se kontrolisati raznim metodama kao što je farbanje površine ili nanošenje sloja metala kao cink i čelik. Ta žrtva korozije površinskog sloja cinka za zaštitu osnovnog čelika zapravo predstavlja oblik galvanske ili bimetalne korozije. Površine nekih metala (poput aluminijuma, nerđajućeg čelika i titana) zaštićene su od ravnomerne korozije izuzetno tankim oksidnim filmom koji se prirodno formira. Mnoga praktična primena materijala zavisi od prisustva ovog zaštitnog oksida. Nažalost, ovaj film može lokalno srušiti, što dovodi do oblika korozije kao što je pucanje aluminijumskih ploča, pukotina od korozije od nerđajućih čeličnih prigušnica ili korozije naprezanja cevi u nuklearnim reaktorima. Zaštita objekata i opreme od ovih oblika korozije je neophodna i moguća. Dostupni pristupi za kontrolu korozije uključuju primenu zaštitnih premaza na metalne površine da bi delovale kao prepreka ili možda pružile zaštitu, dodavanjem hemijskih vrsta u životnu sredinu radi sprečavanja korozije, promenu hemijske legure kako bi ona bila otpornija na koroziju, i tretiranje površine metala da bi se povećala otpornost na koroziju. Organski premazi obično predstavljaju prvu liniju odbrane od korozije. Ovi premazi se koriste za izolaciju metala iz okoline i njihove barijere su od posebnog interesa. Neke vrste, kada se dodaju elektrolitu, prelazno selektuju do anodnih i/ili katodnih mesta usporavajući proces korozije. Hromati, fosfati, nitrati, molibdati i razna organska jedinjenja pružaju zaštitu od korozije sistemima cevovoda u elektranama, postrojenjima za hemijsku preradu i naftnoj i gasnoj industriji. Isto tako, sprečavate koroziju čelika kada prskate VD-40 TM na površini. Nerđajući čelici su klasični primeri legiranja za poboljšanje otpornosti na koroziju. U većini okruženja sveobuhvatna rđa čelika olakšava dodavanjem najmanje 12% hroma. Hrom promeni sastav prirodnog formirajućeg oksidnog filma na površini metala i koncentracije hroma veći od 12%, film sadrži dovoljno hromovog oksida da bi se značajno smanjila korozija. Zaštitne folije na drugim metalima (poput aluminijuma i magnezijuma) takođe mogu biti poboljšane legiranjem dodataka. Pošto korozija obično potiče na površini metala, mnoge uspešne metode kontrole korozije uključuju tretman ili promenu metalne površine. Ovi tretmani mogu biti sasvim uobičajeni kao što je pucanje površina metala da bi se poboljšala otpornost na korozijski zamor, ali oni mogu biti visokotehnološki poput talasanja laserske površine kako bi se obezbedila glatka, kompozicijski izmenjena površina. Budući trendovi u istraživanju korozije uključuju razvoj ekološki benignih inhibitora, precizno predviđanje životnog veka strukture i pronalaženje načina da korozija postane dobra stvar. Ogromne sume novca troše se na inhibitore u širokom spektru industrija. Jedini cevovod može potrošiti milion dolara godišnje na inhibitore koji se dodaju na ulje pre transporta. Dok je hromat moćan inhibitor korozije na mnogim metalnim površinama, on je kancerogeničan. Prema tome, pretraga je bila da pronađe inhibitor koji je jednako efikasan kao i hromat, ali ekološki benigni. Ovo zahteva interdisciplinarni rad u oblasti hemije, elektrohemije, površinske nauke i metalurgije. Budući da infrastruktura industrijalizovanih zemalja i dalje stara, sve više i više kvarova usled korozije se dešavaju. Zamena svih mostova i cevovoda (gas, ulje, voda) bi bila izuzetno skupa i nepotrebna jer je većina u dobrom stanju i može pružiti mnogo više godina rada. Saznati koji od njih ne funkcionišu i koliko dugo mogu trajati je funkcija predviđanja životnog veka. Ovo područje podrazumeva rad sa računarskim naučnicima, inženjerima svih vrsta (civilnih, mehaničkih, hemijskih, električnih, informacija), kao i ekonomista. Upečatljiv primer velikog izazova u ovoj oblasti je predviđanje korozionog ponašanja kanistara izabranih za držanje radioaktivnog otpada visokog nivoa za 10.000 godina ili više. Korozija može biti dobra stvar. Može se koristiti rastvor za selektivno uklanjanje jedne komponente iz materijala (poznatog kao dealloiing), ostavljajući poroznu strukturu koja se može koristiti za držanje i polako eluirati lekove kada se implantira struktura. Unošenje takvog materijala na površinu koronarnog stena može dozvoliti zamenu trenutno korišćenih polimernih filmova koji mogu pucati na širenje stenta. U sličnoj veni magnezijumski stentovi pronalaze aplikacije kao bioabsorbable stentove. Ovo istraživanje je omogućilo uvid u prirodu korozije - zbog čega se to dešava i kako se može sprečiti. Dostupne su mogućnosti za produženje životnog veka različitih struktura i komponenti, od automobila i kamiona do brodova za zadržavanje nuklearnog otpada.

7. Stopa korozije

Približno 85% proizvedenog čelika je ugljenični čelik i stoga je podložan prirodnoj oksidaciji i galvanskoj koroziji. Stopa korozije je dobro shvaćena u tipičnim atmosferskim uslovima, ali za inženjera dizajna, precizni lokalni uslovi ili uslovi mikro-okruženja moraju biti dobro shvaćeni za njega/nje da imaju poverenje u krajnju trajnost modela. Druga mikro-okruženja uključuju izlaganje svežoj i slanoj vodi (u ili u neposrednoj blizini) ili u tlu. Korozija ugljeničnog čelika i čak legiranih čelika u mikro-okruženjima može biti vrlo složena. Na primer, pH, sadržaj vlage i nivo hlorida su samo tri varijable koja određuju stopu korozije pocinkovanog čelika u tlu. Korozivne grafike se teško razvijaju zbog mnogih varijabli prisutnih u datom mikro-okruženju.

Na primer, korozija u vodi mora uzeti u obzir faktore kao što su sadržaj kiseonika, stepen agitacije, dejstvo talasa, temperatura, nivo hlorida i više. Na taj način se razvija tabela koja predviđa stope korozije za bilo koju određenu lokaciju koja je ekstenzivna, a ponekad i skupa, i zašto postoje mnogi grafikoni stope korozije, ali samo za jedinstvene lokacije i uslove.

8. Testiranje korozije

Postoje tri opšte metode ispitivanja korozije: istorija servisa, performanse na terenu i ubrzani testovi korozije. Istorija servisa tokom dužeg vremenskog perioda je najpouzdanija i dostupnija, ali podaci možda ne odražavaju tačne uslove kojima je materijal trenutno izložen. Testiranje korozije na terenu je slično istoriji servisa, ali obično podrazumeva ispitivanje promenljive performansi u kraćem periodu od jednog do pet godina. Kada se podaci prikupe, može se ekstrapolirati da bi se donekle naučno predviđalo performanse na 10, 20 ili čak 50 godina. Ekstrapoliranje varijabilne performanse na 10, 20 ili čak 50 godina onda daje donekle naučno predviđanje dugoročnih performansi. Kombinovanje istorije servisa sa performansama na terenu može biti vrlo efikasno. Na primer, ako se okolina oko projekta promeni u poslednjih 5 godina svog života, ispitivanje ukupne istorije servisa, kao i razlike u performansama polja nakon promene u okruženju, može prouzrokovati predviđanje za novi projekat u tom okruženju. Oznake inspekcije na ovom mostu pokazuju razaranja korozije.

Ubrzano testiranje korozije se obično koristi zbog bržih rezultata. Međutim, teško je dizajnirati test da odgovori na sve korozivne mehanizme koji su uključeni, te stoga rezultati mogu biti kompromitovani. Na primer, 1.000 časova testa za raspršivanje magnezijuma na proizvodima od cinka, kao što je galvanizirani čelik, ne dozvoljavaju vlažne/suve cikluse normalne atmosferske ekspozicije. Ovi vlažni/suvi ciklusi su neophodni za razvoj cinka patina cink-oksida, cink-hidroksida i cink-karbonata koji daje decenijama izdržljivost od pocinkovanih proizvoda. Postoje dva zajednička metoda ispitivanja koja se koriste za ispitivanje korozije na komadu čelika. Ultrazvučno ispitivanje je ispitivanje bez razaranja sa veoma visokom osjetljivošću otkrivanja unutrašnjih mana u čeliku i promena debljine. Veoma kratki ultrazvučni impulsni talasi se šalju u čelik kako bi se utvrdilo da li je bilo kakva korozija promenila zvučni potpis komada, što ukazuje na pojavu korozije. Elektronski mikroskop za skeniranje (SEM) fokusira snop elektrona na površinu koji, kada se reflektuje nazad, daje prikrivene informacije o površinskom stanju i topografiji uzorka koji se testira.

9. Metode zaštite od korozije

Korozijski procesi sa kojima se svakodnevno susrećemo u suštini su spontani procesi između metala i komponenata okoline pri čemu metali prelaze u termodinamički stabilnije stanje. Korozija tako neminovno smanjuje upotrebnu vrednost metala, pa tako i proizvoda koji su napravljeni od njega. Ekonomsko značenje korozije je veliko i ono raste sa industrijalizacijom privrede. Iz navedenog proizlazi da je pravovremena i adekvatno odabrana metoda zaštite od korozije ključna za ekonomsku isplativost objekata napravljenih od metalnih komponenata. Metal se može zaštititi od procesa korozije različitim metodama. Postoji mnogo podela zaštite od korozije - na aktivne i pasivne metode, presvlačenje metalom ili galvanizaciju, bojadisanje zaštitnim bojama, anodnu i katodnu zaštitu...

9.1. Elektrohemijska metoda zaštite

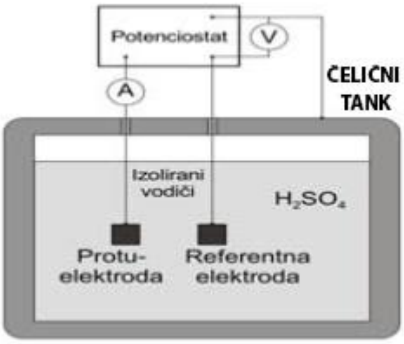
Temelje elektrokemijske zaštite postavio je 1824. godine Sir Hamfri Dejvi, koji je upotrebio cink kao zaštitu bakarnih oklopa na drvenim brodovima ratne mornarice. Glavni polazni podaci za primenu elektrohemijske metode zaštite od korozije daju Pourbaikovi dijagrami koji pokazuju zavisnost potencijala metala o pH vrednostima vodenih rastvora. Danas se elektrokemijske metoda zaštite od korozije upotrebljava tamo gde nije moguće ili je otežana primena ostalih metoda zaštite. Vrlo često se koristi i kao sekundarna zaštita metala. Neki od primera gde se upotrebljava Elektrohemijske zaštita su: brodovi, cevovodi, kablovi, lučka postrojenja, rezervoari, izmenjivači toplote, kondenzatori. Danas poznajemo dve metode elektrokemijske zaštite koje zavise o načinu polarizacije, a to su: katodna zaštita i anodna zaštita.

9.2. Anodna zaštita

Princip anodne zaštite metala vrlo je sličan principu katodne zaštite. Postoje dva osnovna načina zaštite:

- Zaštita jednosmernom strujom - jednosmerna struja deluje pasivizirajuće na metal
- Zaštita protektorom - zaštita se ostvaruje tako da se metal koji se želi zaštititi spaja sa protektorom koji je u pravilu pozitivno nabijen

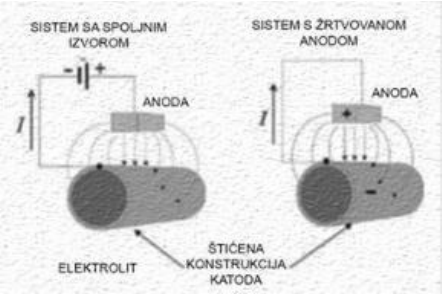
Anodna elektrohemijska zaštita ima uveliko manju primenu u praksi u poređenju s katodnom zaštitom. Tako se na primer anodna zaštita najviše upotrebljava za pasivizaciju čelika, aluminijuma, hroma te titanijuma, odnosno njihovih legura. Jedna od najčešćih primena anodne zaštite od korozije je zaštita čelika koji se nalazi u agresivnoj sredini u kojoj prevladavaju kiseline. Uslov za uspeh svih oblika elektrohemijske, anodne i katodne zaštite jeste održavanje dobrog metalnog kontakta radi provođenja električnih struja između osnovne konstrukcije i anoda/katoda. Ova metoda se vrlo često koristi za zaštitu velikih metalnih konstrukcija, kao što su kopneni cevovodi, naftovodi, naftne platforme i brodovi. Suština dejstva metode jeste da se u procesu korozije troši "žrtvena" anoda, koja ima veći afinitet prema koroziji od metala osnovne konstrukcije.



Slika 1. Prikaz anodne zaštite pomoću spoljašnjeg izvora struje na čeličnom spremniku

9.3. Katodna zaštita

Katodna zaštita je tehnika zaštite metala od korozije čiji je osnovni princip polarizacija metalne konstrukcije na potencijal kod kojeg proces razaranja metala prestaje ili se odvija prihvatljivo malenom brzinom, odnosno dovođenje metala osnovne konstrukcije u poziciju da u električnom krugu ima ulogu katode. Katodna zaštita se može sprovesti na dva načina: 1. Potencijal metala pomoću spoljnjeg izvora, povezanog za inertnu elektrodu, održava se na potencijalu nižem od ravnotežnog, tj. pri uslovima kod kojih ne dolazi do njegova razaranja. 2. Metal koji se štiti dovede se u kontakt sa metalom nižeg potencijala (protektorom) koji će se u električnom kolu ponašati kao anoda. Katodna zaštita je efikasna jedino ako je materijal između protektora, odnosno inertne elektrode, i objekta koji se štiti provodljiv - ako postoji metalni kontakt. Katodna zaštita se obično koristi kao sekundarni zaštitni sistem, i veoma je slična elektrohemijskoj zaštiti koja je već opisana.



Slika 2. Princip katodne zaštite

9.4. Zaštita inhibitorima korozije

Inhibitori su materije koje dodane u korozivnu okolinu smanjuju brzinu korozije do tehnološki prihvatljivih iznosa. Dodaju se povremeno ili kontinuirano u zatvorene ili ređe u otvorene prostore. Prema hemijskom sastavu inhibitori su neorganska ili organska jedinjenja. Inhibitorima korozije smanjuje se efekat korozije na sistem. Najčešće se koriste u motorima sa unutrašnjim sagorevanjem - tačnije dodaju se u rashladnu tečnost motora, gde pokazuju efikasnost od 90-99 %. Naime, u savremenim motorima prisutni su različiti metali, deo su većih konstrukcija, kroz njih teku slabe struje, prisutne su visoke temperature, ima zavarenih spojeva svi uslovi za pojačanu koroziju su tu, pa je zbog toga vrlo izražena potreba za zaštitu delova motora od korozije.

Za zaštitu od korozije izazvane mikro-organizmima, koriste se antiseptička sredstva, kao benz-alkon-hlorid i slična. Osim u rashladnu tečnost, inhibitori korozije dodaju se i u goriva, hidraulične fluide, vodu koja se koristi u parnim kotlovima, motorno ulje za motore i mašine i mnoge druge fluide koji se koriste u industriji. Isto tako, dodaju se i u boje kojima se u cilju zaštite premazuju metalne konstrukcije. Za ovu svrhu najčešće se koristi cink-fosfat.

9.5. Zaštita prevlakama i premazima

Metalne i nemetalne zaštitne prevlake i premazi su najčešći oblik zaštite od korozije. Metalne prevlake mogu imati galvansko delovanje ili su otpornije na koroziju od osnovnog materijala pa deluje kao barijera prema uticajima okoline. Nemetalne prevlake mogu biti oksidi npr. aluminijuma, netopljive soli na gvožđu i čeliku te keramika i organski premazi.

Komponente zaštitnog premaza su: vezivo, otapalo, pigmenti (daju boju i neprovidnost), punila i ostalo (sikativi - ubrzivači sušenja i slično). Razvrstavanje premaza može se sprovesti prema broju komponenata, trajnosti, načinu sušenja, generičkim tipovima itd. Premazi mogu biti jednokomponentni ili dvokomponentni. Obzirom na način sušenja premaza možemo ih podeliti na: konvertibilne premaze - premazi koji se suše oksidacijom ili polimerizacijom; nekonvertibilne premaze - premazi koji se suše isparavanjem otapala i koji nakon nanošenja ne prolaze kroz neke značajnije hemijske promene. Prevlakama i premazima razdvaja se materijal konstrukcije od agresivnog delovanja okoline i tako štiti od korozije.

9.6.Galvanizacija

Proces galvanizacije patentirao je u Parizu 1837. godine Stanislav Sorel. Galvanizacija je elektro-hemijski proces nazvan po italijanskom naučniku Luiđiju Galvaniju, u kojem se na metalni deo (najčešće od gvožđa i čelika) nanosi elektrolizom tanak sloj nekog drugog metala koji je otporniji na koroziju - najčešće cink, mada se često koriste i plemenitiji metali - srebro, zlato, platina, kao i drugi metali.

9.7. Zaštita metalizacijom

Pod metalizacijom (nanošenjem metalne prevlake) podrazumeva se vrsta zaštite čelične konstrukcije od korozije ostvarene prskanjem rastopljenog metala pištoljem. Za metalizaciju se upotrebljavaju rastopljeni metali, cink, aluminijum i olovo. Metalna prevlaka mora se naneti neposredno posle čišćenja čelične površine mlazom abraziva, pre nego što se uočljivo promeni izgled površine. Ako se pri upoređivanju sa izgledom sveže očišćene površine uoči promena, površina se mora ponovo pripremiti za metalizaciju na propisani način. Prevlaka se nanosi najdocnije u roku od četiri časa od izvršene pripreme površine. Pri radu na gradilištu metalna prevlaka se ne sme nanositi pri kišnom ili maglovitom vremenu niti ako je relativna vlažnost iznad 80%. Prevlaka se nanosi pomoću uređaja koji omogućava potpuno topljenje metala u oksiacetilenskom odnosno oksibutanskom plamenu ili u električnom luku i njegovo nabrizgavanje na čeličnu površinu strujom vazduha pod pritiskom.

10. Zaključak

Zaštita od korozije kao takva vrlo je važna karika funkcionalnosti, produktivnosti i sigurnosti kako postrojenja tako i ljudi i okoline u kojoj se konstrukcija nalazi. Daljim razvojem tehnologije, očekuje se veliki napredak u tehnologiji zaštite od korozije koji bi u budućnosti trebalo da prati trendove zaštite životne sredine proizašlih iz globalnih klimatskih i atmosferskih promena. Pravilnom upotrebom savremenih tehnologija zaštite od korozije postiže se planirana trajnost i funkcionalnost, a isto tako zaštita od korozije značajno utiče na cenu konstrukcija, stoga i najmanje unapređenje u primeni tehnologije zaštite od korozije može značiti i velike uštede. Uprkos velikim štetama koje se javljaju kao posledice delovanja korozije još uvek se korozijskoj zaštiti ne pridaje dovoljna pažnja čemu svedoče brojne havarije uzrokovane korozijskim razaranjem. Danas je najvažnija i najzastupljenija metoda zaštite mašinskih konstrukcija od korozije zaštita primenom premaza. Zaštita primenom premaza vrlo je zahtevna, a tržište nam pruža vrlo velike mogućnosti odabira različitih vrsta i sistema premaza. Kod odabira je potrebno voditi računa o nameni konstrukcije i uslovima eksploatacije.

11. Literatura

1. Mladenović, S., Petrović, M., Rikovski, G., Korozija i zaštita metala, „Rad“, Beograd,1985.
2. SRPS ISO 1461, Prevlake cinka koje se nanose toplim postupkom na proizvode od gvožđa i čelika, Institut za Standardizaciju Srbije, Beograd, 2005.
3. Ema Stupnišek-Lisac: "Korozija i zaštita konstrukcijskih materijala", Fakultet kemijskog inženjerstva i tehnologije, Zagreb, 2007.
4. Površinska zaštita čeličnih konstrukcija, IGH, Zagreb, 1994.
5. Stupnišek-Lisac, E., Korozija i zaštita konstrukcijskih materijala, Fakultet kemijskog inženjerstva i tehnologije, Sveučilište u Zagrebu, Zagreb, 2007.
6. Ivan Esih: "Osnove površinske zaštite", Sveučilište u Zagrebu, Fakultet strojarstva i brodogradnje, Zagreb 2003.g.
7. I. Juraga, V. Šimunović, I. Stojanović: "Primjena inhibitora u zaštiti od korozije u brodogradnji",Opatija, Sorta 2006.
8. Ivan Juraga, Vesna Alar, Ivan Stojanović: "Korozija i zaštita premazima", Denona d.o.o., Zagreb, 2014.

Electrochemical behavior of zirconium in NaOH solutions

Zagorka Koneska, Ruzica Manojlovic, Dafinka Stoevska-Gogovska

University St. Kiril and Metodij, Faculty of Technology and Merallurgy, Rudjer Boskovic 16,
10000 Skopje, R.Macedonija

Abstract

This work has been carried out to investigate the electrochemical behavior of Zr metal in aqueous NaOH solutions at room temperatures. Conventional electrochemical techniques such as open-circuit potential measurements, potentiodynamic polarization and potentiostatic method were used in this stady. The (Eoc) in NaOH solutions is in accordance with the passive behavior of metals. The thickening of chemical pure native oxide film occurs practically during the first 5-10 min in all investigated solutions. From the polarization study quantitative values of corrosion parameters, corrosion potential (E_{corr}), corrosion current density (i_{corr}) and corrosion rate were obtained. The oxide thickness was calculated from the charge flow measured during the anodic polarization for all applied potentials at 10 min. immersion time.

Key words: *zirconium, oxides, anodic oxidation, electrochemistry,*

INTRODUCTION

Both zirconium and zirconium oxide are technologically important materials. Due to their specific physical and chemical properties, they are widely used in a large number of application areas. One of the main uses of zirconium alloys is in nuclear technology, as cladding of fuel rods in nuclear reactors, especially water reactors because of their low capture cross-section for thermal neutrons, high hardness, ductility and good mechanical and corrosion properties. Pods of fuel elements and many of the structural components operating in nuclear power reactors are manufactured with Zircaloy-4 (Zry-4), alloy base zircon reference for the nuclear industry [1,2] Zirconium is used extensively by the chemical industry due to high resistance to corrosion by many common acids and alkalis, and by seawater. The metal is also used as an alloying agent in steel, and as a "getter" in vacuum tubes and in lamp filaments. Zirconium oxide is an important wide band gap transition metal oxide. Its current applications range from jewellery, semiconductor substrates, fuel cells and oxygen sensors to nuclear fuel rods.

Zirconium oxide possesses many highly desired materials qualities useful for structural and electrical applications such as fracture toughness, chemical robustness, thermal stability, and biocompatibility.

Zirconia has been widely studied because of its attractive technological properties, including high thermal and chemical stability, good mechanical strength and wear resistance, excellent dielectric properties (as oxide of a “valve metal”) and good ion-exchange properties.

Due to their prominent physical and chemical properties, zirconia (ZrO_2) ceramic materials have been widely used in modern engineering and industry fields, such as chemical sensors [3,4], fuel cells [5], thermal barrier coatings [6], refractory materials, catalysts [7], biomedical applications [8,9].

Zirconium oxide (ZrO_2) films have attracted immense attention as an important ceramic material because of their superior chemical, mechanical, and optical properties. They have high chemical stability, hardness among those of steel and other alloys, dielectric constant among the highest for metallic oxides, low absorption of light and high index of refraction.

When valve metals such as zirconium and its alloys like Zr-2, Zr-4, etc. are anodically polarized, interference colored oxide films is formed. These smooth and mechanically perfect anodic films can act as dielectrics in capacitors. The phenomenon of anodic oxidation plays a basic role in micro - circuitry and in thin film methods. Anodic oxide films formed on valve metals are useful in the field of electrical and electronic components (such as capacitors, resistors, dioxides and photoelectric devices), corrosion protection and for decorative purposes [10].

Anodic growth of zirconium oxides has been extensively studied in a wide variety of media and growth conditions. Electrolyte anions are more readily incorporated in films during anodisation in acid compared with alkaline electrolytes and this can affect film structure, growth kinetics, dielectric behaviour and surface defect density [11].

EXPERIMENTAL

Electrochemical investigations were carried out at room temperature in NaOH solution using three-electrode electrochemical cell consisting of Zr as working electrode, Pt wire as a counter electrode, and SCE as a reference electrode. The working electrode was a rod of polycrystalline (99,2%+Hf) zirconium purchased from Alfa, fixed in a Teflon holder. The exposed area of the working electrode was 1,2 cm^2. The chemical composition of the specimen (wt%) is presented in Table 1. Previous to any experiment, the working electrodes were polished with silicon carbide paper of grade 2000. After abrasion with silicon carbide paper, the sample was polished with diamond pasteof 9 and 3 μm. Among the different polishing session, the electrode was subject to ultrasonic cleaning.

All electrochemical measurements were carried out with a HEKA (potentiostat/galvanostat).

Table 1 Chemical composition of the specimen (wt%)

Hf	Fe+Cr	N	O	H	C	Zr
1	0,08	0,005	0,16	0,0003	0,02	balance

RESULTS AND DISSCUSION

Open circuit potential measurements

The chemical formation and behavior of native zirconia, Figure 1 presents the evolution of open circuit potential (Eoc) of Zr electrode against immersion time for NaOH aqueous electrolytes. As shown in figure 1, in the first 5-10 min., Eoc for all concentrations shifts to more electropositive values, suggesting the formation of the oxide layer onto the surface. After that, open circuit potential remained almost constant, due to the established equilibrium between chemical dissolution and chemical oxidation processes. The results can be explained on the bases of natural formation of thick oxide film of barrier type passive film, which leads to a shift in potential to more noble values [12]. The (Eoc) in NaOH solutions is in accordance with the passive behavior of metals (open circuit potential of the Zr electrode is stabile and decrease to less noble values with increasing the NaOH concentration). The thickening of chemical pure native oxide film occurs practically during the first 5-10 min in all investigated solutions.

Potentiodynamic polarization

After analyzing open circuit potential, potentiodynamic polarization test was carried out in 1M NaOH solution at room temperature The electrode potential was ramped at a rate of 1 mV/s from -1.3V up to -0.2 V (SCE).

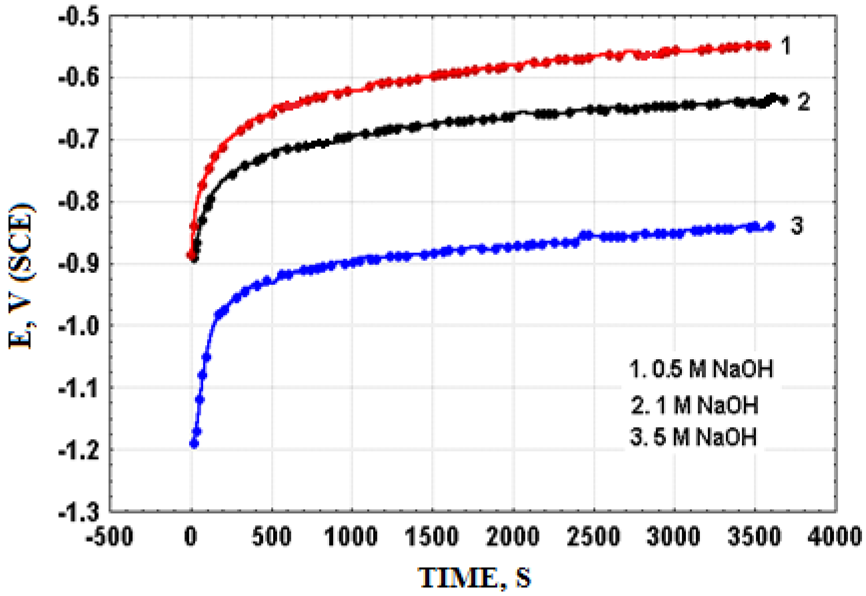


Fig.1 Evolution of EOC with time at different NaOH concentrations

The results for potentiodynamic anodic polarization study in 1M NaOH are as shown in Figure 2.

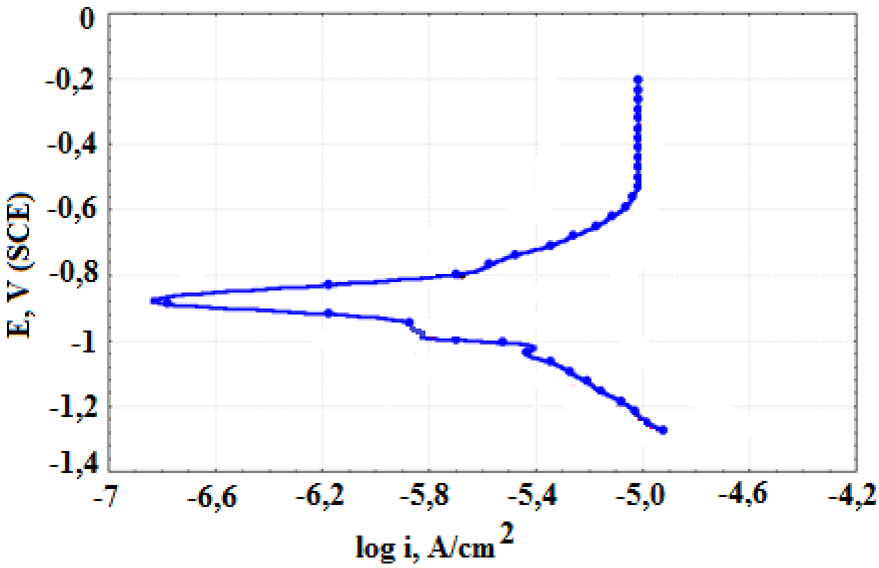


Fig.2 Potentiodynaimcs polarization of zirconium in 1 M NaOH

From the polarization study quantitative values of corrosion parameters, corrosion potential (E_{corr}) and corrosion current density (i_{corr}), were obtained, (Table 2).

Table 2 Corrosion parameters of Zr in 1 M NaOH

E_{corr}, V	i_{corr}, A/cm^2	corrosion rate, mpy
-0,880	$1{,}66 \cdot 10^{-7}$	0,076

Calculated corrosion rate of the zirconium in 1 M NaOH was 0,076 mpy.

Potentiostatic growth of passive film

Figure 3 shows the current transients (I–t curve) at different anodizing potentials (0 to 9 V) recorded during the anodization process in 1 M NaOH. In the first stages of the anodization process, the current increases rapidly owing to the increases of the voltage applied. Then the current drops drastically owing to the formation of a compact barrier layer of oxide on the surface of the Zr electrode. The oxide thickness was calculated from the charge flow measured during the anodic polarization for all applied potentials at 10 min. immersion time.

$$L = \frac{M \cdot Q}{z \cdot F \cdot \rho} \qquad (1)$$

Where:
M - molecular weight of the ZrO_2, (123,2 g/mol)
ρ - density of the oxide, (5,89 g/cm^3)
Q - charge flow, (C/cm^2)
z – transferred electrons (4)
F – Faraday constant (96 500 C/mol)

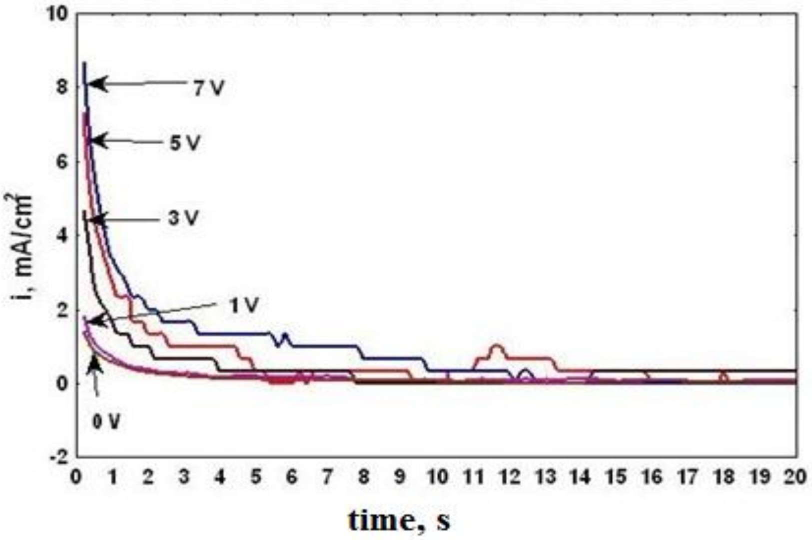


Fig.3 Curve of current density vs time during anodization of Zr in 1 M NaOH

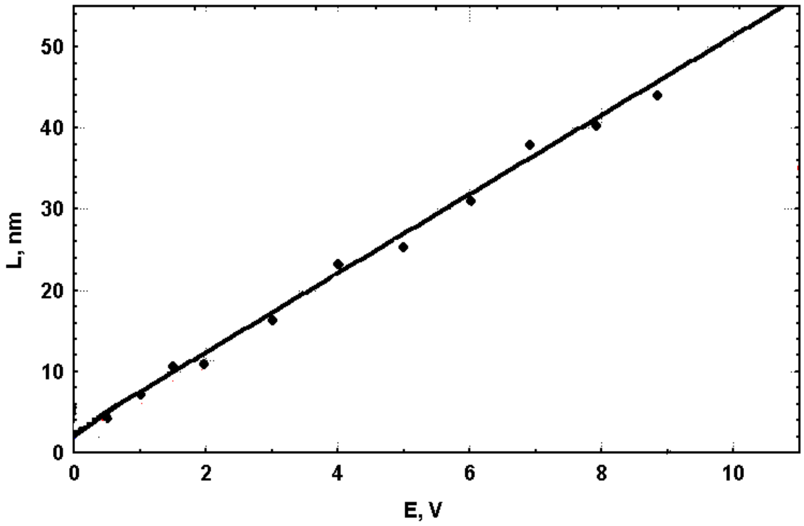


Fig.4 Dependence of zirconium film thickness on anodic potential at 10 min immersion time

Dependence of the oxide film thickness on the applied potential is shown in figure 4. The results show that, the oxide layer increase in thickness with increasing the applied anodic potential. The oxide growth with rate 4,5 nm/V.

CONCLUSIONS

Zirconium has a natural covering of very thin oxide layer, ZrO_2. Such film is responsible for the apparent behavior of the metal under open circuit conditions or under the influence of an alternating field.

The (Eoc) in NaOH solutions is in accordance with the passive behavior of metals (open circuit potential of the Zr electrode is stabile and decrease to less noble values with increasing the concentration). The thickening of chemical pure native oxide film occurs practically during the first 5-10 min in all investigated solutions.

Corrosion rate of the zirconium in 1 M NaOH is 0,076 mpy.

The oxide layer increase in thickness with increasing the applied anodic potential. The oxide growth rate is 4,5 nm/V.

LITERATURE

1. B. Cox, V. Kritsky, C. Lemaignan, et al. Water-Side Corrosion of Zirconium Alloys in Nuclear Power Plants. IAEA-TECDOC-996, 1998.
2. Griffiths M., Gilbert R.W., Fidlers V. Zirconium in the nuclear industry: Eighth International Symposium, ASTM STP 1023, American Society for Testing Materials, Philadelphia, 658- 677, 1989.
3. Shimizu K., Chinzei I., Nishiyama H., et al., “Hydrogen sensor based on WO_3 subnano-clusters and Pt ”, Solid State Ionics , n.177, pp. 2261–2267, oct. 2006.
4. Park H.J., Choi G.M., “Oxygen permeation characteristics of zirconia with surface modification*”, Solid State Ionics* , n.177, pp. 2261–2267, oct. 2006.
5. Laukaitis G., Dudonis J., Milcius D., “YSZ thin films deposited by e-beam technique”, Thin Solid Films, n.515 , v.2, pp. 678-682, oct. 2006.
6. Kitazawa R., Kakisawa H., Kagawa Y. “Anisotropic TGO morphology and stress distribution in EB-PVD Y_2O_3-ZrO_2 thermal barrier coating after in-phase thermo-mechanical test”, Surface and Coating Technology , v.238, pp. 68-74, jan. 2014.

7. Atribak I., Such-Basaniez I., Bueno-lopez A., et al, “Comparison of the catalytic activity of MO_2 (M = Ti, Zr, Ce) for soot oxidation under NOx/O_2”, Journal of Catalysis, v. 250, n.1, pp. 75-84, aug. 2007.
8. Park N.R., Song CH.G., Shon I.J. “Fast low-temperature consolidation of a nanostructured 2Ti– ZrO2 composite for biomedical applications”, Ceramics International , v. 40, n. 4, pp. 6311–6317, may 2014.
9. Liu X., Huang A., Ding C.,et al, “Bioactivity and cytocompatibility of zirconia (ZrO_2) films fabricated by cathodic arc deposition “, Biomaterials , n. 27**,** pp. 3904–3911, july 2006.
10. V. Jeevanana Jyothi and Ch. Anjaneyulu, Growth Kinetics of Anodic Oxide Films Formed on Zircaloy-2 in Various Electrolytes, E-Journal of Chemistry http://www.e-journals.net 2009, **6(3),** 880-886
11. Gomez Sanchez et al., Structure and Dielectric Properties of Electrochemically Grown ZrO_2 Films, Acta Chim. Slov. **2014,** 61, 316–327
12. Adrian Cristian Manea, Liana Aniai, Stadis on the Formation of Zirconia Films in Some Aqueous Solutions, REV. CHIM. (Bucharest), 66, No.6, 2015, http://www.revistadechimie.ro

The disposal of waste sludge from the technological process of paper production

Zbrinjavanje otpadnog mulja iz tehnološkog procesa proizvodnje papira

Veljko Đukić

PanEuropean University “Apeiron”- Banja Luka, Pere Krece 13. Banja Luka, Republic of Srpska, Bosnia and Herzegovina

Panevropski univerzitet Apeiron Banja Luka, Pere Krece 13. Banja Luka, Republika Srpska, Bosna i Hercegovina

Abstract

The pulp and paper industry is one of the largest water consumers in the technological process and is considered one of the largest polluters in terms of the amount and composition of wastewater generated. Due to the satisfaction of economic and ecological requirements, it is necessary to find an optimal process of purification of these wastewaters, and also to fulfill the legal regulations.

In the wood chemical processing plant there is a wastewater treatment plant where one of the segments of its work and the formation of waste sludge. The paper presents the technological process of paper production, the characteristics and process of purification of wastewater, and ultimately the disposal of waste sludge from the process of purification of wastewater.

After chemical treatment and dehydration of the sludge on the strips filter presses, a "cake" is formed with a dry matter content of more than 30%, and as such it is suitable for incineration. The produced heat energy is used to start steam turbines and produce electric current.

Key words: *sludge, paper machine, wastewater treatment.*

Izvod

Industrija celuloze i papira se nalazi među najvećim potrošačima vode u tehnološkom procesu, a smatra se i jednim od najvećih zagađivača s obzirom na količinu i sastav otpadnih voda koje nastaju. Zbog zadovoljenja ekonomskih i ekoloških zahtjeva, potrebno je pronaći optimalan postupak prečišćavanja ovih otpadnih voda, a isto tako ispuniti i zakonske propise.

U pogonu hemijske prerade drveta nalazi se i postrojenje za tretman otpadnih voda gdje je jedan od segmenata njegovog rada i nastanak otpadnog mulja. U radu je prezentovan tehnološki proces proizvodnje papira, karakteristike i proces prečišćacvanja otpadnih voda i na kraju zbrinjavanje otpadnog mulja iz procesa prečišćavanja otpadnih voda.

Poslije hemijske obrade i dehidracije mulja na trakastoj filter presi se formira „kolač“ koji ima sadržaj suhe materije veći od 30%, i kao takav je pogodan za spaljivanje. Proizvedena toplotna energija se koristi za pokretanje parnih turbina i proizvodnju električne struje.

Ključne riječi: *mulj, papir mašina, tretman otpadnih voda.*

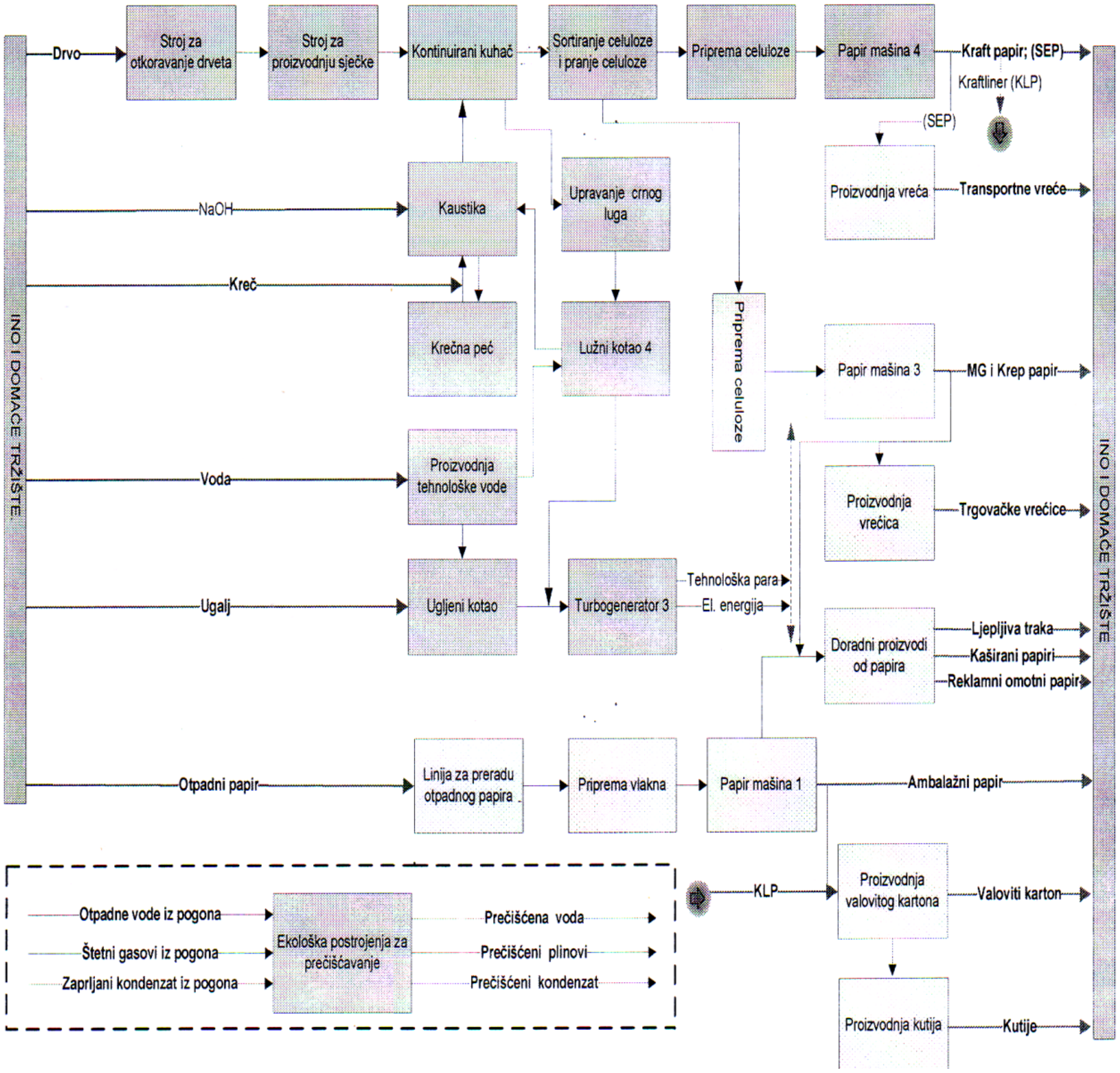
Uvod

Industrijske otpadne vode predstavljaju potencijalnu opasnost za vodotoke, a naročito vode koje potiču iz industrije celuloze i papira koja se nalazi među najvećim potrošačima vode u tehnološkom procesu a smatra se i jednim od najvećih zagađivača s obzirom na količinu i sastav otpadnih voda koje nastaju[1].

U kompaniji Natron-Hayat koja se bavi proizvodnjom celuloze i papira sulfatnim postupkom, nastaju znatne količine industrijskih otpadnih voda koje se po svom sastavu i porijeklu dijele na crne i bijele otpadne vode. S obzirom na količinu nastalih otpadnih industrijskih voda i njihove fizičko-hemijske karakteristike one zahtjevaju tretman prije ispuštanja u recipijent.
U postrojenju za tretman otpadnih voda vrši se kondicioniranje otpadnih voda u fazama: primarni treman, sekundarni treteman, tercijarni tretmana i na kraju procesa obrada nastalog mulja.
Mulj koji nastaje tokom tretmana otpadnih voda i čija količina zavisi od rada papir mašina, nakon hemijske obrade i dehdriatcije na trakastoj filter presi gdje se formira tzv. „kolač“ koji ima sadržaj suhe materije veći od 30%. Kao takav je pogodan za spaljivanje u kotlu za spaljivanje gdje njegovim sagorjevanjem nastaje određena količina energije koja se koristi za pokretanje parnih turbina i proizvodnju električne energija, dok se filtrat koji je nastao prilikom dehidratacije vraća u egalizacioni bazen na početak procesa obrade otpadnih voda[2].

Tehnološki proces proizvodnje papira

U tehnološkom procesu dobijanja celuloze i papira po sulfatnom postupku kao sirovine koriste se četinari: bor, jela, smreka (slika 1)[3].



Slika 1. Shema tehnološkog procesa proizvodnje celuloze i papira (Izvor: Envirotek,2007)

Danas je sulfatni postupak voma zastupljen, zbog činjenice da je kvalitet proizvoda bolji u odnosu na tzv. natron postupak (razlika između natron postupka i sulfanog postupka je u načinu regeneracije alkalija odnosno bijelog luga koji se upotrebljava za kuhanje drveta, dok se kod natron postupka nadoknada izgubljenih hemikalija vrši upotrebom kalcinisane sode-Na_2CO_3 ili lužinom-NaOH, dok se kod sulfatnog postupka koristi natrijev sulfat-Na_2SO_4 po kome je postupak i dobio ime) a u potpunosti je riješeno i pitanje regeneracije hemikalije čime je osim tehnološkog, zadovoljen i ekonomski aspekt.

Bez obzira koji se tehnološki proces primjenjuje za preradu drveta uvijek je potrebno obaviti fazu tzv. pripreme drveta koja obuhvata sljedeće korake: uskladištenje drveta, otkoravanje drveta i proizvodnja i sortiranje sječke.

Dobijena sječka ide na separaciju i prihvatljivi dio se šalje na kuhanje u Kamyr kuhač gdje se ubrizgava tzv. bijeli lug u čiji sastav ulaze natrijum hidroksid NaOH i natrijum sulfid Na_2S (sulfatni postupak kuhanja). Zadatak NaOH jeste da odvoji lignin od celulozne mase, a Na_2S ima ulogu da čuva celulozna vlakna na okupu.

Celulozna masa nakon kuhanja ide na pranje i separaciju te nakon sto prođe svu neophodnu obradu šalje se na papir mašinu u finalnoj koncentraciji od 4,5% - 5%.

Nakon što se celulozna masa prebaci na papir mašinu (PM-4) šalje se na prese gdje dolazi do ugušćavanja mase na cca 33% suhe materije a zatim se melje na mlinovima za visoku koncentraciju, nakon čega se ponovo razređuje na koncentraciju cca 4-5% te se dodaje sumporna kiselina (H_2SO_4) radi regulacije pH pri čemu se vrijednost pH obara sa 9 na 7. Nakon ovoga masa se prebacuje na mlinove za mljevenje u tzv. niskoj koncentraciji.

Mljevenje predstavlja bitnu operaciju pripreme papirnih vlakana čime se uveliko mogu poboljišati fizička svojstva papira. Smatra se da mljevenje dovodi samo do fizičke promjene vlakana ali ne i hemijske što je dokazano nepromjenjenom difrakcijom svjetlosti (odnosno lomom svjetlosnih zraka) uz pomoć rentgenskih zraka.

Najvažnije fižičke promjene koje se dešavaju na vlaknima prilikom mljevenja su razdvajanje i skraćivanje vlakana po dužini.

Poslije mljevenja celulozna masa se šalje na centriklinere. Funkcija centriklinera je grubo odvajanje nečistoća uz pomoć diferencijalne razlike pritisaka nakon čega se masa ponovo razređuje sa velikom količinom vode i šalje na tzv. selektifajere koji služe za fino prečišćavanje.

Poslije svih obrada celuloza konačno dolazi na stroj za izradu papira (papir mašinu).

Karakteristike otpadnih voda iz procesa proizvodnje celuloze i papira

Otpadne vode u tehnološkom procesu čine:

- crne otpadne vode
- bijele otpadne vode

Crne otpadne vode potiču iz pogona proizvodnje celuloze, regeneracije alkalija i pripreme hemikalija. One sačinjavaju efluent kuhaonice, praonice, separacije, uparivaone, lužnih kotlova i kaustike.

Sanitarne vode ovih pogona se takođe ulijevaju u kolektor crnih otpadnih voda.

Bijele otpadne vode potiču iz pogona proizvodnje papira, te pomoćnih pogona (priprema vode, energana, pogon prerade). U kanalizacioni sistem bijelih voda ulijevaju se i sanitarne vode ovih pogona. Otpadne vode koje nastaju na papir mašini po sastavu pripadaju bijelim otpadnim vodama, ali su zbog lokacije mašine pripojene kanalizacionom sistemu crnih otpadnih voda.

Karakteristike crnih otpadnih voda predstavljene su u tabeli 1.

Tabela 1. Količina i karakteristike crnih otpadnih voda

Karakteristike otpadnih voda	Količina
količina	18.000 m^3/dan
ukupna BPK_5	7.000-12.000 kg/dan
ukupna HPK	14.000-35.000 kg/dan
ukupne SM	3.500-7.000 kg/dan
maksimalna BPK_5	700 mg/l
maksimalna HPK	2.000 mg/l
maksimalna koncentracija SM	400 mg/l

Karakteristike bijelih otpadnih voda predstavljene su u tabeli 2.

Tabela 2. Količina i karakteristike bijelih otpadnih voda

Karakteristike otpadnih voda	Količina
količina	22.000 m^3/dan
ukupna BPK	3.000-6.000 kg/dan
ukupna HPK	6.000-13.000 kg/dan
ukupne SM	6.000-13.000 kg/dan
maksimalna BPK	350 mg/l
maksimalna HPK	750 mg/l
maksimalna koncentracija SM	750 mg/l

Sve otpadne vode se obrađuju na postrojenju za prečišćavanje otpadnih voda.
U tabeli 3. predstavljena je ukupna količina otpadnih voda prilikom proizvodnje celuloze i papira (crne + bijele otpadne vode) i njihove karakteristike.

Tabela 3. Ukupna količina i karakteristike otpadnih voda (bijele+crne)

Karakteristike otpadnih voda	Količina
ukupna količina otpadnih voda	40.000 m^3/dan
ukupna BPK_5	10.000-18.000 kg/dan
ukupna HPK	20.000-48.000 kg/dan
ukupne SM	9.500-20.000 kg/dan

Ukupna proizvodnja celuloze je 450 tona vazdušno suhe celuloze/dan (300 t/dan kontinuirani + 150 t/dan u serijama).
Otpadna voda (crna voda) može se količinski izraziti kroz jediničnu vrijednost od 40 m^3/t celuloze.
Proizvodnja papira odvija se na više papir mašina. U tabeli 4. dat je proizvodni kapacitet svake papir mašine pojedinačno.

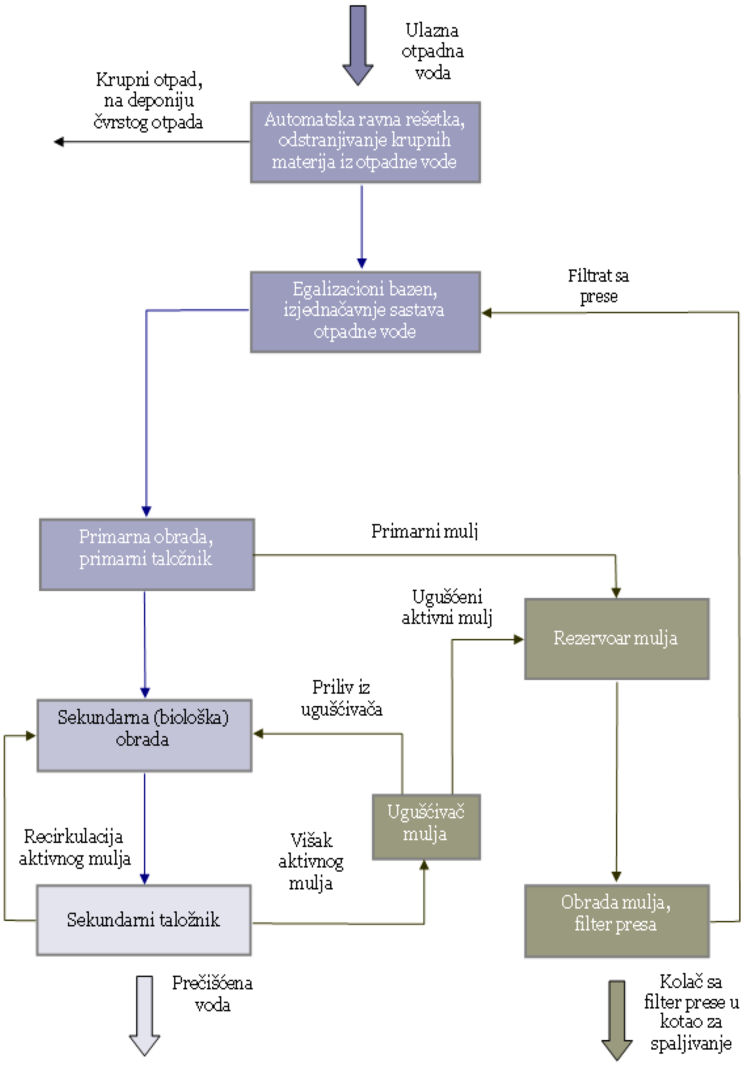
Tabela 4. Kapacitet mašina za proizvodnju papira

Mašina za proizvodnju papira	Količina
PM1	175 t/dan
PM3	30 t/dan
PM4	300 t/dan
Ukupna proizvodnja	505 t/dan

Prečišćavanja otpadnih voda iz procesa proizvodnje celuloze i papira

Tretman otpadne vode iz procesa proizvodnje celuloze i papira (slika 2) se sastoji od:

- primarne obrade,
- sekundarne obrade,
- tercijarne obrade (po potrebi) i
- obrade mulja.



Slika 2. Shematski prikaz postupka obrade otpadnih vodaiz procesa proizvodnje celuloze i papira (Izvor:Đukić,2009)

Zbrinjavanje otpadnog mulja iz postrojenja za prečišćavanje otpadnih voda papir mašina

U samom procesu kako primarnog tako i sekundarnog prečišćavanja otpadnih voda sa papir mašina nastaju znatne količine mulja ili taloga koji ide na dalju obradu i zbrinjavanje.

Primarni mulj koji nastaje u primarnom taložniku vodi se direktno u rezervoar mulja, dok se mulj koji je nastao u sekundarnoj obradi ili takozvani „aktivni mulj“ šalje prvo na ugušćivač mulja gdje se miješa uz pomoć rešetkastog zgrtača-ugušćivača, a potom se odvodi u rezervoar za mulj.

Slika 3. Ugušćivač mulja

U rezervoaru (tanku za mulj) se primarni mulj te pristigli višak biološkog mulja od sekundarne obrade miješaju i održavaju u svježem stanju pomoću miksera odakle se dalje putem pumpi transportuju na filter presu radi ugušćavanja.

Slika 4.Tank za mulj

Količine nastalog mulja zavise od količine prerađene vode, odnosno rada papir mašina.
Količine prerađene vode kao i količine nastalog mulja variraju u zavisnosti od rada pojedinih papir mašina, tj. da sa radom papir mašine br.1 čija se proizvodnja zasniva na preradi otpadnog papira nastaju veće količine mulja zbog većeg broja suspendovanih čestica koje dolaze zajedno sa otpadnom vodom na tretman, dok sa radom papir mašine br. 3 te papir mašine br. 4 to nije slučaj pošto iste proizvode papir od svježe napravljene celuloze.

Iz tanka za mulj, mulj se transportuje na filter presu, a zbog velike količine vode koja se nalazi u mulju i postizanja boljih efekata dehidratacije prije nego li dospije na filter presu, mulj se tretira sa kationiskim polielektrolitom u cilju povećanja efikasnost dehidratacije.
Dehidratacijom na filter presi dobija se „kolač“ od mulja sa sadržajem suhe materije većim od 30% koji se potom šalje na kotao za spaljivanje (skupa sa korom od procesa odkornjavanja drveta), dok se filtrat putem kanalizacione mreže vraća u egalizacioni bazen na početak procesa.

Slika 5. Trakasta filter presa

Slika 6. Odloženi mulj poslije filter prese koji se transportuje na spaljivanje

Slika 7.Kotao za spaljivanje

Zaključak

Industrija celuloze i papira se nalazi među najvećim potrošačima vode u tehnološkom procesu, a smatra se i jednim od najvećih zagađivača gledano prema količini i sastavu otpadnih voda koje nastaju. Zbog zadovoljenja ekonomskih i ekoloških zahtjeva, potrebno je pronaći optimalan postupak prečišćavanja ovih otpadnih voda, a isto tako ispuniti i zakonske propise.

U kompaniji Natron-Hayat koja se bavi proizvodnjom celuloze i papira sulfatnim postupkom, nastaju znatne količine industrijskih otpadnih voda koje se po svom sastavu i porijeklu dijele na crne i bijele otpadne vode. S obzirom na količinu nastalih otpadnih industrijskih voda i njihove fizičko-hemijske karakteristike one zahtjevaju tretman prije ispuštanja u recipijent.

U samom procesu kako primarnog tako i sekundarnog prečišćavanja otpadnih voda sa papir mašina nastaju znatne količine mulja ili taloga koji ide na dalju obradu i zbrinjavanje.

Mulj koji nastaje tokom tretmana otpadnih voda i čija količina zavisi od rada papir mašina, nakon hemijske obrade i dehdriatcije na trakastoj filter presi formira se tzv. „kolač“ koji ima sadržaj suhe materije veći od 30%. Kao takav “kolač” je pogodan za spaljivanje u kotlu za spaljivanje gdje njegovim sagorjevanjem nastaje određena količina energije koja se koristi za pokretanje parnih turbina i proizvodnju električne energija, dok se filtrat koji je nastao prilikom dehidratacije vraća u egalizacioni bazen na početak procesa obrade otpadnih voda.

Literatura

13. Đukić V.,Upravljanje otpadnim vodama”, Panevropski univerzitet Apeiron Banaj Luka, Banja Luka, 2009, 51-55.
14. Simičić H., Procesi obrade otpadnih voda, Biblioteka Lukavac i Eko zeleni Tuzla, 2004.
15. Envirotek H., Nostrifikacija Hidrotehnološkog dijela glavnog projekta: Postrojenje za tretman otpadnih voda Natron-Hayat Maglaj–dopuna do nivoa izvedbenog projekta, Univerzitet u Sarajevu, Građevinski fakultet, Institut za materijale i konstrukcije Sarajevo, br.507-17/06, 2007.
16. Jakupović E.,Đukić V., Monitoring otpadne deponijske vode sa aspekta uticaja na kvalitet vode prijemnika, Međunarodna naučna konferencija“Savremeni materijali 2016“,Akademija nauka i umjetnosti RS,2016.

Solution of a complex problem in the field of chemical effect of atmosphere on steel products by graphicial method

Rešavanje jednog složenog problema u oblasti hemijskog dejstva atmosfere na čelične proizvode grafičkom metodom

Branko Pejović, Slavko Smiljanić, Miladin Gligorić, Marija Riđošić, Aleksandar Došić

University of East Sarajevo, Faculty of Technology Zvornik, Republic of Srpska, Bosnia and Herzegovina

Univerzitet u Istočnom Sarajevu, Tehnološki fakultet Zvornik, Republika Srpska, BiH

Abstract

Oxidation and decarburization as an undesired phenomena, which are particularly evident for steel, is caused by increased temperatures due to the chemical effects of the atmosphere in the furnaces in which steel products are thermally treated by different methods. Exact knowledge of the thickness of the oxidation and decarburization layer is of great practical importance, especially in mechanical engineering and technology.

In the paper, the existing procedure for determining the depth of oxidation, which is valid for stationary, and used for a non-stationary region in an experimentally determined time-temperature diagram. In addition, the non-stationary area of the heating curve is divided into a number of segments in which for the calculation are responsible the corresponding middle temperatures which are defined in the operation. In order to take the effect of oxidation of the previous segment in the next segment, the so-called fictitious time was introduced, considering the given temperature of the next segment. In the execution of the main relationship, started with the individual or specific solutions, and on the basis of these solutions, laws were set for general solutions of the problem. Based on the fictitious time which is calculated for all segments of the area, a general model for determining the depth of the oxidation layer at the end of any segment is performed, which is a solution to the problem. The resulting approximate solution enables the graphical solution of the set problem, with regard to the entire non-stationary area, and it is much simpler than the existing analytical solution.

The depth of the decarbonization layer can also be determined on the basis of the previous method with minor changes.

Key words: *steel productions, adverse events (advents), depth of oxidation, depth of decarburization, termical treatment, diffusion process, heating diagram, graphical methods.*

Izvod

Oksidacija i razugljeničenje kao neželjene pojave, koje su posebno izražene, odnosno značajne kod čelika, nastaje na povišenim temepraturama usled hemijskog dejstava atmosfere u pećima u kojima se čelični proizvodi termički obrađuju različitim postupcima. Tačno poznavanje debljine oksidacionog i razugljeničnog sloja je od velikog praktičnog značaja, posebno u mašinskoj tehnici i tehnologiji.

U radu je postojeći postupak za određivanje dubine oksidacije, koji važi za stacionarno, iskorišćen za nestacionarno područje u eksperimentalno određenom dijagramu vreme-temperatura. Pri tome, nestacionarno područje krive zagrevanja podeljeno je na veći broj segmenata kod kojih su za proračun merodavne odgovarajuće srednje temperature, koje su definisane u radu. Da bi se kod narednog segmenta uzeo učinak oksidacije prethodnog segmenta uvedeno je tzv fiktivno vreme, s

obzirom na temperaturu narednog segmenta. Pri izvođenju glavne relacije, pošlo se od pojedinačnih, odnosno posebnih rešenja i na bazi tih rešenja postavljeni su zakoni za opšta rešenja postavljenog problema. Na bazi fiktivnog vremena koje je izračunato za sve segmente područja, izveden je opšti model za određivanje dubine oksidacionog sloja na kraju bilo kog segmenta, što predstavlja rešenje postavljenog problema. Dobijeno aproksimativno rešenje, omogućava grafičko rešavanje postavljenog problema, s obzirom na celo nestacionarno područje, i ono je znatno jednostavnije od postojećeg analitičkog rešenja.
Dubina razugljeničnog sloja se može takođe odrediti na bazi prethodne metode uz neznatne izmene.

Ključne reči: *čelični proizvodi, nepoželjne pojave, dubina oksidacije, dubina razugljeničavanja, termička obrada, difuzioni procesi, dijagram zagrevanja, grafičke metode.*

1. UVOD

Svi procesi termičke obrade čelika obavljaju se na povišenim temperaturama u pećima raznih vrsta u kojima se nalazi određena gasovita atmosfera, tečno sredstvo za zagrevanje ili vakuum. U svim ovim slučajevima sredina u kojoj se vrši zagrevanje ima manji ili veći hemijski uticaj na površinu čelika. Ovo predstavlja utoliko veći problem ukoliko se procesi obavljaju na višim temepraturama [1,2]. Oksidacija i razugljeničenje površine su sigurno najvažnije nepoželjne pojave koje su ovde prisutne, te ove pojave oduvek predstavljaju problem termičke obrade [2], [3]. Njene posledice su od velikog značaja, posebno sa ekonomskog aspekta procesa obrade. Prema nekim istraživanjima, od ukupne količine čelika koja se podvrgava termičkoj obradi 2-3% predstavlja gubitak na oksidaciju [1,3,4]. Gubici na razugljeničenje su nešto manji. Ove pojave imaju veliki uticaj na povećanje obima poslova oko čišćenja površina posle termičke obrade, da bi se uklonili produkti oksidacije ili nataloženi ugljenik. Pored ekonomskog značaja, treba imati u vidu da će kao posledica ove pojave doći do smanjenja mehaničkih osobina i veka delova za 15-20% [2,5], što se ne sme zanemariti.
Uticaj atmosfere peći na čelične proizvode istražuje se jako dugo. Tražena su bolja rešenja od postojećih postupaka. Pomenućemo pakovanje čeličnih delova u sanduke od sivog liva, regulisanje strujanja produkata sagorevanja u peći, a u savremenim uslovima problem se rešava kontrolisanom atmosferom i vakuumom[3,6].
Tačno poznavanje debljine oksidacionog kao i razugljeničnog sloja je od velikog praktičnog značaja. U mašinstvu, pored moguće deformacije pri termičkoj obradi, ova debljina je glavni faktor koji odlučuje o veličini dodatka za obradu posle termičke obrade [4,7]. Kao što je poznato ovaj dodatak se predviđa unapred i kasnije se naknadno nepovratno odstranjuje, što sve utiče na troškove proizvodnje.
Glavni faktori koji utiču na oksidaciju su [1,5,8]: hemijski sastav, dejstvo atmosphere, temepratura procesa, vrsta čelika i vreme zagrevanja, odnosno žarenja.
Zbog regulisanja dodatka za mehaničku obradu posle termičke obrade, od velike važnosti je poznavanje dubine oksidacije odnosno razugljeničenja [3,9]. Kod niskougljeničnih čelika, sa sadržajem ugljenika ispod 0,3%, najveći značaj ima baš oksidacija površine [1,5,10]. Brzina oksidacije kod ugljeničnih čelika naglo raste sa porastom temperature [4]. Zagrevanje čelika u praksi najčešće se obavlja u vazdušnoj atmosferi, zagrevanje produktima sagorevanja, kao i toplim kupatilima sa rastopljenim solima [6,10].

2. DIJAGRAM STANJA OKSIDA FeO

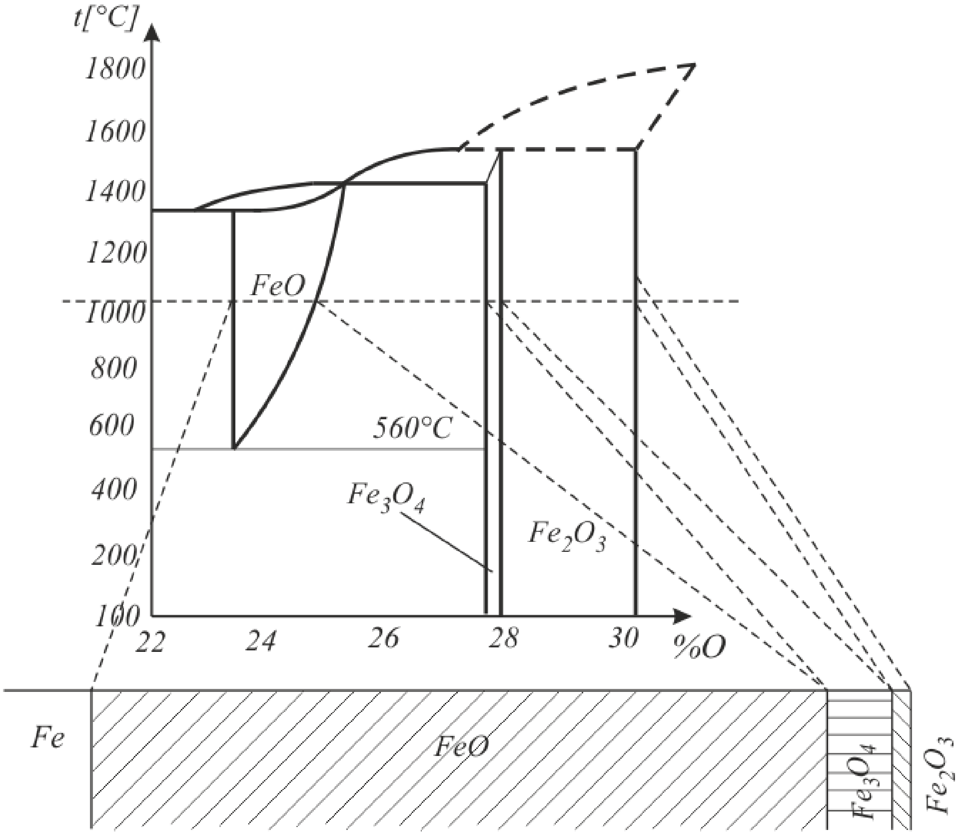
Prema nekim ispitivanjima najpovoljnija atmosfera za niskougljenične čelike je primena mešavine azota i vodonika koja sme da sadrži najviše 0,06% vlage [4,11]. Teorijske mogućnosti oksidacije čelika mogu se videti na dijagramu ravnotežnih stanja gvožđe-kiseonik, prikazanom na slici 1. [3,12,13].

Sa slike 1. se, pre svega, vidi da ispod 500 ^{0}C nema praktično opasnosti od oksidacije, jer se na ovim temperaturama može obrazovati samo tanki sloj oksida Fe_2O_3 ili Fe_3O_4. Prvi od njih se javlja na površini oksidnog sloja, a drugi ispod ovog sloja. Na višim temperaturama od 570 ^{0}C prisutna su sva tri oksida: Fe_2O_3, Fe_3O_4 i FeO, čije su debljine približno u odnosu 1:10:100, što pokazuje da najbrže nastaje oksid FeO [1,4,14].

Do naglog ubrzanja procesa oksidacije posle prekoračenja temperature 570 ^{0}C dolazi zbog nastajanja oksida FeO, što teče vrlo brzo [7,15,16,17]. Proces oksidacije je samo na početku čisto hemijska reakcija čiji je produkt čvrst oksid koji se nalazi na površini komada [9,11,18,19]. Prisustvo ovog sloja prouzrokuje u daljem procesu pojavu difuzije bilo kiseonika ka gvožđu bilo gvožđa kroz oksidni sloj. Najčešći slučaj je difuzija gvožđa.

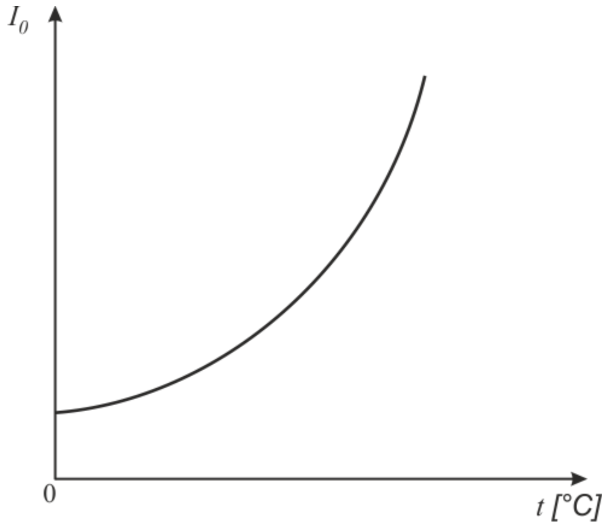
Pošto oksidni sloj ne mora biti kompaktan, to se kroz pukotine u njemu može nastaviti i direktna hemijska reakcija, ali je oksidacija čelika u najvećoj meri zavisna od brzine difuzionog procesa [2,8,20].

Razugljeničenje čelika zavisi takođe od difuzije.



Slika 1. Dijagram stanja FeO [3,12,37]

Uticaj temperature na tok oksidacije prikazan je na slici 2.



Slika 2. Zavisnost intenziteta oksidacije i razugljeničavanja od temperature

U ovom slučaju intenzitet oksidacije raste sa portastom temperature komada [7,10,15]. U opštem slučaju ovo se može reći i za razugljeničenje.

3. DUBINA OKSIDACIJE I RAZUGLJENIČENJA ZA STACIONARNO STANJE

Do dubine prodiranja oksidacije i dubine razugljeničenja može se teorijski doći polazeći od diferencijalne jednačine difuzije, napisane u skraćenom, odnosno pogodnom matematičkom obliku:

$$\frac{\partial C}{\partial \tau} = D(\tau) \cdot div(gradC) \qquad (1)$$

gde je $D(\tau)$ koeficijent difuzije u funkciji vremena [7,9,15,21].
Pri upotrebi jednačine (1) mora biti poznata promena temperature u funkciji vremena.
Za slučaj izotermskog toka pri $t = const$, biće $D(\tau) = const$, pa se do rešenja $S = S(\tau)$ dolazi na relativno jednostavniji način [8,16,22].
Iz relacije (1) došlo se do izraza za dubinu razugljeničenja:

$$S = S(\tau) = \sqrt{12 \int_0^\tau D(\tau) \cdot d\tau} \qquad (2)$$

Za izotermni tok razugljeničenja, za slučaj konstantne temperature, biće:

$$S = \sqrt{12D\tau} \qquad (3)$$

Koeficijent difuzije može se izraziti u zavisnosti od procenta sadržaja ugljenika i temperature u empirijskom obliku:

$$D = 0{,}07 + 0{,}06(\%C) \cdot \exp(-\frac{32000}{1{,}99 \cdot T}) \qquad (4)$$

Oksidacija čelika u najvećoj meri zavisi od brzine difuzionih procesa pri zagrevanju, usled hemijskog dejstva atmosfere, koji je neophodno držati pod kontrolom [6], [17], [23]. Na bazi prethodnih relacija dolazi se do analitičkog rešenja postavljenog problema [34,35,37]. Za približno izračunavanje dubine oksidacije samo u zavisnosti od vremena, u teoriji i praksi često se koristi empirijski obrazac [8,12,18,24].

$$S = a\sqrt{\tau} + b\tau \qquad (5)$$

Ovde su odvojena dva osnovna zbivanja, odnosno procesa od kojih zavisi brzina oksidacije. Prvi član sa desne strane jednačine $a\sqrt{\tau}$ uzima u obzir difuziju kroz oksidnu koru, a drugi kinetiku hemijske reakcije [19,20,21,25].

Množitelji a i b zavise od stanja oksidne kore na površini čelika. Njihove vrednosti, najčešće se daju tabelarno za pojedine vrste čelika, zavisno od stacionarne temperature t_{St}, tabela 1. [13,15,20,26].

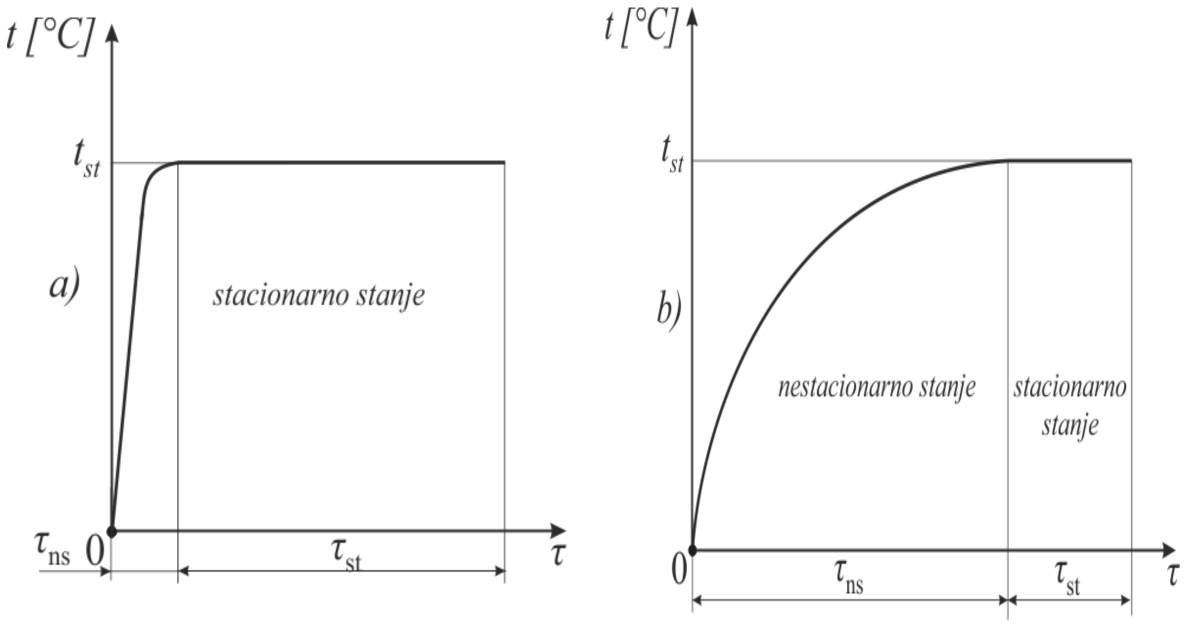
Tabela 1. Principijelna tabela za određivanje koeficijenata a i b

Množitelj	Temperatura t_{St}[°C]				
	t_1	t_2	t_3	t_{n-1}	t_n
$a\ [mm/min]^{-\frac{1}{2}}$	a_1	a_2	a_3	a_{n-1}	a_n
$b\ [mm/min]^{-1}$	b_1	b_2	b_3	b_{n-1}	b_n

Ova vrsta oksidacije pri $t = const$, u teoriji i praksi često se naziva izotermska oksidacija. Za slučaj da se uticaj nestacionarnog stanja, kao relativno malog, s obzorom na vreme trajanja, može zanemariti (slika 3.a), na dubinu oksidacije utiče prvenstveno stacionarno stanje τ_{St}, koja se može odrediti prema (5) kao:

$$S_{St} = a\sqrt{\tau_{St}} + b\tau_{St} \tag{6}$$

gde se a i b određuju prema stacionarnoj temperaturi t_{St}, tabela 1. [11,18,21,23,27].
Treba zapaziti, prema (5) da dubina oksidacije raste sa porastom temperature t i vremena zagrevanja τ.

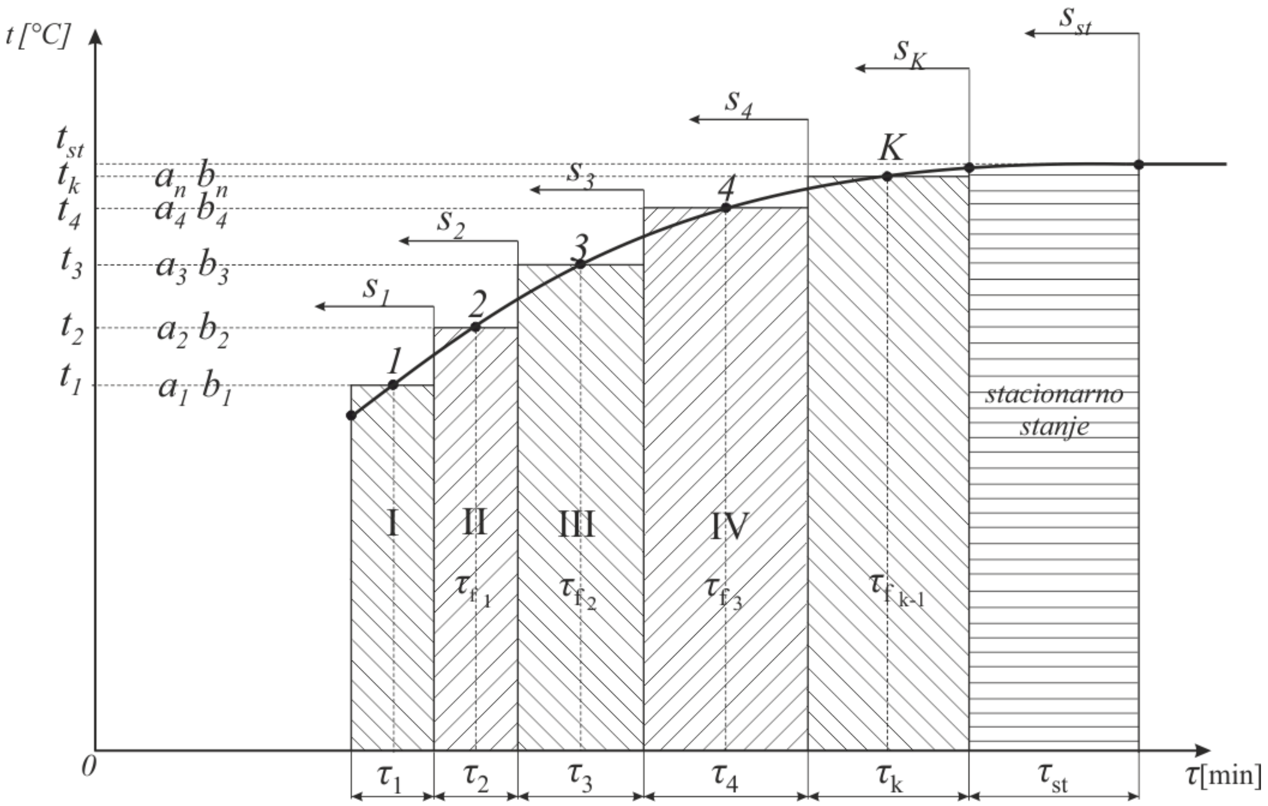


Slika 3. Dva karakteristična slučaja zagrevanja čelika u dijagramu $t = f(\tau)$, a)- stacionarno zagrevanje, b) – nestacionarno zagrevanje

U praksi, češći slučaj je prema slici 3.b kada se uticaj nestacionarnog stanja ne može zanemariti [11,14,24,28], jer bi to izazavalo određenu grešku ako bi smo želeli dobiti upotrebljive rezultate. Očigledno za ovaj slučaj zbog $t \neq const$ tokom τ_{ns}, relacija (5) se ne može primeniti za određivanje dubine oksidacije. Ideja rada je da se jednačina (5) primeni i za slučaj nestacionarnog stanja.

4. OPŠTI MODEL ZA REŠAVANJE PROBLEMA

Ako prema slici 4., za poznati dijagram *τ-t*, područje nestacionarnog zagrevanja podelimo na k segmenata $\tau_1, \tau_2, \tau_3, \tau_{4,} \dots \dots, \tau_k$, odgovarajuće temperature biće u tačkama na sredini svakog segmenta t_1, t_2, t_3, t_4, t_k. Ova aproksimacija zadovoljava za slučaj da segmenti nisu suviše veliki.
Tačke 1, 2, 3, 4, k su na sredini segmenta s obzirom da ako je uzet dovoljan broj segmenata luk u segmentu se može aproksimirati sa pravom linijom tako da odgovarajuće površine ispod luka i prave budu jednake, sl. 5. Pri ovome intervali segmenata τ_k ne moraju biti jednaki, dok će srednje temperature t_k, merodavne za proračun (k=1, 2, 3, 4...). Na ovaj način, dijagram zagrevanja $t = f(\tau)$ aproksimiran je tzv. „stubastim“ dijagramom (histogramom), koji je konstruisan na bazi odgovarajućih srednjih temepratura $t_k(k = 1, 2, 3, 4 \dots)$.
Završetak nestacionarnog stanja, određuje se grafički tako da porast temeprature ne bude veći od 2-3 ^{0}C [23,25,29], što za praksu zadovoljava.
Prema tome, za stacionarno stanje je $t_{st} = const$ dok je vreme stacionarnog zagrevanja t_{st} i ono se obično zadaje, zavisno od konkretne termičke obrade.



Slika 4. Kriva zagrevanja u dijagramu $t = f(\tau)$ podeljena na odsečke u nestacionarnom području [1]

Na slici 4. S_k (k=1, 2, 3, 4...), strelicama su označene dubina oksidacije na kraju posmatranog segmenta. Isto tako fiktivna vremena τ_{fk-1}(k=1, 2, 3, 4) označena su na onom segmentu kod koga se koristi za proračun dubine oksidacije odnosno na koju srednju temperaturu se odnose. Množitelji a_k, b_k odnose se na srednje temperature t_k(k=1, 2, 3, 4) posmatranih segmenata. Za prvi interval, odnosno na kraju prvog intervala, dubina oksidacije biće prema jednačini (5):

$$S_1 = a_1 \sqrt{\tau_1} + b_1 \tau_1 \qquad (7)$$

Ovde je τ_1 vreme prvog (I) segmenta, dok se množitelji a_1 i $b_1$uzimaju za srednju temperaturu t_1, slika 5. Uvedimo zamišljeno fiktivno vreme τ_{f_1} pri kome će dubina oksidacije biti jednaka S_1 ali pri srednjoj temperaturi drugog (II) segmenta t_2. S obzirom na prethodno prema (7) sledi da je:

$$a_1\sqrt{\tau_1} + b_1\tau = a_2\sqrt{\tau_{f_1}} + b_2\tau_{f_1} \tag{8}$$

Fiktivno vreme u (8) τ_{f_1}, odredićemo uvođenjem smene:

$$\sqrt{\tau_{f_1}} = x^2 \rightarrow \tau_{f_1}=x^4 \tag{9}$$

Odnosno prema (8):

$$a_1\sqrt{\tau_1} + b_1\tau = a_2x^2 + b_2x^4 \tag{10}$$

odavde dobijamo jednačinu četvrtog stepena po x:

$$b_2x^4 + a_2x^2 - a_1\sqrt{\tau_1} - b_1\tau = 0 \tag{11}$$

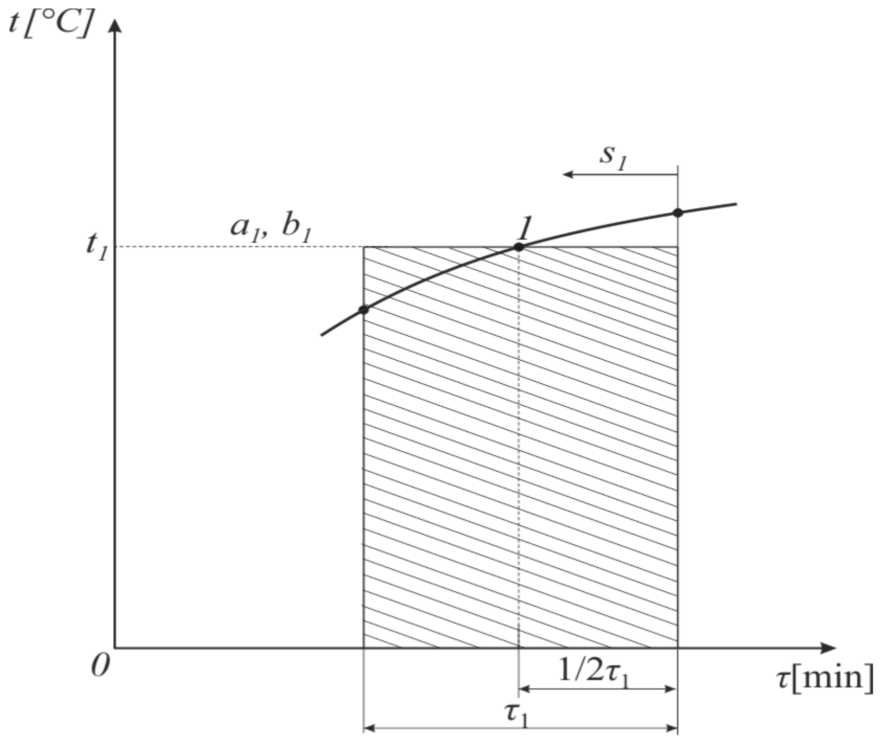
čije je rešenje, s obzirom na (9):

$$x^2 = \frac{-a_2 \pm \sqrt{a_2^2 + 4b_2\cdot(a_1\sqrt{\tau_1} + b_1\tau)}}{2b_2} = \sqrt{\tau_{f_1}} \tag{12}$$

$$\tau_{f_1} = \frac{\left[-a_2 \pm \sqrt{a_2^2 + 4b_2\cdot(a_1\sqrt{\tau_1} + b_1\tau_1)}\right]^2}{4b_2^2} \tag{13}$$

U relaciji, množitelji a_2, b_2 određuju se za temperaturu narednog, odnosno drugog (II) intervala t_2. Zbog ovoga τ_{f_1} je označena na ordinati drugog (II) segmenta.

Radi preglednijeg i jednostavnijeg proračuna dubine oksidacije u nestacionarnom području, u tabeli 2., uneseni su svi neophodni parametri za svaki segment, uključujući i fiktivno vreme τ_f.



Slika 5. Prvi segment krive zagrevanja pri proračunu dubine oksidacije [1]

Tabela 2. Parametri za proračun dubine oksidacije u nestacionarnom području

Interval	1	2	3	4	k-1	k
Temperatura t_k	t_1	t_2	t_3	t_4	t_{k-1}	t_k
Vreme τ_k	τ_1	τ_2	τ_3	τ_4	τ_{k-1}	τ_k
Fiktivno vreme τ_f	τ_{f_1}	τ_{f_2}	τ_{f_3}	τ_{f_4}	$\tau_{f_{k-1}}$	τ_{f_k}

Dubina oksidacije na kraju drugog (II) intervala S_2, dobija se prema relaciji (5) gde se mora dodati izračunato fiktivno vreme τ_{f_1}. Razlog za ovo je očigledan jer se mora dodati uticaj oksidacije tokom prvog intervala.
Odavde sledi da je:

$$S_2 = a_2\sqrt{(\tau_2 + \tau_{f_1})} + b_2(\tau_2 + \tau_{f_1}) \qquad (14)$$

Fiktivno vreme τ_{f_1} u relaciji je poznato i određeno je prema (13). Množitelji a_2, b_2 uzimaju se prema temperaturi t_2.
Kao i u prošlom slučaju, uvedimo fiktivno vreme τ_{f_2} je s obzirom na temperaturu t_3. Izjednačenjem dubine oksidacije prema (14) biće:

$$a_2\sqrt{(\tau_2 + \tau_{f_1})} + b_2(\tau_2 + \tau_{f_1}) = a_3\sqrt{\tau_{f_2}} + b_3\tau_{f_2} \qquad (15)$$

Odavde, fiktivno vreme τ_{f_2} biće:

$$\tau_{f_2} = \frac{\left[-a_3 \pm \sqrt{a_3^2 + 4b_3\left[a_2\sqrt{\tau_2 + \tau_{f_1}} + b_2(\tau_2 + \tau_{f_1})\right]}\right]^2}{4b_3^2} \qquad (16)$$

Na isti način za treći interval biće:

$$S_3 = a_3\sqrt{(\tau_3 + \tau_{f_2})} + b_3(\tau_3 + \tau_{f_2}) \qquad (17)$$

Odnosno nakon izjednačavanja relacije:

$$a_3\sqrt{(\tau_3 + \tau_{f_2})} + b_3(\tau_3 + \tau_{f_2}) = a_4\sqrt{\tau_{f_3}} + b_4\tau_{f_3} \qquad (18)$$

Odavde, fiktivno vreme, s obzirom na temepraturu t_4 biće:

$$\tau_{f_3} = \frac{\left[-a_4 \pm \sqrt{a_4^2 + 4b_4\left[a_3\sqrt{\tau_3 + \tau_{f_2}} + b_3(\tau_3 + \tau_{f_2})\right]}\right]^2}{4b_4^2} \qquad (19)$$

Odavde sledi opšti zakon za bilo koji segment odnosno odsečak:

$$\tau_{f_k} = \frac{\left[-a_{k+1} \pm \sqrt{a_{k+1}^2 + 4b_{k+1}\left[a_k\sqrt{\tau_k + \tau_{f_{k-1}}} + b_k(\tau_k + \tau_{f_{k-1}})\right]}\right]^2}{4b_{k+1}^2} \qquad (20)$$

Iz prethodne analize, s obzirom na (19) sledi da će dubina oksidacije na kraju proizvoljnog k-tog intervala biti:

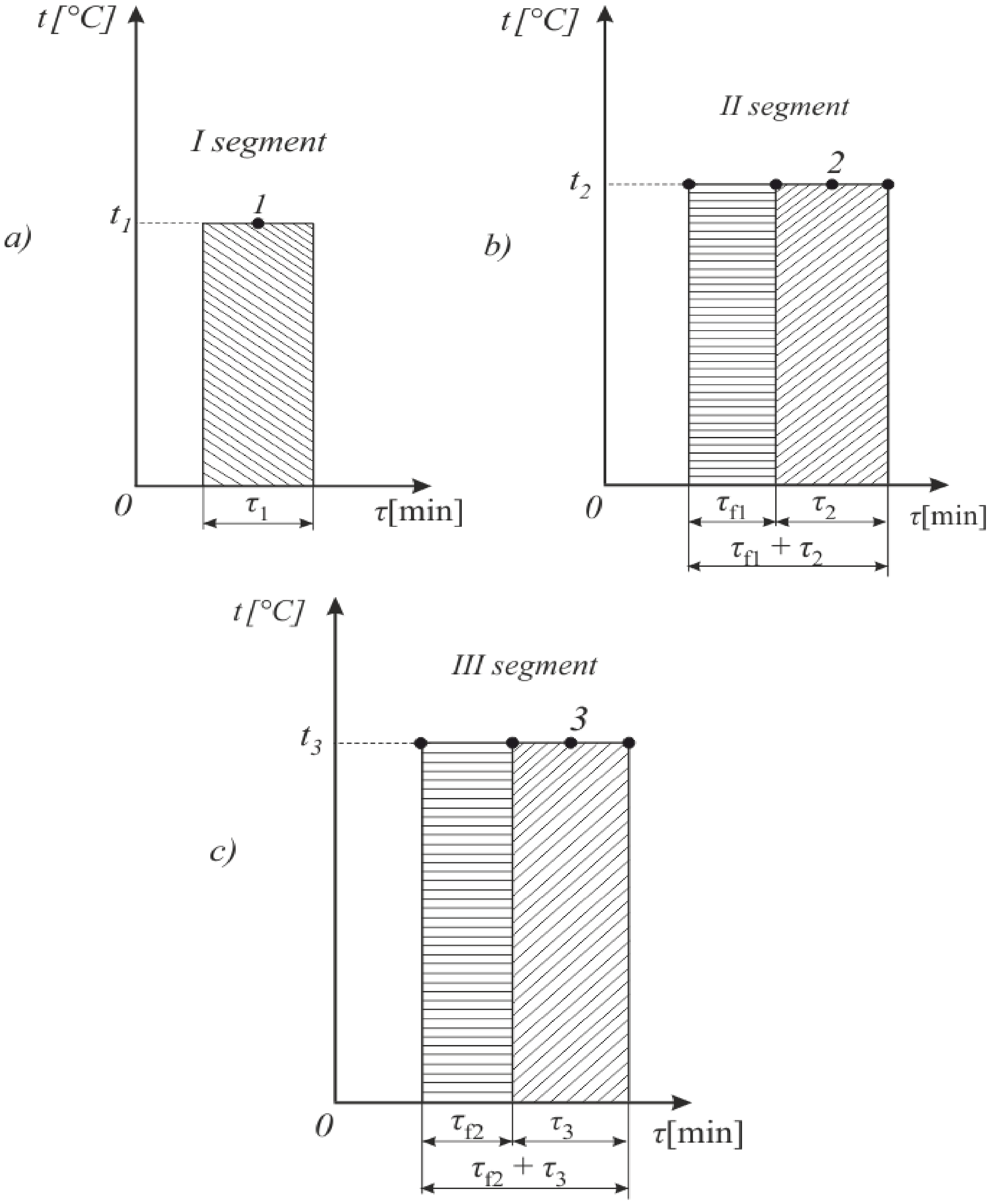
$$S_k = a_k\sqrt{(\tau_k + \tau_{f_{k-1}})} + b_k(\tau_k + \tau_{f_{k-1}}) \qquad (21)$$

Izvedene opšte zavisnosti (20) i (21) predstavljaju glavne relacije za rešavanje postavljenog problema, sa aspekta dubine oksidacije, za proizvoljno vreme nestacionarnog procesa [1].
Pokazaćemo kasnije da se ovaj model može primeniti i za određivanje dubine razugljeničenja.

16.1. APROKSIMACIJA KRIVE ZAGREVANJA SEGMENTIMA

Na slici 6., za prva tri segmenta (I, II, III) prikazane su merodavne temeprature i vremena za proračun dubine oksidacije S_1, S_2 i S_3 za nestacionarno područje. Pri ovome uključeno je i odgovarajuće fiktivno vreme.

Treba zapaziti da se dubina oksidacije za prvi segment S_1, određuje kao za slučaj stacionarnog stanja gde je merodavna srednja temperatura segmenta S_1. Ovo je jedini segment gde se u proračunu ne uključuje fiktivno vreme.

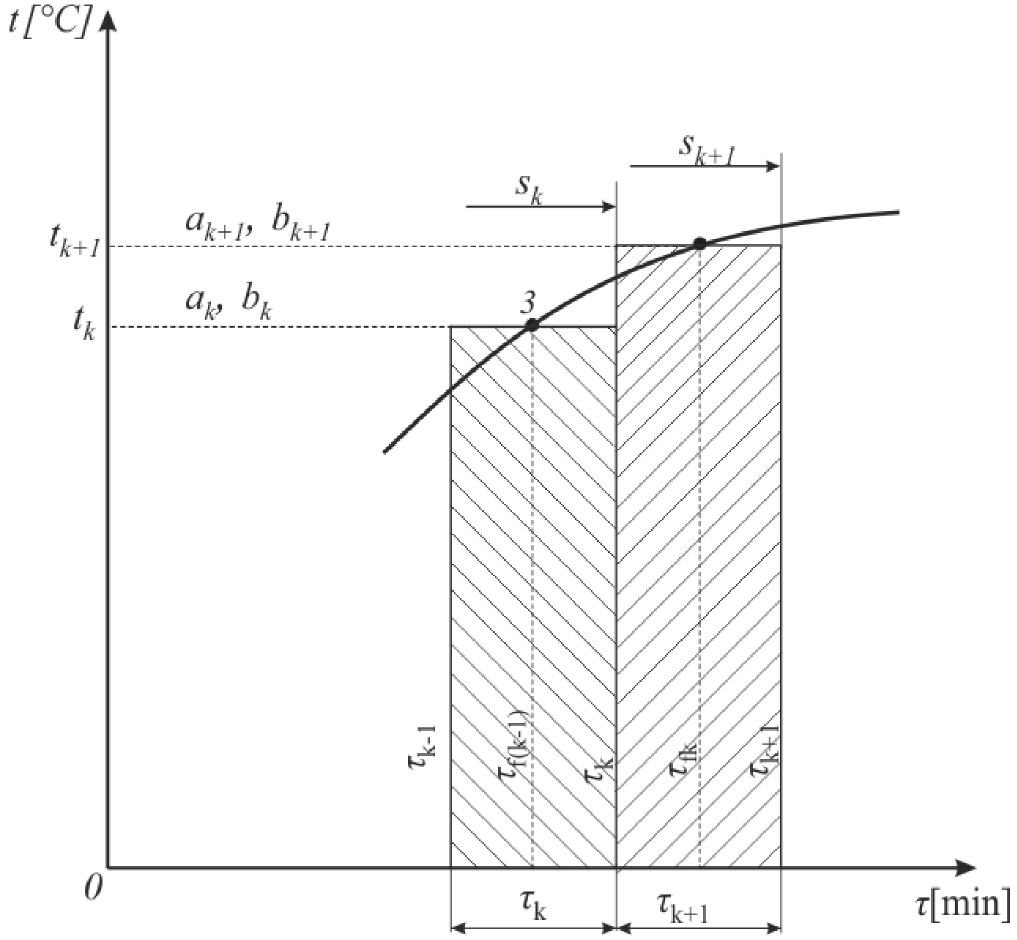


Slika 6. Odsečci krive zagrevanja za prvi, drugi i treći segment sa merodavnim fiktivnim vremenom [1]

Kod proračuna dubine oksidacije drugog intervala S_2 uključuje se fiktivno vreme τ_{f_1}, kod proračuna S_3 uključuje se τ_{f_2} itd. do poslednjeg segmenta. Prema tome dubina oksidacije S_2 ostvaruje se pri temperaturi t_2 za fiktivno vreme τ_{f_1}, dubina oksidacije S_3 pri t_3 za τ_{f_2} itd., do kraja poslednjeg segmenta nestacionarnog stanja.

Na bazi prethodne analize, na slici 7. prikazani su u opštem slučaju parametri za proračun dubine oksidacije u dijagramu (t, τ) za slučaj nestacionarnog stanja. Oznaka „k“ odnosi se na proizvoljni segmnet, a oznaka „k+1“ na sledeći, odnosno naredni, segment. Očigledno, oznaka S_k odnosi se na dubinu oksidacije na kraju k-tog segmenta.

Napomenimo da kada bi se izvršilo direktno sabiranje dubine oksidacije svih segmenata, to ne bi odgovaralo realnom stanju, što je očigledno iz prirode problema.



Slika 7. Zamena krive zagrevanja segmentima, odnosno stubastim dijagramom u nestacionarnom području [1]

5. POSTUPAK ZA REŠAVANJE DUBINE RAZUGLJENIČAVANJA ZA NESTACIONARNO STANJE

Na sličan način, može se izračunati i dubina razugljeničenja u toku zagrevanja, pri čemu se period zagrevanja deli na *k* intervala, pa je i ovde dubina razugljeničenja na kraju *k*-tog intervala:

$$S = a_k \sqrt{[\tau_k + \tau_{f(k-1)}]} \qquad (22)$$

gde je fiktivno vreme:

$$\tau_{fk} = \left(\frac{a_k}{a_{k-1}}\right)^2 \qquad (23)$$

Važno je, za razliku od prethodnog slučaja, da se ovde množitelj a odnosi na difuziju atoma ugljenika u čeliku i treba ga računati u približnim računima prema relaciji [34,36,37]:

$$a = \sqrt{12D} \qquad (24)$$

Napomenimo da su autori ovog rada u radu [1] dali prikaz jednog grafo-analitičkog postupka koji se može koristiti kao približno aproksimativno rešenje postavljenog problema a koje je manje tačno od predloženog.

U istom radu [1] prikazan je detaljno i jedan karakterističan računski primer iz prakse gde je verifikovana prikazana metoda, pri čemu je određena dubina oksidacije kako za stacionarno tako i za nestacionarno stanje.

6. REDOSLED PROCEDURE PRIMENE IZVEDENOG MODELA

Uzimajući prethodno, određivanje dubine oksidacionog sloja, odnosno dubine razugljeničenja sprovodimo po sledećem redosledu:

1. Konstruisanje krive zagrevanja (dijagram τ - t) u određenoj razmeri, koja se određuje eksperimentalno, za zadate uslove.
2. Podela nestacionarnog područja, koje je određeno grafički, na određeni broj segmenata (koji ne moraju biti jednaki po veličini).
3. Utvrđivanje vremena τ_i za svaki segment tako da je $\tau_{ns} \geq \tau_i$.
4. Određivanje temperature t_i u svakoj tački na sredini segmenta, sa konstruisanog grafika.
5. Određivanje množitelja a i b prema odgovarajućoj literaturi za zadati čelik i za temperature iz tačke 4.
6. Određivanje fiktivnog vremena (τ_f) prema relaciji (13) odnosno (20) za svaki temperaturni interval.
7. Određivanje ubine oksidacije nestacionarnog područja, prema realciji (21) za poslednje područje.
8. Dubina oksidacije stacionarnog stanja se određuje jednostavno kao $S_{ts} = a_{st} \cdot \sqrt{\tau \cdot st} + b_{st} \cdot \tau_{st}$.
9. Ukupna dubina oksidacije se određuje kao zbir dubine nestacionarnog i stacionarnog područja.
10. Dubina za razugljeničenje se određuje na sličan način prema relacijama (22) – (24).

7. ZAKLJUČAK

Za regulisanje dodatka za mehaničku obradu posle termičke obrade od velike je važnosti poznavanje dubine oksidacije i razugljeničenja. Obe ove pojave imaju različit značaj u zavisnosti od vrste čelika i njihove namene. Kod niskougljeničnih čelika sa sadržajem ugljenika ispod 0,3 % najveći značaj ima oksidacija površine, dok su kod čelika predviđenih za kaljenje značajne obe pojave. Od niskougljeničnih čelika treba izuzeti kaljene čelike za cementaciju, gde su izuzetno obe pojave značajne. Isto tako, razugljeničenje se javlja i kod niskougljeničnih čelika ali je manje značajno.

Dobijeno opšte rešenje za određivanje dubine oksidacije, odnosno dubine razugljeničenja kod čelika, zbog zamene krive zagrevanja sa „stubastim“ dijagramima je aproksimativno, ali u mnogim slučajevima u praksi zadovoljava, sobzirom da spada u grafička rešenja. Tačnost rešenja se može povećati usvajanjem većeg broja segmenata ali je tada vreme računanja duže.

Pri praktičnoj primeni modela, kao što je pokazano, radi preglednosti i praćenja rezultata, odnosno inženjerskog pristupa problemu, treba sprovoditi uporedo grafički i tabelarani prikaz veličina. Radi jednostavnijeg rešavanja problema uvedeno je neko zamišljeno, odnosno fiktivno vreme, što znatno uprošćava rešavanje postavljenog složenog problema. Treba zapaziti da se pri primeni modela određuje dubina oksidacije samo za poslednji segment, koja predstavlja predstavlja traženo rešenje, dok se fiktivno vreme mora odrediti za svaki segment, s obzirom da ono uzima u obzir učinak oksidacije prethodnih segmenata. Pri ovome odabrana vremena segmenata τ_k, ne moraju biti jednaka, što jednim delom olakšava proračun.

S obzirom da je predloženi model opšteg karaktera može se direktno primeniti u praksi. Isto tako model je pogodan za izradu računskog programa čime bi se analize i vreme računanja znatno skratili. Na ovaj način, mogao bi se uvesti u proračun proizvoljan broj segmenata i tako izvršila analiza njihovog uticaja na tačnost dobijenih rezultata.

Tačnost dobijenih rezultata prvenstveno zavisi od tačnosti konstruisane krive zagrevanja i tačnosti množitelja a i b, koji se eksperimentalno određuju za pojedine čelike, ili se uzimaju iz odgovarajuće literature za date uslove. Prikazana metoda na bazi uvođenja fiktivnog vremena postavljeni složeni problem određivanja dubine oksidacije i razugljeničenja rešava na relativno jednostavan način. S obzirom da se oksidacija kod čelika javlja u intervalu 550-1200 ^{0}C, to je prema predloženom modelu za proračun dovoljno uzeti 6-7 segmenata u razmaku od 100 ^{0}C. Slična situacija je i kod razugljeničenja. Množitelji *a* i *b*, u literaturi se obično određuju za isti temperaturski razmak. Za ovaj slučaj tačnost metode je najveća jer ne treba izvoditi interpolaciju.

Dobijeno rešenje, u odnosu na postojeće teorijsko analitičko rešenje, je znatno pogodnije i brže, a time i efikasnije za praktičnu primenu. Razlog za ovo je taj što je teorijsko rešenje znatno složenije i komplikovanije s matematičkog aspekta.

Razugljeničenje, kao nepoželjna pojava kod čelika pri visokim temperaturama, kao što je pokazano, može se analizirati i proračunavati prema datom modelu koji se odnosi na dubinu oksidacije, relacije (22-24).

Treba konstatovati da se zagrevanje čeličnih proizvoda najčešće obavlja u vazduhu. Isto tako oksidacija i razugljeničenje čelika nastaju i pri zagrevanju produktima sagorevanja, kao i u toplim kupatilima sa rastopljenim solima. Ovi uslovi znatno utiču kako na krivu zagrevanja, tako i na množitelje *a* i *b*.

8. LITERATURA

1. M. Riđošić, B. Pejović, M. Tomić, S. Smiljanić, Određivanje dubine oksidacije niskougljeničnih čelika pri nestacionarnim uslovima uvođenjem fiktivnog vremena, Zaštita materijala 58 (1) (2017) 104-115.
2. A.P. Guljaev (2010) Termičeskaje obrabotka, Mašgiz, Moskva.
3. D. Clark (2010) Physikal Metallurgy for Engineer, New York.
4. A.D. Assonov (2000) Tehnologija termičeskoj obrabotki detolej mašin, Moskva.
5. M.A. Balter (2003) Uproćnenie detalej mašin, Mašinostroenie, Moskva.
6. M.A. Berništejn (2004) Termonohaničekaja abrabotka metalov i splavov I, II, Učpetgiz, Moskva.
7. U. Dehlinger (2008) Teoretische Metallkunde, Springer, Berlin.
8. E. Bickel (2004) Die metalischen Werkstoffe des Maschinenbaes, Shringer, Berlin.
9. C. E. Bleckmann, (2010) Die Härterei, Springer, Berlin.
10. R. W. Cahn (2011) Physikal Metallurgy, VTN, Amsterdam.
11. P. R. Roberge,Handbook of Corrosion Engineering, McGraw-Hill, New York, 2000.
12. W. Hanfe (2012) Schenellstähle, München.
13. G.V. Karpenko (2000) Vlijanie difuzionih pokritij na pročnost stalnih izdelij, VŠ, Kiev.
14. G.A. Kašenko (2000) Osnovi metalovedenija, Mašgiz, Leningrad.
15. I.S. Kozlovskij (1995) Himiko-termičeskaja obrabotka šesteren, Mašinostroenie, Moskva.
16. M. Antonijević, M.G. Pavlović, Č. Lačnjevac, S. Mladenović, Korozija i zaštita čelika, SITZAMS, Beograd (1988).
17. R.E. Reed-Hill (2010) Physical Metallurgy Principles, New York.
18. I. Eish, Osnove površinske zaštite, Fakultet strojarstva i brodogradnje, Sveučilište u Zagrebu, Zagreb (2003).
19. S. Mlađenović, Zaštita materijala, Beograd 42(3) (2001) 15.
20. V.A. Dobrovoljskij, K.I. Zblonskij, S.L. Mak, A.S. Radčik, L.B. Erlih, Detali Mašin Mašinostroenije, Moskva (1972).
21. S. Đorđević, Metalne prevlake, Tehnička knjiga Beograd (1970).
22. R. Bunker, J. Bailey (2001) Effect of Squealer Cavity Depth and Oxidation on Turbine Blade Tip Heat Transfer, ASME Turbo Expo 2001: Power for Land, Sea, and Air Volume 3: Heat Transfer; Electric Power; Industrial and Cogeneration, New Orleans, Louisiana, USA, June 4–7.
23. G. Schuerman, Verbindungsellemente VEB Fachbuchverlag, Leipsig (1972).

24. X. Liao, D. Zhao, X. Yan (2011) Determination of potassium permanganate demand variation with depth for oxidation–remediation of soils from a PAHs-contaminated coking plant, Journal of Hazardous Materials, Volume 193, Pages 164–170.
25. K.I. Popov, B.N. Grgur, Osnovi elektrometalurgije, Tehnološko-metalurški fakultet, Beograd (2002).
26. V. Vujičić, Korozija i tehnologija zaštite metala, Vojna akademija, Beograd (2002).
27. Y. Li, T. Qiu (2007) Oxidation behaviour of boron carbide powder, Materials Science and Engineering: Volume 444, Issues 1–2, Pages 184–191.
28. D. Blowes, E. Reardon, J. Jambor, J. Cherry (1991) The formation and potential importance of cemented layers in inactive sulfide mine tailings, Geochimica et Cosmochimica Acta, Volume 55, Issue 4, Pages 965-978.
29. C.S. Liu, S.N Atluri (2009) A Fictitious Time Integration Method for the Numerical Solution of the Fredholm Integral Equation and for Numerical Differentiation of Noisy Data, and Its Relation to the Filter Theory, CMES, vol.41, No.3, pp.243-261.
30. S.D. Cramer, B.S. Covino, ASM Handbook, vol 13A, Corrosion Fundamentals, Testing and Protection, ASM International; Materials Park, Ohio (2003).
31. C.S. Liu, S.N. Atluri (2008) A Fictitious Time Integration Method (FTIM) for Solving Mixed Complementarity Problems with Applications to Non-Linear Optimization, CMES, vol.34, No.2, pp.155-178.
32. M.S. Hashemi, D. Baleanu (2016) Numerical approximation of higher-order time-fractional telegraph equation by using a combination of a geometric approach and method of line, Journal of Computational Physics, Volume 316, Pages 10–20.
33. L. Sun, W. Chen, A.H.-D. Cheng (2016) Method of fundamental solutions without fictitious boundary for plane time harmonic linear elastic and viscoelastic wave problems, Computers & Structures, Volume 162 Pages 80–90.
34. M. E. Blanter, Metallovedenije i termičeskaja obrabotka, Mašgiz, Moskva (1989).
35. A. P. Guljajev, Metallovedenije, Metallurgija, Moskva (2001).
36. N. Malešević, Osnove nauke o metalima, Tehnička knjiga, Zagreb (1999).
37. V. A. Butalov, Tehnologija metallov, Mašgiz, Moskva (2005).

Development of biological procedure of wastewater emulsion from metalworking process

Razvoj biološkog postupka prečišćavanja otpadne vodene emulzije iz procesa obrade metala

Vesna Lazarević[1], Ivan Krstić[2]

[1]Military hospital, Nis, Serbia,

[2]University of Niš, Faculty of Occupational Safety, Niš, Serbia

[1]Vojna bolnica, Niš, Srbija

[2]Univerzitet u Nišu, Fakultet zaštite na radu, Niš, Srbija

Abstract

Research carried out within this paper had the aim of developing a process of biological treatment of waste water emulsion obtained in the technological metalworking process. What was performed was the isolation of strains with the ability of degradation and rapid growth in the water emulsions of mineral oil, as well as the isolation of a strain of the microorganism in the waste oil-in-water emulsion and the identification to the level of the genus. Based on the biochemical characteristics of the isolate and comparison with the properties of Gram-negative bacteria, it is assumed that an isolated bacterium belongs to the genus Pseudomonas.

Key words: *metalworking, wastewater emulsion, biological treatment.*

Izvod

Istraživanja sprovedena u okviru rada imala su cilj razvoj postupka biološkog prečišćavanja otpadne vodene emulzije iz tehnološkog procesa obrade metala. Izvršeno je izolovanje sojeva sa sposobnošću razgradnje i brzog rasta na vodenim emulzijama mineralnog ulja, kao i izolacija soja mikroorganizma iz otpadne vodene emulzije i identifikacija do nivoa roda. Na osnovu biohemijskih karakteristika izolata i poređenja sa osobinama Gram negativnih bakterija pretpostavljeno je da izolovana bakterija pripada rodu Pseudomonas.

Ključne reči: *obrada metala, otpadna vodena emulzija, biološko prečišćavanje.*

1. UVOD

Iscrpljene vodene emulzije iz procesa obrade metala sadrže, po pravilu, ulja i masti, organska jedinjenja, kao i sekundarna ulja i antikorozivna sredstva, jone metala i drugo. Pošto mogu imati negativan efekat na životnu sredinu, one se moraju obraditi pre odlaganja. Primarni postupak prečišćavanja otpadnih vodenih emulzija koristi se za separaciju slobodnih i neemulgovanih ulja, kao i za uravnotežavanje toka otpadne vode i koncentracije ulja. U fazi sekundarnog prečišćavanja otpadnih emulzija ulje-voda, postiže se uklanjanje emulgovanog ulja i velike frakcije rastvorenog ulja [1]. Nakon toga primenjuje se tercijalno biološko prečišćavanje koje se zasniva na osnovnim biološkim procesima koji se javljaju u prirodi. U principu biološki procesi prečišćavanja otpadnih voda su:

- procesi aktivnim muljem,
- procesi biološke filtracije i

- procesi u jezerima i lagunama.

U ovim procesima, polarna biodegradabilna ulja i masti uklanjaju se do nivoa od 2-8 mg/dm^3 u prerađenoj otpadnoj vodi, dok se nepolarna ulja i masti uklanjaju primarnom klarifikacijom ili se inkorporiraju u biološke flokule.

Biološki procesi prečišćavanja otpadnih voda baziraju se na nekim osnovnim principima:

- populacija aktivnog mulja sastoji se od različitih mikroorganizama prirodnih sredina čiji se rast i razvoj ne odigravaju u optimalnim fiziološkim uslovima,
- supstrat predstavljaju otpadne vode koje po hemijskom sastavu i ostalim karakteristikama mogu biti veoma različite i
- koncentracije supstrata obično su niske u odnosu na vrednosti za gajenje mikroorganizama i proces je usmeren ka razgradnji organskih materija, koje je teško ukloniti hemijskim i mehaničkim putem, kao što su masne kiseline i amini, a ne na stvaranju biomase ili korišćenju produkata metabolizma [2, 3].

Najvažniji inženjerski problemi u biološkom prečišćavanju otpadnih voda vezani su za obezbeđenje velike kontaktne površine i efikasno rastvaranje kiseonika. Pored njih, značajni su i problemi vezani sa flokulaciju čestica i taloženje mikroorganizama.

Vodene emulzije pokazuju visoku osetljivost na dejstvo mikroorganizama, pod čijim se uticajem razlažu. Mikroorganizmi prouzrokuju kvarenje emulzija nakon razblaživanja mineralnog ulja sa vodom. Mineralno ulje je, uglavnom, bez mikroorganizama zbog sadržaja mikrobiocida, ali se u toku pripreme emulzije (razblaživanjem sa vodom) i rada kontaminira iz okoline. Broj i vrsta mikroorganizama u radnoj emulziji zavise od uslova rada, prisutne mikroflore u radnim prostorijama i tankovima, kao i mikrobiološke kontrole. Zbog svog sastava, mali broj mikroorganizama može preživeti u emulziji. Mikroorganizmi pronađeni u emulzijama pripadaju Gram negativnim bakterijama iz rodova: *Aeromonas, Pasteurella, Acinetobacter, Moraxella, Bacteroides, Citrobacter, Desulfovibrio, Alcaligenes, Serratia, Pseudomonas, Enterobacter, Escherichia, Proteus* i *Providencia*. Gram pozitivne bakterije se ređe nalaze u emulzijama, ali ponekad su prisutne: *Bacillus, Micrococcus* i *Mycobacteria* [4].

Za svoj razvoj bakterije zahtevaju vodu, organske supstance i odgovarajuće uslove temperature i pH. Uslovi primene vodenih emulzija, u odsustvu inhibitora, povoljni su za mikrobni rast i razmnožavanje, a rezultati njihove aktivnosti su razgradnja emulzije, smanjenje pH, povećanje korozije, degradacija sastojaka i gubitak moći podmazivanja. Aerobne bakterije zahtevaju kiseonik u metaboličkim procesima i efikasno troše ulje, dok anaerobne bakterije rastu u okruženju sa nedostatkom kiseonika, hrane se mineralnim uljem i produkuju škodljive sporedne proizvode, kao što je vodonik-sulfid. Bakterije mogu, takođe, uzrokovati povećanu penušavost i separaciju ulja i prouzrokovati začepljenje vodova, filtera i ventila. Među aerobnim bakterijama najčešće se u emulzijama javljaju bakterije iz roda *Pseudomonas* koje su striktni aerobi. Aerobi, obično, ne izazivaju neprijatan miris emulzuje. Anaerobne bakterije se razmnožavaju u uslovima kada aerobne bakterije potroše sav kiseonik iz emulzije. Izazivaju, najčešće, neprijatan miris na “pokvarena jaja”, odnosno oslobađanje vodonik-sulfida [5].

Najčešće posledice rasta mikroorganizama u vodenim emulzijama mineralnih ulja su tamnjenje emulzije i delova na mašinama, razdvajanje vodene i uljane faze (narušavanje stabilnosti emulzije, što često prouzrokuje začepljenje vodova), povećana penušavost i narušavanje antikorozivne osobine emulzije [6]. U cilju uklanjanja mogućih problema izazvanih mikroorganizmima, potrebno je vršiti stalnu kontrolu vodenih emulzija, čistiti mašine i rezervoare, aerisati emulzije radi odstranjivanja neprijatnog mirisa i, u krajnjem slučaju, naknadno dodavati aditive koji sprečavaju rast mikroorganizama.

Neki od kontaminanata, na primer bakterije *Pseudomonas* sp., imaju sposobnost razgradnje uljanih komponenata vodenih emuzija [4]. Ova osobina može biti iskorišćena za potencijalnu primenu kontaminanata u procesima prečišćavanja otpadnih vodenih emulzija.

Usled mikrobiološke razgradnje emulgovana ulja su podložna kvarenju. Zbog toga su u njihovim formulacijama neophodne komponente koje će regulisati i sprečavati rast bakterija, gljiva, kvasaca, baktericida i fungicida, prikazano u tabeli 1. Iz ove grupe dodataka najpoznatija su jedinjenja formaldehida i fenola od kojih visoku efikasnost pokazuje 3-metil-hlorfenol [7].

Tabela 1. Komponente vodenih emulzija za obradu metala [7,8,9]

Komponenta	Primer
Emulgatori	Anjonski emulgatori (soli sulfonske kiseline, soli karbonske kiseline, estri fosforne kiseline, sarkozin) Katjonski emulgatori (soli amida masnih kiselina, kvaternarne amonijačne soli) Nejonogeni emulgatori (poliglikol etri, fenoli, masne kiseline masni amini)
Antikorozivni dodaci	Nirtriti, borati, amidi i estri borne kiseline, karbonske i dikarbonske kiseline, N-acil sarkozin, sulfonamido karbonske kiseline
Biocidi	Fenoli, hlorfenoli, formaldehid, triazini, derivati kvaternarnih amonijačnih soli
EP-aditivi	Polialkilenglikoli, estri fosforne kiseline iz etoksilovanih alkohola, hlorovani parafini, sumporna jedinjenja

2. EKSPERIMENTALNI DEO

Za izolaciju mikroorganizama korišćena je metoda iscrpljivanja ploča i serijskih razblaženja na podlozi sledećeg sastava (g/dm^3): mineralno ulje - 1, agar - 1 i destilovana voda (do 1 dm^3).
Izolati su identifikovani bojenjem po Gramu, analizom rasta na različitim temperaturama i biohemijskim testovima: katalaza test, rast na argininu i stvaranje kiseline na podlogama sa različitim šećerima.
Da bi se došlo do sojeva mikroorganizama, potencijalno upotrebljivih za biološko prečišćavanje otpadne vodene emulzije, izvršena je izolacija mikroorganizama kontaminanata otpadne vodene emulzije. Izolovanje mikroorganizama je vršeno na selektivnoj podlozi koja je sadržala mineralno ulje kao izvor nutritijenata za mikrobni rast. U ovom pristupku je pretpostavljeno da izolati koji rastu na podlozi sa mineralnim uljem imaju mogućnost razgradnje njegovih komponenata, a time i potencijalnu primenu za biološko prečišćavanje otpadnih vodenih emulzija.

3. REZULTATI I DISKUSIJA

Poznato je da u vodenim emulzijama mineralnih ulja i otpadnim vodenim emulzijama dolazi do smanjenja koncentracije komponenata ili do nestanka nekih od njih, kao rezultat fizičkih, hemijskih i bioloških procesa. Efekat smanjenja koncentracije nekih komponenata vodenih emulzija pod uticajem biološkog agensa mogao bi se, pod određenim uslovima, iskoristiti za prečišćavanje otpadnih vodenih emulzija ili za dalje prečišćavanje otpadne vode iz procesa hemijskog prečišćavanja. Biološko prečišćavanje bi se zasnivalo na primeni sojeva mikroorganizama koji se odlikuju dobrim rastom u vodenim emulzijama mineralnih ulja u toku primene ili u otpadnim vodenim emulzijama u toku skladištenja.
Na selektivnoj podlozi sa mineralnim uljem, nakon inkubacije od 48 sati, uočene su jedino bele, sjajne, neprozirne, ispupčene kolonije sa nepravilnom ivicom, veličine 3-5 mm. Na mikroskopskom preparatu uočeni su Gram negativni kratki štapići sa zaobljenim krajevima, pojedinačno ili u paru.

Biohemijske karakteristike izolata date su u tabeli 2. Bakterija izolovana iz otpadne emulzije jako slabo raste na šećerima, što je razumljivo s obzirom na sredinu iz koje je izdvojena. Upoređivanjem rezultata iz tabele 2 sa osobinama Gram negativnih bakterija [5], može se pretpostaviti da izolovana bakterija pripada rodu *Pseudomonas* [10]. Na ovakvu pretpostavku upućuju rezultati mikroskopskog istraživanja (bojenje po Gramu i oblik ćelija), kao i činjenica da raste na malom broju ugljenih hidrata (tabela 2) i ne zahteva organske faktore rasta (izolat je pokazao rast samo na 1 % rastvoru emulzije). Sve ostale Gram negativne bakterije koje su, prema literaturi [8] pronađene u otpadnoj emulziji mineralnog ulja zahtevaju ogranske faktore i šećere za svoj rast.

Tabela 2. Karakteristike izolata iz otpadne vodene emulzije

Karakteristika	Izolat	*Pseudomonas* sp.[**]
Bojenje po Gramu	-	-
Oblik ćelije	Kratki štapići sa zaobljenim krajevima	Štapići ili kokobacili
Rast na (°C)		
20	+	Zavisno od vrste
30	+	
40	-	
Katalaza	+	+
Arginin	+	+
Gas iz glukoze	-	- ili +
Stvara kiselinu iz		Zavisno od vrste s zajedničkom karakteristikom da ne zahtevaju organske faktore rasta
trehaloze	+	
manitola	+	
glicerola	+	
arabinoze	-	
saharoze	-	
rafinoze	-	
riboze	-	
sorbitola	-	
ksiloze	-	
maltoze	-	
rafinoze	-	
galaktoze	-	
manoze	-[*]	
glukoze	-[*]	
fruktoze	-[*]	
laktoze	-[*]	

[*] Rast bez stvaranja kiseline

[**] Bergey's Manual of Determinative Bacteriology [11]

4. ZAKLJUČAK

Iz otpadne vodene emulzije izolovan je jedan soj koji, na selektivnoj podlozi sa mineralnim uljem, stvara bele, sjajne, neprozirne, ispupčene kolonije sa nepravilnom ivicom, veličine 3-5 mm. Na mikroskopskom preparatu uočeni su Gram negativni kratki štapići sa zaobljenim krajevima, pojedinačno ili u paru. Na osnovu biohemijskih karakteristika izolata i poređenja sa osobinama Gram negativnih bakterija pretpostavljeno je da izolovana bakterija pripada rodu Pseudomonas. Zbog dobrog rasta na vodenoj emulziji mineralnog ulja, izolovani soj, kao potencijalni industrijski mikroorganizam u postupcima prečišćavanja otpadnih vodenih emulzija, treba podvrgnuti daljem proučavanju. Preduslov daljih istraživanja je prethodno ispitivanje patogenosti izolovanog soja.

5. LITERATURA

1. Brinksmeiera, E., Meyera, D., Huesmann-Cordesa, A. G., Herrmannb, C., Metalworking fluids-Mechanisms and performance, CIRP Annals - Manufacturing Technology 2015, 64 (2), 605-628.
2. Fakhru’l-Razia, A., Pendashteha, A., Abdullaha, L. C., Biaka, D. R. A., Madaenic, S. S., Grady, Z. Z. A., Review of technologies for oil and gas produced water treatment, Journal of Hazardous Materials, 2009, 170(2-3), 530-551.
3. Grady, C. P. L., Daigger, Jr. G. T., Love, N. G., Filipe, C. D. M., Biological Wastewater Treatment, Third Edition, CRC Press, CRC Press Taylor and Francis Group, London, UK, 2011. pp. 3-26.
4. Trafny, E., Microorganisms in metalworking fluids: Current issues in research and management. Int. J. Occup. Med. Environ. Health. 2103, 26(1), 4-15.
5. Cyprowski, M., Piotrowska, M., Zakowska, Z., Szadkowska-Stanczyk, I., Microbial and Endotoxin Contamination of Water-Soluble Metalworking Fluids, Int. J. Occup. Med. Environ. Health 2007, 20(4), 365-71.
6. Byers, J. P., Metalworking Fluids, CRC Press, Taylor and Francis Group, Boca Raton, Florida, US, 2006.
7. Van Der Gast, C. J., Whiteley, A. S., Lilley, A., Knowles, C. J., Thompson I. P., Bacterial community structure and function in a metal-working fluid, Environmental Microbiology 2003, 5(6), 441-535.
8. Glasse, B., Zerwas, A., Guardani, R., Fritsching, U., Refractive indices of metal working fluid emulsion components, Measurement Science and Technology 2014, 25(3).
9. Rudnick, L. R., Synthetics, Mineral Oils, and Bio-Based Lubricants: Chemistry and Technology, Second Edition, CRC Press Taylor and Francis Group, Boka Raton, FL, 2013, pp. 3-123.
10. Azhdarpoor, A., Mortazavi, B., Moussavi, G. J. Oily wastewaters treatment using Pseudomonas sp. isolated from the compost fertilizer, Environ. Health. Sci. Eng. 2014, 12, 77.
11. Bergey, D. H., Holt, J. G. Bergey's manual of determinative bacteriology, 9th ed, Lippincott Williams and Wilkins, Philadelphia, 2000.

Novel method for synthesis of biocompatible hydroxyapatite/passive oxide layer on modified titanium surface

Zoran Janković[1], Marijana R. Pantović Pavlović[2], Anto Gajić[3], Veljko Marić[4], Jasmina Stevanović[2], Sanja Eraković[2], Miroslav M. Pavlović[2]

[1]V&Z Zaštita, d.o.o., Banja Luka, Republic of Srpska, Bosnia and Herzegovina

[2]University of Belgrade, ICTM-Department of Electrochemistry, Belgrade, Serbia

[3]Rudnik i termoelektrana Ugljevik, Republic of Srpska, Bosnia and Herzegovina

[4]University of East Sarajevo, Faculty of Medicine Foča, Republic of Srpska, Bosnia and Herzegovina

Abstract

Hydroxyapatite (HAp) is the most suitable biocompatible material for bone implant coatings. However, its brittleness is a major obstacle, and that is why, recently, research focused on creating composites. In this study, a novel in situ synthesis of HAp coating on titanium was presented. HAp was anaphoretically deposited from alkaline-ethanol suspension in one step process. Morphology of the coating was investigated by optical microscopy, while deposited HAp was characterized using ATR-FTIR. It was concluded that HAp has excellent coverage of the surface without delamination. The obtained coating can be good material for bone implants due to solving HAp brittleness.

Introduction

In recent years, new materials for use in orthopedic surgery have been the subject of extensive research. The main challenges of biological implants have an appropriate hardness, adhesion, biocompatibility and corrosion resistance. Titanium is one of a small number of biocompatible metals which has been successfully used as dental and medical implants, since it has advantageous properties such as strength, toughness, density, low Young's modulus, corrosion resistance and biocompatibility, which makes it suitable material for biomedical applications [1-6]. However, it was shown that titanium is not an ideal replacement for bone tissue due to differences in its physical and chemical characteristics in relation to the bone, which is reflected in poor osteoconductivity and osteoinductivity [7, 8]. On the other hand, the titanium can cause an adverse reaction of the body upon its implantation [9]. Although little of this problem is reported in the literature, there are isolated cases and studies to prove it.

In order to increase osteointegration and improve regeneration of the bone tissue on the implant, modification of titanium surface is required with a biologically active material. The most commonly used biocompatible material is a hydroxyapatite (HAp, $Ca_{10}(PO_4)_6(OH)_2$) [10]. Hydroxyapatite has the chemical structure that resembles bone mineral composition with similar release of Ca^{2+} и PO_4^{3-} ions and it can be used during the formation of new bone formation [11-13]. HAp has porous structure and due to its bioactivity HAp leads to its partial resorption and replacement of natural bone cells [14]. It has the possibility of creating a strong chemical bonds with bones.

The literature contains numerous methods for the synthesis of HAp. A microwave method leads to formation of suitable HAp coating with the composition and structure similar to bones [15-19]. HAp nucleation is favored by electrostatic binding with the hydroxyl groups of calcium ions [20, 21]. Many researchers have reported that in systems with polar molecules, microwave irradiation can be significantly speed up the chemical reaction by reducing the activation energy [22, 23].

Microwave hydrothermal method can be used as an alternative, which has been found to be suitable solution for preparation of the mesoporous HAp nanoparticles without the use of a template (mold) [24, 25]. Another way of obtaining of hydroxyapatite is direct or indirect chemical deposition, and chemical precipitation method consists of the reaction between $Ca(NO_3)_2 \cdot 5H_2O$, $(NH_4)_2HPO_4$, $NH_3 \cdot H_2O$ and C_2H_5OH, which forms HAp of controlled morphology and particle size [26].

Electrophoretic deposition (EPD) is another method of surface modification that is used for improving the bioactivity of the surfaces by deposition of calcium phosphate (CaP) particles on TiO_2 electrode under high voltage [27-29]. The advantages of this method are rapid formation of the coating, simple instrumentation, deposition of very pure stoichiometric coatings on complex surfaces. However, the EPD technique does not provide good adhesion of the coating to the substrate. For this reason, two step process - plasma electrolytic oxidation coupled with electrophoretic deposition - PEO-EPD for obtaining the porous hydroxyapatite coatings with incorporated particles of TiO_2 particles on titanium can be found in the literature. [29]. Electrolytic plasma oxidation is one the most useful methods for the surface modification of titanium since the porous and adherent coatings of nanotubular layer are obtained [29].

Due to major differences between the properties of the bioactive material and the metal substrate, adhesion of the coating to the substrate remains a major problem. During review of the literature it has been observed that most of the works dealing with a modification of the coating and the surface of the substrate without adhesion tests between them [7, 10, 29-31], nor adequate adhesion testing were performed which include mechanical testing [32]. The problem of poor adhesion of the coating appears in the form of delamination, poor mechanical properties and poor connections between the ceramic and metal. A potential solution to this problem is seen in the methods of surface modification of the substrate and/or HAp coatings in order to improve adhesion. Papers that have dealt with the adhesion of the coatings and substrate modifications [33-35] did not suggest a process which would, in the same time, modify the coating and substrate, regardless of the relatively positive obtained results of adhesion.

Spontaneous passive oxide layer of titanium is very sluggish and it takes a long time after implantation until osteointegration. The modification of the surface, thereof, leads to the increase in roughness of the implant surface, and hence adhesion of bioactive ceramic coating on a substrate [36]. Most of the titanium implants are treated with bioactive ceramic material, in order to improve biocompatibility, osteointegration and the adhesion of coatings on the substrate [36-38].

Anodizing the substrate surface has proven to be a promising method of modifying metals. One of the most commonly used method is the anodization of surface with simultaneous treatment in an acidic environment, and a bioactive electrodeposition of HAp coating. On the other hand, it was shown that pre-treatment of alkali nanotubular titanium oxides (ATi) accelerates the formation of HAp, having the characteristics and structure as the bone tissue [39]. Nanostructured HAp is formed on the pretreated and ATi ATi (P-ATi), in contrast with conventional Ti [39].

The aim of the work was novel process of *in situ* synthesis and characterization of anaphoretic hydroxyapatite coatings on modified titanium surfaces by anodization process.

Experimental

A chemical precipitation method was used to prepare hydroxyapatite powder by the reaction of calcium oxide (obtained by calcination of $CaCO_3$ for 5 h at 1000 °C in air) and phosphoric acid. A stoichiometric amount of the resulting calcium oxide was mixed and stirred in distilled water for 10 min and phosphoric acid was added dropwise to the suspension in order to obtain hydroxyapatite powder, $Ca_{10}(PO_4)_6(OH)_2$. When all the necessary quantity of phosphoric acid was introduced, the pH reached a value of 7.4−7.6. The obtained suspension was preheated to 94 ± 1 °C for 30 min and stirred for another half an hour. After sedimentation, the upper clear solution layer was decanted. The suspension was then spray-dried at 120 ± 5 °C into granulated powder [40]. HAp powder was then suspended in a solution containing 5 wt.% of NaOH with 50% of C_2H_5OH.

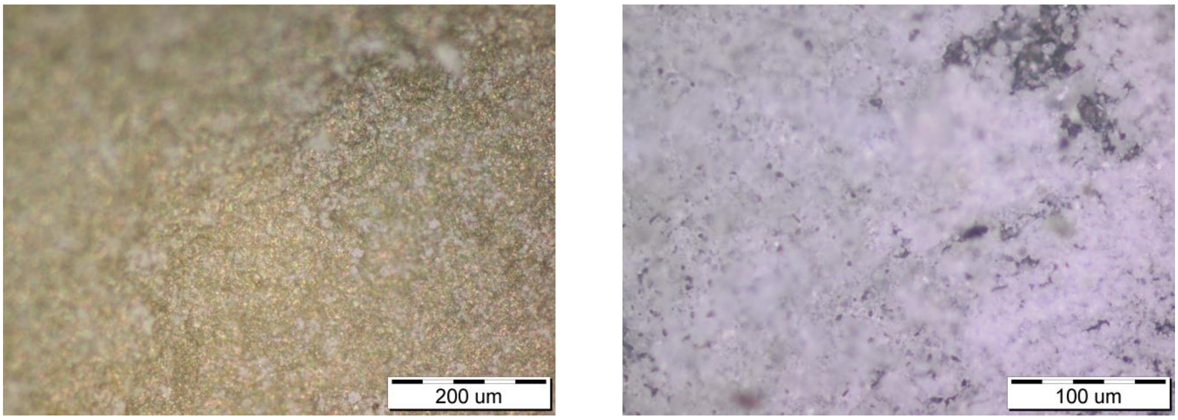
Electrochemical measurements were performed in a two-electrode cell. For this purpose, an electrochemical work station (Hewlett Packard HP6024A) having potentiostat/galvanostat provided with corrosion and physical electrochemistry software and a desktop computer (HP) was used. A platinum wire was used as counter electrode. The working electrode geometric area exposed to electrolyte was 0.39 cm^2. The cell was filled with HAp suspension and purged with N_2 for 30 min prior to electrochemical measurements.

Morphology of the obtained HAp coatings was determined by optical microscope Olympus BX41.

Fourier transform infrared spectroscopy (FTIR) was recorded on anodized titanium and on anaphoretic deposited HAp coating composite. Michelson MB Series Bomen FTIR was used (Hartmann Braun), scanning from 400 to 4000 cm^{-1}.

Results and discussion

In order to obtain *in situ* HAp coating and to compare it with pure Ti after anodzation, two sets of experiments were performed, i.e. pure titanium anodization and anaphoretic HAp coating deposition from alkaline solution. For HAp to be anaphoreticaly deposited, it needs to be in a form of suspension with negatively charged micelle. Pure ethanol in 5 % NaOH was proven to be excellent solution of choice for this task, making HAp suspension stable for a long period of time. Both anodization and anaphoretic deposition were performed from 50-70 V at 0.5 mA in galvanostatic regime for 5 min. Obtained anodized titanium surface and deposited HAp coating are shown in Figure 1.



(a) *(b)*

Figure 1. Optical images of (a) anodized titanium and (b) HAp coating on titanium.

It can be seen that HAp has excellent coverage of the surface with a firm deposite that is not delaminating. The obtained coating can be good material for bone implants due to solving HAp brittleness.

Further evidence of presence of HAp coating on titanium, and hence its functional groups is characterized by ATR-FTIR spectrum which is shown in Figure 2.

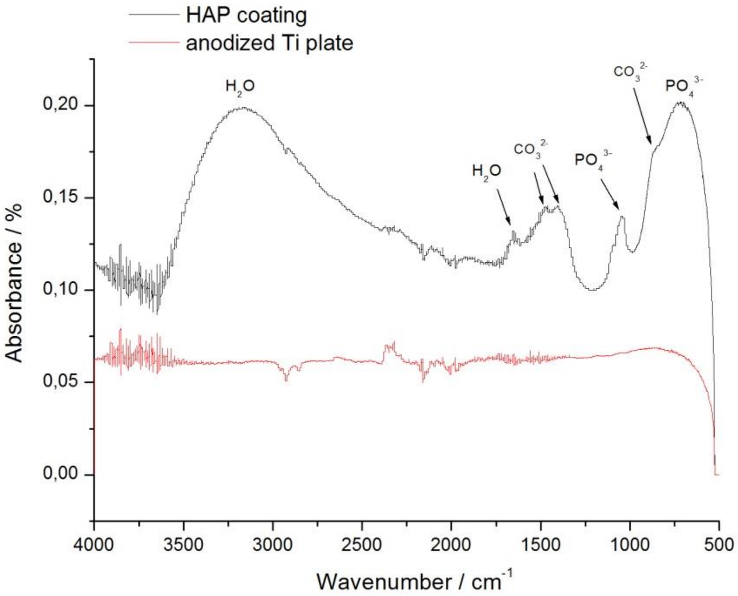


Figure 2. ATR-FTIR spectrum of anodized titanium (bottom red line) and HAp coating (top black line).

The spectra display typical PO_4^{3-} characteristic bands of hydroxyapatite coating. Two absorption bands were clearly distinguished at the following wave numbers 1041 and around 718 cm^{-1} in the ν_3 and ν_1 phosphate mode region. Additional weak bands at 872, 1402, and 1476 cm^{-1} are assigned to carbonate species (CO_3^{2-}) in the apatite lattice [41]. These peaks in the FTIR spectrum can be attributed to the reaction between CaO and CO_2 from the atmosphere. In the FTIR spectrum of HAp coating (Figure 2), the wide band at 3170 cm^{-1} is attributed to the OH stretching of H_2O molecules. The band at cca. 1650 cm^{-1} is from water (bending modes). The observed functional groups and their corresponding assignments are presented in Table 1.

Table 1. Some important functional groups assignments of HAp coating.

Wavenumber cm-1	**Stretching mode**	**Functional group**
3170	Ion Stretching	H_2O/OH-
1650	Out of plane bending mode	H_2O
1402, 1476	Asymmetric stretching	CO_3^{2-}
1041	Asymmetric stretching	PO_4^{3-}
872	Out of plane bending mode	CO_3^{2-}
718	Asymmetric bending vibration	PO_4^{3-}

Conclusions

Nano-hydroxyapatite coating has been successfully synthesized by novel *in situ* method of anaphoretic deposition on titanium substrate. The formation of hydroxyapatite coating was confirmed by optical microscopy and Attenuated Total Reflection Fourier transform infrared spectroscopy (ATR-FTIR). It can be concluded that with good preparation and proper choice of suspension medium leading to stable negative micelle HAp obtains excellent coverage of the surface with a firm deposite that is not delaminating. This coating has good properties to be used as a material for bone implants.

Acknowledgements

This work was financially supported by Ministry of Education, Science and Technological Development of the Republic of Serbia under the research projects: ON172037, ON172046 and ON172060.

References

1. Ahmadi, S.; Mohammadi, I.; Sadrnezhaad, S. K., *Surface and Coatings Technology*, 287, 67-75 (2016).
2. Liu, X.; Chu, P. K.; Ding, C., *Materials Science and Engineering: R: Reports*, 47, 49-121 (2004).
3. Ahmadi, S.; Sadrnezhaad, S. K., *Journal of Alloys and Compounds*, 656, 416-422 (2016).
4. Geetha, M.; Singh, A. K.; Asokamani, R.; Gogia, A. K., *Progress in Materials Science*, 54, 397-425 (2009).
5. Dezfuli, S. N.; Sadrnezhaad, S. K.; Shokrgozar, M. A.; Bonakdar, S., *Journal of Materials Science: Materials in Medicine*, 23, 2483-2488 (2012).
6. Long, M.; Rack, H. J., *Biomaterials*, 19, 1621-1639 (1998).
7. Han, C.; Wang, Q.; Song, B.; Li, W.; Wei, Q.; Wen, S.; Liu, J.; Shi, Y., *Journal of the Mechanical Behavior of Biomedical Materials*, 71, 85-94 (2017).
8. Hamada, K.; Kon, M.; Hanawa, T.; Yokoyama, K. i.; Miyamoto, Y.; Asaoka, K., *Biomaterials*, 23, 2265-2272 (2002).
9. Osman, R.; Swain, M., *Materials*, 8, 932 (2015).
10. Niespodziana, K.; Jurczyk, K.; Jakubowicz, J.; Jurczyk, M., *Materials Chemistry and Physics*, 123, 160-165 (2010).
11. Shen, S.; Cai, S.; Li, Y.; Ling, R.; Zhang, F.; Xu, G.; Wang, F., *Chemical Engineering Journal*, 309, 278-287 (2017).
12. Shadanbaz, S.; Dias, G. J., *Acta Biomaterialia*, 8, 20-30 (2012).
13. Abdal-hay, A.; Vanegas, P.; Hamdy, A. S.; Engel, F. B.; Lim, J. H., *Chemical Engineering Journal*, 254, 612-622 (2014).
14. Williams, D. F., *Journal of Materials Science*, 22, 3421-3445 (1987).
15. Chen, X. B.; Birbilis, N.; Abbott, T. B., *Corrosion Science*, 55, 226-232 (2012).
16. Gray-Munro, J. E.; Strong, M., *Journal of Biomedical Materials Research - Part A*, 90, 339-350 (2009).
17. Zhou, H.; Nabiyouni, M.; Bhaduri, S. B., *Materials Science and Engineering: C*, 33, 4435-4443 (2013).
18. Ren, Y.; Zhou, H.; Nabiyouni, M.; Bhaduri, S. B., *Materials Science and Engineering: C*, 49, 364-372 (2015).
19. Zhou, H.; Goel, V. K.; Bhaduri, S. B., *Materials Letters*, 125, 96-98 (2014).
20. Jongpaiboonkit, L.; Franklin-Ford, T.; Murphy, W. L., *ACS Applied Materials and Interfaces*, 1, 1504-1511 (2009).
21. Barrere, F.; Snel, M. M. E.; van Blitterswijk, C. A.; de Groot, K.; Layrolle, P., *Biomaterials*, 25, 2901-2910 (2004).
22. Yamada, S.; Takasu, A.; Kawamura, K., *Journal of Polymer Science, Part A: Polymer Chemistry*, 51, 3732-3739 (2013).
23. Haque, E.; Khan, N. A.; Kim, C. M.; Jhung, S. H., *Crystal Growth and Design*, 11, 4413-4421 (2011).
24. Zhou, H.; Yang, M.; Hou, S.; Deng, L., *Materials Science and Engineering: C*, 71, 439-445 (2017).
25. Vani, R.; Subramaniya Bharathi, R.; Sridevi, T. S.; Savithri, K.; Devaraj, S. N.; Girija, E. K.; Thamizhavel, A.; Kalkura, S. N., *Nanotechnology*, 22, 285701 (2011).
26. Zuo, G.; Wei, X.; Sun, H.; Liu, S.; Zong, P.; Zeng, X.; Shen, Y., *Journal of Alloys and Compounds*, 692, 693-697 (2017).
27. Albayrak, O.; El-Atwani, O.; Altintas, S., *Surface and Coatings Technology*, 202, 2482-2487 (2008).
28. Biest, O. O. V. d.; Vandeperre, L. J., *Annual Review of Materials Science*, 29, 327-352 (1999).
29. Ulasevich, S. A.; Kulak, A. I.; Poznyak, S. K.; Karpushenkov, S. A.; Lisenkov, A. D.; Skorb, E. V., *RSC Advances*, 6, 62540-62544 (2016).
30. Wen, H. B.; de Wijn, J. R.; Cui, F. Z.; de Groot, K., *Journal of Biomedical Materials Research*, 41, 227-236 (1998).

31. Wang, H.; Eliaz, N.; Xiang, Z.; Hsu, H.-P.; Spector, M.; Hobbs, L. W., *Biomaterials*, 27, 4192-4203 (2006).
32. Eliaz, N.; Shmueli, S.; Shur, I.; Benayahu, D.; Aronov, D.; Rosenman, G., *Acta Biomaterialia*, 5, 3178-3191 (2009).
33. Mostafa, N. Y.; Kamel, M. M., *Surface Engineering and Applied Electrochemistry*, 52, 520-523 (2016).
34. Hieda, J.; Niinomi, M.; Nakai, M.; Cho, K.; Matsubara, A., *Mater. Trans.*, 56, 1703-1710 (2015).
35. Eliaz, N.; Ritman-Hertz, O.; Aronov, D.; Weinberg, E.; Shenhar, Y.; Rosenman, G.; Weinreb, M.; Ron, E., *Journal of Materials Science: Materials in Medicine*, 22, 1741-1752 (2011).
36. Kang, K.; Zakiyuddin, A.; Lee, K., *Journal of Nanoscience and Nanotechnology*, 16, 1708-1710 (2016).
37. Moore, B.; Asadi, E.; Lewis, G., *Advances in Materials Science and Engineering*, 2017, 9 (2017).
38. Yilmaz, B.; Evis, Z.; Tezcaner, A.; Banerjee, S., *International Journal of Applied Ceramic Technology*, 13, 1059-1068 (2016).
39. Parcharoen, Y.; Termsuksawad, P.; Sirivisoot, S., *Journal of Nanomaterials*, 2016, 13 (2016).
40. Eraković, S.; Janković, A.; Veljović, D.; Palcevskis, E.; Mitrić, M.; Stevanović, T.; Janaćković, D.; Mišković-Stanković, V., *The Journal of Physical Chemistry B*, 117, 1633-1643 (2013).
41. Mirzaee, M.; Vaezi, M.; Palizdar, Y., *Materials Science and Engineering: C*, 69, 675-684 (2016).

The roughness of surface of aluminum after chemical and electrochemical treatment

Hrapavost površine aluminijuma nakon hemijske i elektrohemijske obrade

Marija G. Riđošić[1], Milorad V. Tomić[1], Miroslav M. Pavlović[2], Vaso Bojanić[3]

[1]University of East Sarajevo, Faculty of Technology, Zvornik, Republic of Srpska, Bosnia and Herzegovina

[2]University of Belgrade, Institute of Chemistry, Technology and Metallurgy, Belgrade, Serbia

[3]University of Banja Luka, Faculty of Technology, Banja Luka, Republic of Srpska, Bosnia and Herzegovina

[1]Univerzitet u Istočnom Sarajevu, Tehnološki fakultet Zvornik, Zvornik, Republika Srpska, Bosna i Hercegovina

[2]Univerzitet u Beogradu, Institut za hemiju tehnologiju i metalurgiju, Beograd, Srbija

[3]Univerzitet u Banja Luci, Poljoprivredni fakultet, Banja Luka, Republika Srpska, Bosna i Hercegovina

Abstract

In this paper chemical and electrochemical treatment of aluminium and measurement of roughness were carried out. Before chemical or electrochemical treatment of aluminium samples chemical preparation is done to remove oxide coating on surface. Three solutions are used for chemical and two solutions for electrochemical treatment. All used solutions give good results, because after chemical and electrochemical treatment the roughness of surface is decrease for all samples. It is shown by measurements of surface roughness. The surface of aluminium has specific color and visual appearance after treatments. Because of various colours, aluminium can be used in different enterer or exterior, depending of the needs of the market. Some of used solutions are commercial, which is used in d.o.o "Alpro" Vlasenica. Increase of time of treatments leads to decrease of the roughness of surface. The best results were obtained in solutions (H1) and (H2) of all used solutions for chemical and electrochemical treatments of aluminium surface. The samples of aluminium treated in solutions (H1) and (H2) have lower roughness of surface and its value is 0,235-0,268µm. The most intense color is obtained during treatment of samples in solutions (H1) and (H2), i.e. by chemical treatment of aluminium samples.

Key words: *Preparation of surface, chemical treatment, electrochemical (anodic) treatment, roughness of surface.*

Izvod

U ovom radu je vršena hemijska i elektrohemijska obrada aluminijuma, nakon čega je merena hrapavost uzoraka. Pre hemijske ili elektrohemijske obrade uzoraka aluminijuma potrebno je izvršiti hemijsku pripremu i ukloniti zaštitnu oksidnu opnu. Za hemijsku obradu korišćena su tri, a za elektrohemijsku obradu dva rastvora. Svih pet korišćenih rastvora daju dobre rezultate, jer nakon hemijske i elektrohemijske obrade dolazi do smanjenja površinske hrapavosti. To pokazuju izvršena merenja površinske hrapavosti svih uzoraka. Takođe, nakon tretmana u svakom od rastvora dobija se i specifična boja i različit vizuelni izgled površine aluminijuma. U zavisnosti od boje, aluminijum se može uklapati u različite enterijere i eksterijere u zavisnosti od zahteva tržišta. Neki od korišćenih rastvora su komercijalni rastvori koji se već koriste u d.o.o „Alpro“ Vlasenica.

Sa povećanjem vremena obrade dolazi do smanjenja hrapavosti uzoraka aluminijuma. Od pet korišćenih rastvora za hemijsko i elektrohemijsko bojenje aluminijuma, najbolje rezultate pokazali su rastvori (H_1) *i* (H_2)*. Uzorci aluminijuma obrađeni u ovim rastvorima imaju najmanju hrapavosti i ona se kreće od 0,235-0,268µm. Najintezivnija boja je dobijena prilikom obrade uzoraka u rastvoru* (H_1) *i* (H_2) *tj. pri hemijskoj obradi uzoraka aluminijuma.*

Ključne reči: *Priprema površine, hemijska obrada, elektrohemijska (anodna obrada), hrapavost površine.*

Uvod

Aluminijum je veoma postojan u atmosferskim uslovima, zbog velikog afiniteta prema kiseoniku i formiranja pasivne oksidne opne na njegovoj površini, ali je nepostojan u rastvorima većine kiselina i baza [1,3]. Aluminijum spada u grupu metala koji se u industrijskoj praksi mogu malo elektrohemijski obrađivati kako katodnom tako i anodnom polarizacijom. Pre hemijske ili elektrohemijske obrade potrebno je ukloniti pasivnu oksidnu opnu sa površine aluminijuma. Opna se najčešće uklanja hemijskim postupcima. Fenomen poravnavanja metalnih površina procesom anodnog rastvaranja pod određenim uslovima je poznat duže od osamdeset godina. Prema tome, oblast u kojoj je gustina struje praktično nezavisna od napona, a koja je poznata kao plato granične difuzione gustine struje, je oblast u kojoj se javlja maksimalni efekat poravnavanja i zavisi od brzine toka elektrolita oko anode, tj. od debljine hidrodinamičkog graničnog sloja. Na anodnu oksidaciju, kao najzastupljeniji vid antikorozione zaštite aluminijuma i njegovih legura, nadovezuju se postupci elektrohemijskog bojenja, zasnovani na poluprovodničkoj prirodi anodne oksidne prevlake [4-14]. Aluminijum se mnogo koristi u građevinarstvu za izradu stolarije, fasada i uređivanje enterijera. Anodna obrada i bojenje aluminijuma u industriji je veoma zastupljeno, pa je u ovom radu pokušano u laboratorijskim uslovima koristiti komercijalne elektrolite i porediti dobijene rezultate sa novim elektrolitima.
Cilj ovog rada je bio da se, koristeći dosadašnja iskustva iz ove oblasti, kroz eksperimentalni rad, da doprinos u iznalaženju nekih od elektrolita i optimalnih uslova za hemijsko i elektrohemijsko bojenje aluminijuma i njegovih legura. Takođe cilj je bio da se pokaže kako odabrani rastvori za hemijsko i elektrohemijsko bojenje utiču na vizuelni izgled i hrapavost površine aluminijumskih uzoraka.

Eksperimentalni deo

Eksperimenti su rađeni sa aluminijumskim pločicama nepoznatog sastava površine 0,5dm^2 u laboratoriskoj ćeliji zapremine 500cm^3. Za eksperimente u laboratoriji korišćen je i aluminijum koji se koristi u procesu proizvodnje d.o.o. "Alpro" Vlasenica. Pre hemijske i elektrohemijske anodne obrade vršena je hemijska priprema uzoraka aluminijuma u rastvorima koje se koriste u d.o.o. "Alpro" Vlasenica.

1. Rastvor za odmašćivanje: 25% Na_2CO_3, 25% $Na_3PO_4 \cdot 10H_2O$, t = 60 - 70°C, τ = 3-10 min.
2. Rastvor za nagrizanje: 5% NaOH, t =50-55^{0}C, τ = 3-5 min.
3. Rastvor za osvetljavanje: 160-180 g/dm^3 HNO_3, τ = 3-5 min, temperatura sobna
4. Korišćeni rastvori za hemijsko bojenje su komercijalni rastvori koji se koriste u proizvodnom procesu doo "Alpro" Vlasenica :
    - Rastvor (H_1): Alficolor Schwarz 711 (17-18 g/dm^3), pH=4.5, t= 60°C, τ = 3-10 min.
    - Rastvor (H_2): Arficolor gold 603 (1-5 g/dm^3), t= 60°C, τ = 3-10 min.
    - Rastvor (H_3): $SnSO_4$ (15 g/dm^3), H_2SO_4 (18 g/dm^3), aditiv (30 g/dm^3), temperatrura sobna, τ = 6min. [14].

5. Korišćeni rastvori za elektrohemijsko bojenje su [13,14]:

Rastvor (EH_1): $KMnO_4$ (18.5 g/dm^3), H_2SO_4 (150 g/dm^3), τ = 10 min., U=20 V, j=1.0 A/dm^2, katoda: olovo

Rastvor (EH_2): $C_2H_2O_4$ (5%), τ = 40 min., U=36 V, j=1.5 A/dm^2, katoda: olovo

6. Siliranje: destilovana voda, t= 98°C, , τ = 3 min.

Hemijska priprema svih uzoraka pre elektrohemijske obrade rađena je na isti način: hemijsko odmašćivanje 6 min, nagrizanje 4 min., osvetljavanje 4 min., a između svake od operacija vršeno je ispiranje u protočnoj i destilovanoj vodi.

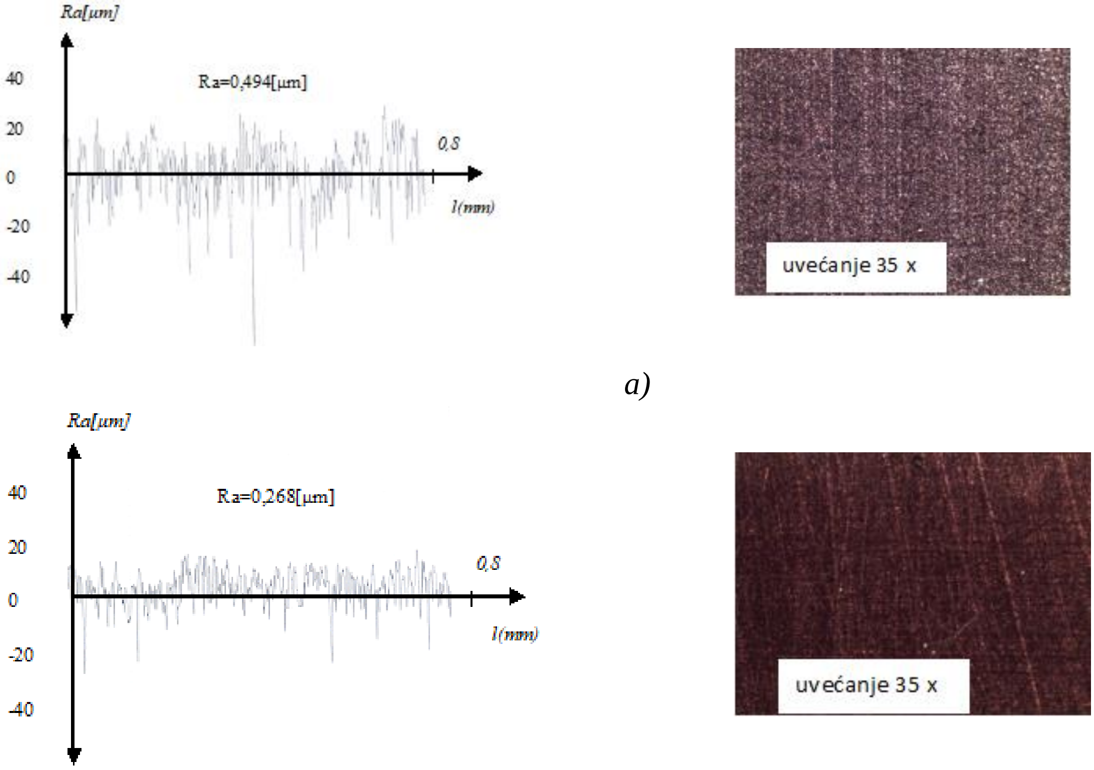
Ovako hemijski pripremljeni uzorci bili su podvrgnuti hemijskoj ili elektrohemijskoj obradi u rastvorima H_1, H_2, H_3, EH_1 i EH_2 uz mešanje elektrolita, ispiranje u protočnoj i destilovanoj vodi, siliranje i sušenje.

Merenje hrapavosti vršeno je ručnim taster uređajem TR 200. To je novi proizvod razvijen od strane kompanije Time Group Inc. Veoma je pogodan za brzo i precizno merenje hrapavosti proizvedenih predmeta i u pogonskim uslovima. TR 200 preračunava parametre po izabranim mernim uslovima i jasno prikazuje parametre i grafike profila na LCD ekranu. Uređaj ima mogućnost softverske podrške i upravljanja preko računara. Mogućnosti multi–parametarsko merenje: *Ra, Rz, Ry, Rq, Rp, Rm, Rt, St, S, Sm, tp*

Površina uzoraka aluminijuma nakon hemijskog i elektrohemijskog bojenja, ispiranja, siliranja i sušenja snimana je optičkim mikroskopom Leica EZ4 HD. Aparat karakteriše kvalitetno 4,4:1 zumiranje odnosno uvećanje od 8-35 puta.

Rezultati i diskusija

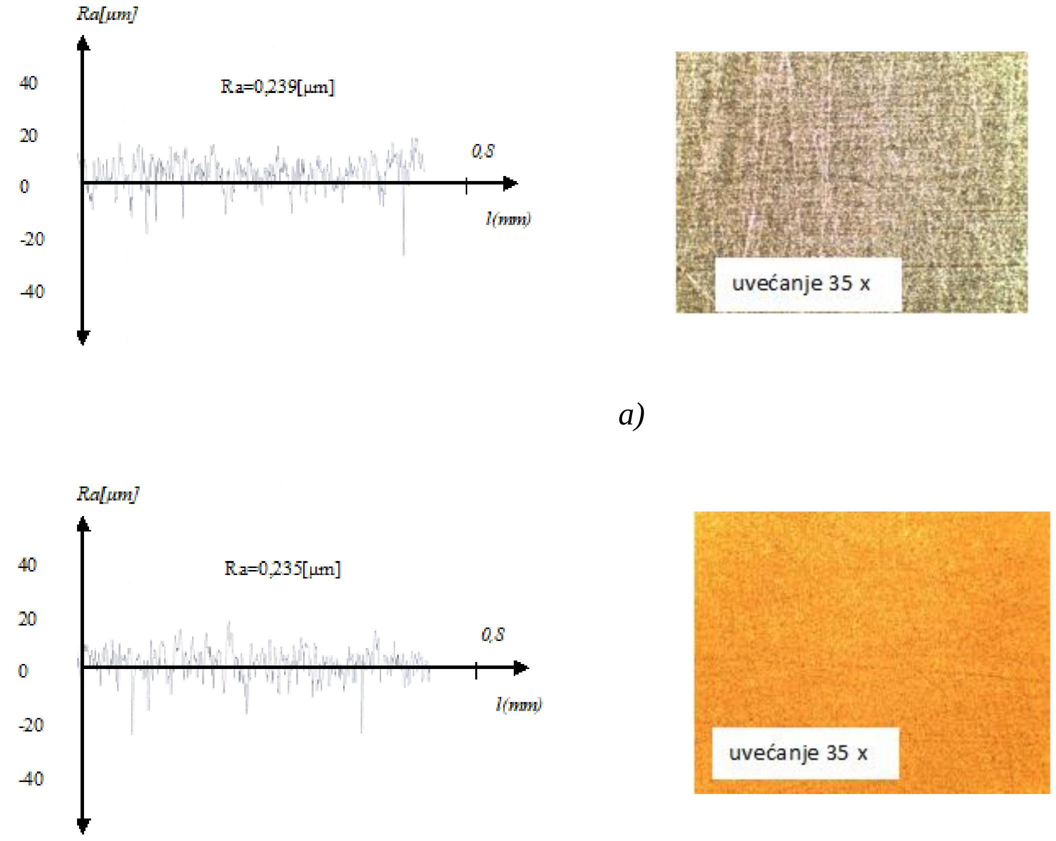
Na slici 1. prikazan je izgled hemijski pripremljenih uzoraka aluminijuma u rastvorima 1-3, a nakon toga uzorci su tretirani u rastvoru (H_1) u vremenskom intervalu: a) τ =5 min; b) τ= 10 min.



b)

Slika 1.Grafički i fotografski prikaz hrapavosti i izgleda uzoraka aluminijuma nakon tretmana u rastvoru (H1) u vremenu: a)5 min. i b)10 min.

Na slici 2. prikazan je izgled hemijski pripremljenih uzoraka aluminijuma u rastvorima 1-3, a nakon toga uzorci su tretirani u rastvoru (H_2) u vremenu: a) τ =5 min; b) τ= 10 min;

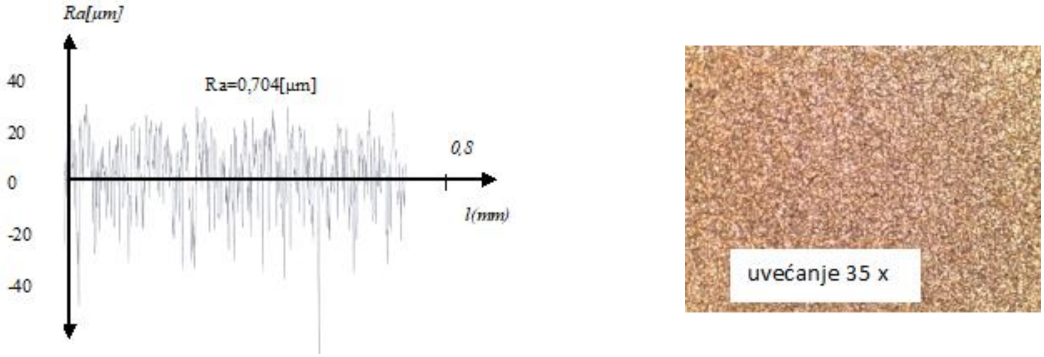


a)

b)

Slika 2.Grafički i fotografski prikaz hrapavosti i izgleda uzoraka aluminijuma nakon tretmana u rastvoru (H2) u vremenu: a)5 min. i b)10 min.

Na slici 3. prikazan je izgled hemijski pripremljenog uzorka aluminijuma u rastvorima 1-3, a nakon toga uzorak je potopljen u rastvor (H_3), τ =6 min.



Slika 3.Grafički i fotografski prikaz hrapavosti površine uzorka aluminijuma nakon tretmana u rastvoru (H3), τ=6 min.

Sa slika 1-3 može se videti da se iz različitih rastvora dobija površina aluminijuma različitih boja, kao i različite hrapavosti. Takođe, može se primetiti da i vreme tretmana tj. zadržavanja uzorka u rastvoru bitno utiče na izgled (boju), a ponekad i na hrapavost površine.

Nakon tretmana u rastvoru (H_1) (slika 1), dobija se površina tamno zlatne boje, a tamnija braon nijansa nakon tretmana uzorka 10 minuta. Primetno je i smanjenje površinske hrapavosti sa vremenom tretmana. Nakon 5 minuta Ra=0.494 µm, a nakon 10 minuta Ra=0.268 µm.

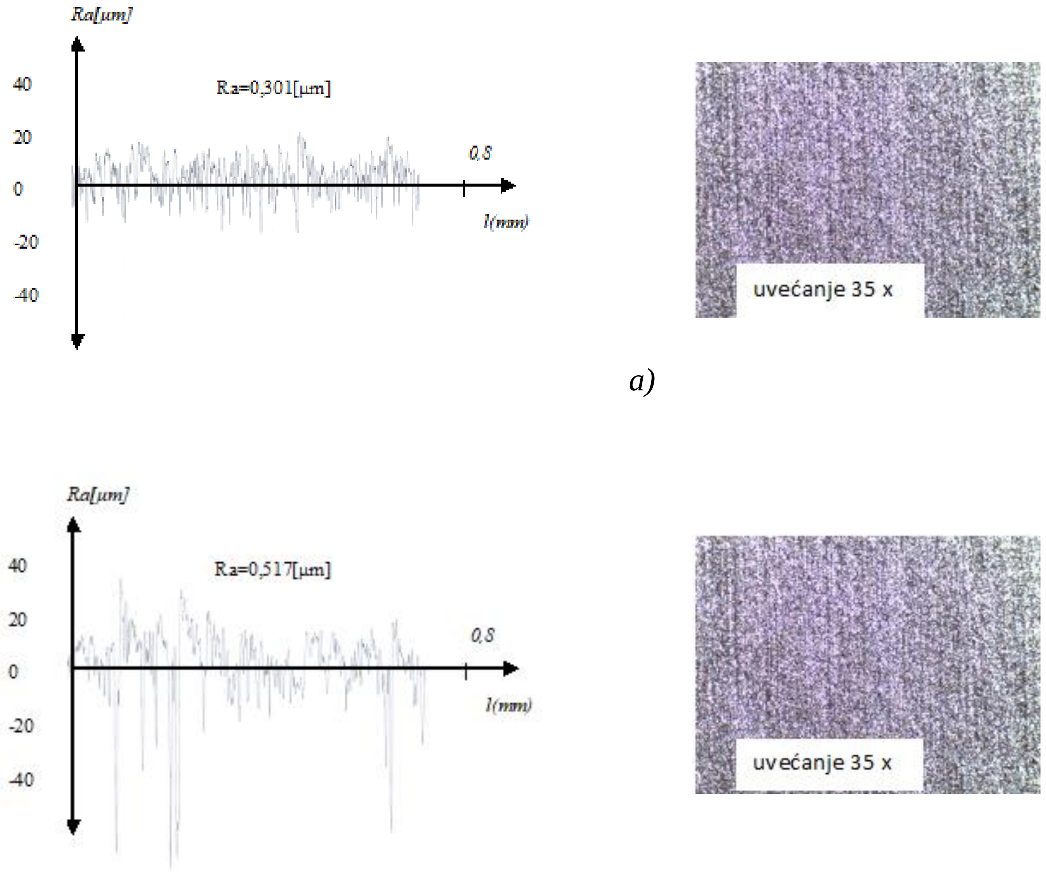
Sa slike 2. može se videti da se iz istog rastvora (H_2) nakon 5 minuta dobija površina aluminijuma zelenkaste boje, a nakon 10 minuta površina ima zlatno-žutu boju. Može se primetiti da vreme tretmana bitno ne utiče na hrapavost površine, jer ona je nakon 5 minuta Ra= 0.239 µm, a nakon 10 minuta Ra=0.235 µm.

Iz rastvora (H_3) (slika 3) dobija se površina aluminijuma obojena svetlo braon i vidi se krupnozrnija struktura na površini. To je pokazao i rezultat izmerene hrapavosti površine Ra=0,704 µm.

Iz dobijenih rezultata može se zaključiti da se najmanja hrapavost površine dobija iz rastvora (H_1) pri vremenu 10 min., i iz rastvora (H_2) bez obzira na vreme tretmana i kreće se od 0,235 – 0,268 µm.

Za bojenje površine aluminijuma mogu se koristiti sva tri rastvora, u zavisnosti koja boja površine se želi dobiti.

Na slici 4. prikazan je izgled površine uzoraka aluminijuma nakon hemijske pripreme i anodne obrade u rastvoru (EH_1) 10 minuta, pri gustini struje j_a =1.0 A/dm^2 : a) alpro uzorak i b) obična pločica



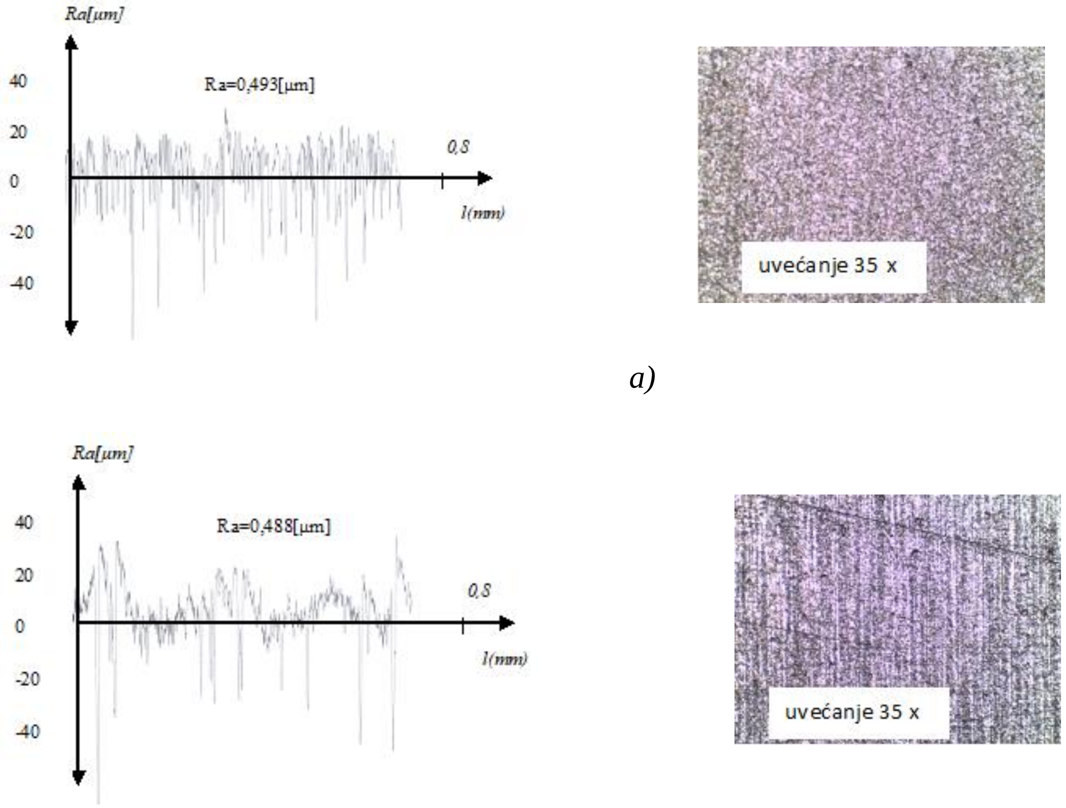
a)

b)

Slika 4. Grafički i fotografski prikaz izmerene hrapavosti nakon anodne obrade u rastvoru (EH1), 10 minuta, ja =1.0 A/dm2: a) alpro uzorak i b)obična pločica

Sa slike 4. može se videti da je boja površine oba uzorka nakon elektrohemijskog tretmana pri struji j=1 A/dm^2 skoro ista, ljubičasto-zelena i da je hrapavost uzoraka aluminijuma koji je nabavljen iz d.o.o. "Alpro" znatno manja Ra=0,301 µm. To ukazuje da uslovi skladištenja, transporta, kao i sam hemijski sastav uzorka utiču na površinsku hrapavost.

Na slici 5. prikazan je izgled površine uzoraka aluminijuma nakon hemijske pripreme i elektrohemijskog tretmana (anodne obrade) u rastvoru (EH$_2$) pri gustini struje j$_a$=1,5 A/dm^2 a) alpro uzorak i b) obična pločica



a)

b)

Slika 5.Grafički i fotografski prikaz izmerene hrapavosti nakon anodne obrade u rastvoru (EH2), 40 minuta, ja=1,5 A/dm2: a) alpro uzorak i b)obična pločica

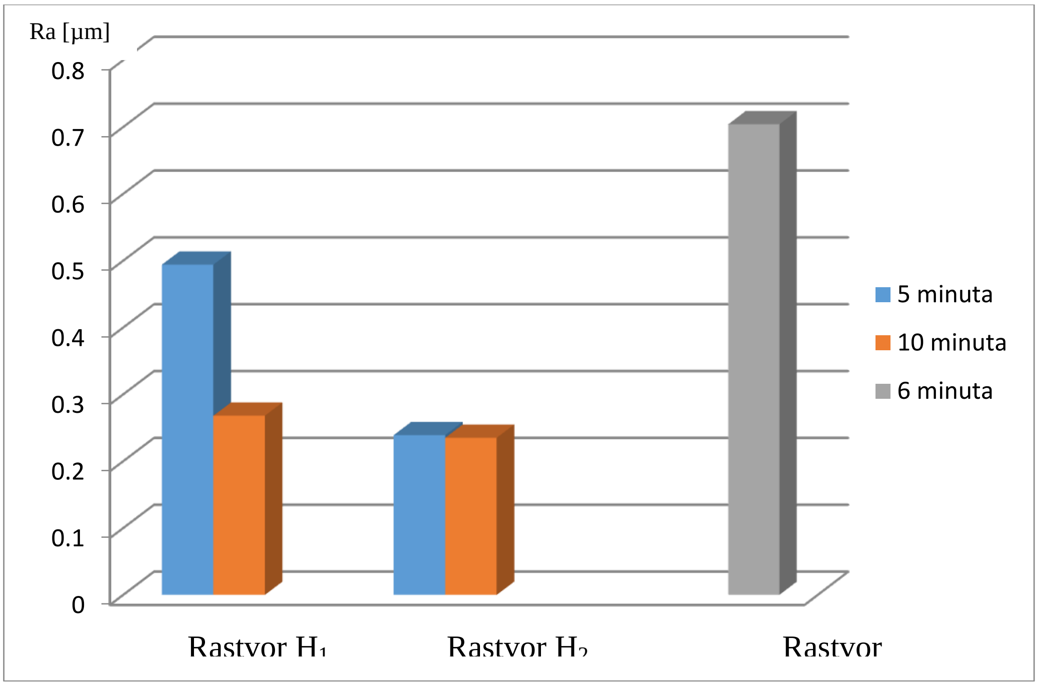
Sa slike 5. može se videti da je boja površine aluminijuma veoma slična onoj koja se vidi na slici 4. tj. ljubičasto zelena. To govori da se iz dva različita rastvora i pri različitim uslovima anodne obrade može dobiti slična boja površine aluminijuma i hrapavost površine se puno ne razlikuje. Kod rastvora (EH$_1$) hrapavost se kreće od 0,301 do 0,517 µm, a kod rastvora (EH$_2$) od 0,488 do 0,493 µm.

U tabeli 1. dat je prikaz izmerenih parametara hrapavosti hemijski i elektrohemijski obrađivanih uzoraka aluminijuma.

Tabela 1. Parametri izmerene hrapavosti u svih 5 korišćenih rastvora za hemijski i elektrohemijski tretman

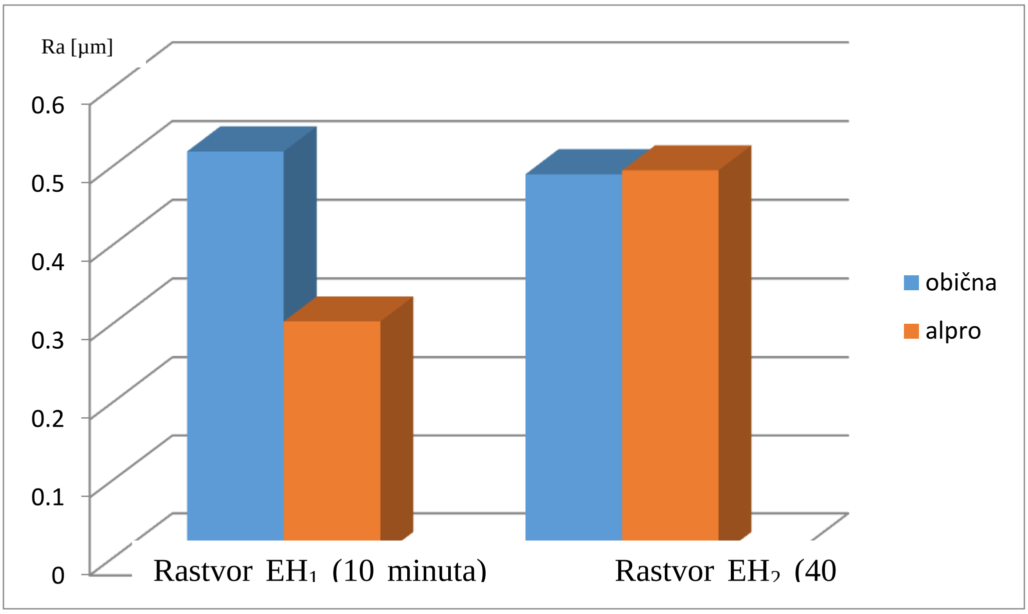
Rastvor	Vreme (min)	Ra(µm)
H_1	5	0.494
	10	0.268
H_2	5	0.239
	10	0.235
H_3	6	0.704
EH_1	10	0.517 (obična) 0.301 (alpro)
EH_2	40	0.488 (obična) 0.493 (alpro)

Na slici 6 dat je prikaz izmerene hrapavosti uzoraka aluminijuma nakon obrade u rastvorima H_1, H_2 i H_3 u zavisnosti od vremena tretmana uzoraka u pojedinim rastvorima.



Slika 6. Prikaz hrapavosti nakon obrade u rastvorima H1, H2 i H3 u zavisnosti od vremena

Sa slike 6. može se videti da je najmanja hrapavost izmerenje na uzorcima koji su hemijski bojeni (tretirani) u rastvoru H_2 i da vreme obrade ne utiče na hrapavost površine. Kod tretmana u rastvoru H_1 hrapavost površine se smanjuje sa vremenom i za 10 minuta hrapavost je približno ista, kao kod uzoraka tretiranih u rastvoru H_2. Najveća hrapavost je izmerenje kod uzoraka bojenih u rastvoru H_3. Na slici 7. prikazana je izmerenje hrapavost obične pločice i alpro uzorka nakon anodne obrade u rastvorima EH_1 i EH_2 u vremenskim intervalima od 10 i 40 min.



Slika 7. Prikaz hrapavosti obične pločice i alpro uzorka nakon anodne obrade u rastvorima EH1 i EH2 u zavisnosti od vremena

Sa slike 7. može se videti da je hrapavost uzorka aluminijuma koji je nabavljen u d.o.o. "Alpro" Vlasenica nakon anodne obrade od 10 min. u rastvoru EH_1 skoro za duplo manja od hrapavosti drugog uzorka aluminijuma. To ukazuje da sastav i čistoća aluminijuma utiču na hrapavost površine nakon anodnog tretmana u rastvoru EH_1. To se ne može reći za uzorke nakon anodne obrade u vremenu od 40 min. u rastvoru EH_2, jer je hrapavost oba uzorka približno ista i za nijansu manja od uzorka aluminijumskog lima (obična). Najmanju hrapavost Ra=0,301μm, ima uzorak alpro koji je tretiran u rastvoru EH_1, 10 min.

Zaključak

Pre hemijske ili elektrohemijske obrade uzoraka aluminijuma potrebno je uzorke hemijski pripremiti i ukloniti zaštitnu oksidnu opnu. Iz rastvora (H_1) se dobijaju nijanse od tamno zlatne do tamnije braon nijanse, a iz rastvora (H_2) dobijaju se uzorci zelenkaste i zlatno-žutu boje u zavisnosti od vremena tretmana. Najmanja hrapavost na uzorcima koji su hemijski tretirani je u rastvorima (H_1) i (H_2) i kreće se od Ra=0.235-0.268 μm.
Prilikom elektrohemijske obrade u rastvoru (EH_1), hrapavost uzorka aluminijuma koji je nabavljen u d.o.o. "Alpro" Vlasenica je znatno manja od hrapavosti običnog uzorka (aluminijumski lim ≠1mm), i iznosi Ra=0.301μm. Najveća hrapavost je izmerenje kod uzoraka bojenih u rastvoru (H_3) i iznosi Ra=0,704μm, a površina aluminijuma je obojena svetlo braon i vidi se krupnozrnija struktura na površini.Vreme tretmana tj. zadržavanja uzorka u rastvoru bitno utiče na izgled (boju) kao i na hrapavost površine. Tako npr. nakon hemijske obrade u rastvoru (H_1) posle 5 minuta Ra=0.494 μm, a nakon 10 minuta Ra=0.268 μm. Očigledno je da se hrapavost smanjuje, a boja menja sa povećanjem vremena tretmana. U zavisnosti koja se nijansa boje želi dobiti (od zelenkaste, ljubičasto – zelene, zlatno – žute, do raznih nijansi braon) može se koristiti hemijski ili elektrohemijski tretman. Takođe, vreme obrade igra važnu ulogu kada je u pitanju nijansa boje, kao i hrapavost površine aluminijuma. Rezultati hemijskog i elektrohemijskog bojenja u laboratorijskim uslovima i industrijskim uslovima (d.o.o. „Alpro“ Vlasenica) daju približno iste rezultate u nijansi boja i izmerene hrapavosti, za korišćene rastvore.

Literatura

1. Antić,M., Smiljanić,M.: Aluminijum i aluminijumske legure, ZZZ,Beograd, 2003.
2. M. Pourbax, Atlas of Electrochemical Equilibria in Aqueous Solutions, Pergamon London 1966. str. 168 – 176
3. M.J. Pryor, D.S. Keir, J. Electrochem. Soc., 102 (1955) 605.
4. S. Đorđević, M. Maksimović, M.G. Pavlović, K.I. Popov, Galvanotehnika, Tehnička knjiga, Beograd, 2000.,
5. Yu. Ya. Lukomskii, V. K. Gorshkov, ″Galvanicheskie i lakokrasochnye pokrytiya na alyuminii i ego splavakh″, Leningrad, 1985
6. M.V. Tomić, Lj. J. Pavlović, M. G. Pavlović , Zaštita materijala, 46(2005)3,13-16.
7. B. C. Bunker ,G. C. Nelson , K. R. Zavadil , J. C. Barbour , F. D. Wall , J. P. Sullivan, C. F. Windisch Jr., M. H. Engelhardt ,d D. R. Baer J. Phys. Chem. B, 2002, 106 (18), pp 4705–4713
8. Z. Wang, Y.-K. Su, H.-L. Li, Applied Physics A, 74(2002) 4, pp 563–565.
9. M.V. Tomić, Lj. J. Pavlović, M. G. Pavlović, D.Stanojević, M.Gligorić, Zaštita materijala, 47(2006)4, str.23-28.
10. H. Masusda, M. Satoh: Jpn. J. Appl. Phys. 35, (1996), 1126
11. S.I. Krichmar, A.Ya. Pronskaya, Elektrokhimiya 2 (1966).
12. Catherine Y. Han ,Gerold A. Willing , Zhili Xiao , H. Hau Wang , Langmuir, 23(2007)3, pp 1564–1568.
13. P.V. Shchigolev, Elektroliticheskoe i himicheskoe polirovanie metallov, Akafemii nauk SSSR, Moskva, 1959.
14. S.Ya.Grilikhes, Elektroliticheskoe i himicheskoe polirovanie, Mashinostroenie, Leningrad, 1987.

Corrosion processes in the oil and gas industry and methods for their mitigation

Korozioni procesi u industriji nafte i gasa i metode za njihovo ublažavanje

Živče Šarkoćević[1], Bojan Stojčetović[2], Srđan Jović[1], Dragan Lazarević[1]

[1]University of Priština, Faculty of Technical Sciences, Kosovska Mitrovica, Serbia

[2]High Technical School of Vocational Studies Zvečan, Zvečan, Serbia

[1]Univerzitet u Prištin, Fakultet tehničkih nauka, Kosovska Mitrovica, Srbija

[2]Visoka tehnička škola strukovnih studija Zvečan, Zvečan, Srbija

Abstract

To ensure the smooth and uninterrupted flow of oil and gas to end users, it is essential that engineers in the design and construction of oil and gas pipelines are aware of corrosion, because the exploitation and casing pipe as well as transport lines and their components were subject to material degradation due to corrosion. This paper gives a comprehensive overview of the problem of corrosion during oil and gas production and its mitigation. The chemical process of the formation of various types of corrosion occurs in the oil and gas industry. Factors affecting each of the different forms of corrosion are also shown. Methods for reducing corrosion levels are presented in accordance with current low cost technology. It is notable that the principles of corrosion must understand how to effectively select materials and designed, developed and used metal structures for optimal economic life of the plant and operating safety in exploitation of oil and gas. Also, the materials used to build oil and gas pipelines last longer when used together inhibitors and coatings than when using only inhibitors. However, collaboration between engineers of different profiles in the design and construction of oil and gas to save billions of dollars that are spent on elimination of consequences resulting from the operation of corrosion.

Keywords: *Oil and gas, Alloys, Production, Corrosion, Industry, Materials, Inhibitors*

Izvod

Da bi se obezbedio nesmetani i neprekidni protok nafte i gasa krajnjim korisnicima, neophodno je da inženjeri pri projektovanju i izgradnji naftovoda i gasovoda budu svesni korozije, jer bi eksploatacione i zaštitne kolone cevi kao i transportne linije i njihovi elementi bili podložni degradaciji materijala zbog korozije. Ovaj rad daje sveobuhvatan pregled problema korozije tokom proizvodnje nafte i gasa i njegovog ublažavanja. Dat je hemijski proces nastanka različitih vrsta korozije koji se pojavljuju u industriji nafte i gasa. Prikazani su i faktori koji utiču na svaki od različitih oblika korozije. Prikazane su metode za smanjenje nivoa korozije u skladu s trenutnom tehnologijom niskih troškova. Primetno je da se principi korozije moraju razumeti kako bi se efikasno selektovali materijali i projektovali, izradile i koristile metalne konstrukcije za optimalni ekonomski vek postrojenja i sigurnost u radu pri eksploataciji nafte i gasa. Takođe, materijali od kojih se izgrađuju naftovodi i gasovodi traju duže kada se zajedno koriste inhibitori i zaštitni premazi nego kada se koriste samo inhibitori. Međutim, neophodna je saradnja inženjera različitih profila pri projektovanju i izgradnji postrojenja za eksploataciju nafte i gasa kako bi se uštedele milijarde dolara koje se troše na otklanjanje posledica nastalih delovanjem korozije.

Ključne reči: *nafta i gas, legure, proizvodnja, korozija, industrija, materijali, inhibitori*

Introduction

Corrosion is the process of destruction of metals due to chemical or electrochemical effect with the surrounding environment [1] and the danger ftom natural potential associated with the production and transport of oil and gas [2]. Almost every aquatic environment can cause corrosion, which occurs in a number of complex conditions in the production, processing and pipelines and pipelines [3]. This process consists of three elements: anodes, cathodes and electrolytes. Anode is a corroding metal site, the electrolyte is a corrosive medium that allows the transfer of electrons from anode to the cathode, and the cathode forms an electrical conductor in a cell that is not consumed in the corrosion process [4]. Crude oil and natural gas may contain different media that can be highly corrosive. In the case of oil and gas wells and pipelines, such highly corrosive media are carbon dioxide (CO2), hydrogen sulphide (H2S) and free water [5].

The content of CO2, H2S and free water in the oil and gas wells can eventually lead to corrosion damage of the inner surfaces of the pipeline. Bore hole lines as well as lines of exploitation columns of tubes with variable conditions in the well during the drilling process, such as: change in the composition of liquids; Discharging the deposits during the period and changing working conditions with the change of pressure and temperature. Material degradation leads to a reduction in the mechanical properties of the material. Corrosion damages lead to loss of material, reduction in wall thickness of the pipe, and sometimes to breakage. Problems of corrosion in oil and gas wells are a problem of global significance, as they lead to large material losses due to production delays and causing ecological disasters [1].

Corrosion is one of the major problems in the industry of the modern world. Most modern industrial plants can not be designed without taking into account the corrosion effects on the lifetime of the equipment. Recent industrial disaster research shows that many industries have lost billions of dollars for corrosion. Due to the effects of corrosion, there have been leakage of pipelines of some world oil companies, which has led to pollution of the environment and large material costs for elimination of consequences of ecological pollution [6]. The possibility of corrosion in oil and gas production plants is a special problem for engineers who are designing and constructing these plants. It is also known that corrosion can have certain effects on the production process itself and product purity.

Costs related to damage caused by corrosion of all types are estimated at 3% to 5% of gross national product of industrial countries [7]. The total annual cost of corrosion in the oil and gas production industry is estimated at $ 1,372 billion, of which $ 589 million are costs incurred on transport pipelines and plants, $ 463 million per year are costs incurred on oil and gas wells and $ 320 million in Capital expenditures related to corrosion [8]. Costs of the oil and gas industry arising from the elimination of the consequences of the effects of corrosion and the maintenance of pipelines and equipment amount to tens of billions of dollars annually [3]. Costs in the American industry arising from the effects of corrosion are estimated at $ 170 billion a year, of which more than half of these costs relate to costs incurred in the oil and gas industry [9]. The internal corrosion in the wells and pipelines is influenced by the content of CO2 and H2S, temperature, chemical composition of water, flow rate and pipe material quality [10]. Reducing the level of corrosion (mm / year) can significantly increase the lifetime of the equipment, which contributes to the reduction of maintenance costs. Currently, many components are used for the exploitation of oil and gas made of carbon steel. In recent times, there has been a growing demand for oil and gas exploitation plants to be built from corrosion-resistant materials, which require much higher costs in the construction process. The problem of corrosion is a challenge at a global level and must be addressed.

Types of corrosion in the oil and gas industry

The most common form of corrosion in the oil and gas industry occurs when steel contacts the aquatic environment [4].

In the oil and gas industry, carbon dioxide (CO2) and hydrogen sulphide (H2S) are mostly present, and water is their catalyst for corrosion. When water is combined with CO2 and H2S, the environment forms the following reactions [11]:

$$Fe + H_2CO_3 \rightarrow FeCO_3 + H_2 \quad (1)$$

$$Fe + H_2S + H_2O \rightarrow FeS + 2H \quad (2)$$

There may be a combination of the above-mentioned reactions if both gases are present. These resulting molecules are attached to the cathode or released into the electrolyte, and the process of corrosion is continued. The corrosion process is shown in Figure 1.

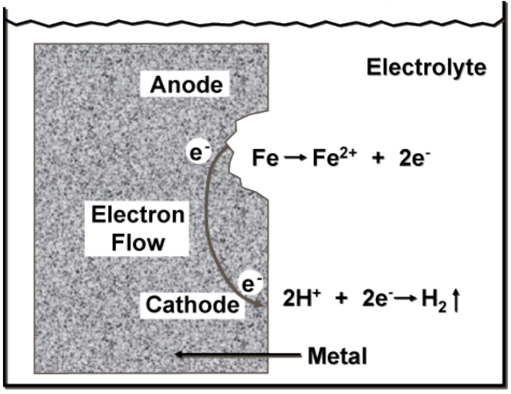


Figure 1. Corrosion process

It is a great challenge to classify the types of corrosion in the oil and gas industry in a unique way. Corrosion can be done based on the appearance of damage from corrosion, mechanism of origin, industrial section and preventive methods. There are many types and causes of corrosion. The mechanism present in the pipeline system varies depending on the composition of the liquid, service location, geometry and temperature. In all cases of corrosion, the electrolyte must be present for the reaction to occur. In the oil and gas industry, the main forms of corrosion include: sweet corrosion, acid corrosion, oxygen corrosion, galvanic corrosion, corrosion in gaps, cavitation corrosion, corrosion caused by microbiological action and voltage corrosion.

Sweet corrosion (CO_2 corrosion)

Corrosion has been recognized for many years in the production and transport of oil and gas [12]. CO2 is one of the main agent for corrosion in the oil and gas production [13]. Dry CO2 by itself is non-corrosive at the temperatures in the system for the production of oil and gas, but is when dissolved in the aqueous phase through promote electrochemical reaction of the contact between the steel and the contact water phase [14]. The most important criteria for the appearance of corrosion due to the presence of CO2 in the gas are the partial CO2 pressure, the presence of water and the pH value of the medium and the characteristics of metals [13, 15] and is by far the most common form of corrosion in the production of oil and gas [2]. In the presence of water and under certain conditions, CO2 is very corrosive, because its dissolution in water creates a carbonic acid that reduces the pH value of water and corrosion occur. The most common forms of corrosion damage due to the action of CO2 on metal are "pitting" (local damage resulting in rapid penetration and removal of metal on a small area) [16], Figure 2 and the form of general corrosion [17], Figure 3.

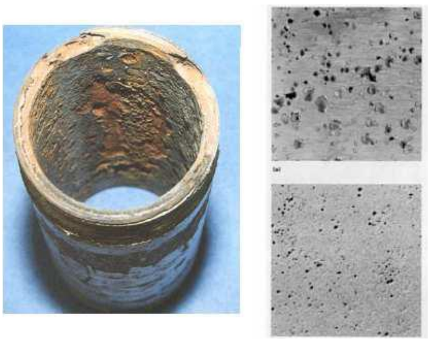


Figure 2. Pitting corrosion

Figure 3. General corrosion

Acid corrosion (H2S corrosion)

Although H2S itself is not corrosive, similar to CO2 and H2S in contact with water becomes a serious corrosive agent [18], which leads to the growth of the gas pipeline [13]. Similar to CO2 and H2S is a gas that becomes corrosive in contact with water. Become especially corrosive if CO2 and O2 are present. Corrosion caused by the content of H2S is also called "sour corosion". Figure 4 shows the degradation of oil and gas pipelines under acid corrosion.

Figure 4. Degradation of oil and gas pipelines under acid corrosion

Iron corrosion in the presence of H2S and water is dependent on the dissociation of the H2S molecule and dissociation of the Fe atoms on the anode.

Anoda:

$$Fe \rightarrow Fe^{+2} + 2e^{-} \qquad (3)$$

Cathode:

$$H_2S+H_2O \rightarrow H^{+} + HS^{-} + H_2O \qquad (4)$$

$$HS^{-} \rightarrow H^{+} + S^{2-} \qquad (5)$$

$$2H^{+} + Se^{-} \rightarrow 2H \qquad (6)$$

$$Fe^{2} + S^{2+} \rightarrow FeS \qquad (7)$$

The general equation of acid corrosion can be expressed as follows [27]:

$$H_2S + Fe + H_2O \rightarrow FeS + 2H + H_2O \qquad (8)$$

Along with tritium (FeS), other ferrous sulfides of the Fex Sy type are formed, which depends on the conditions, among which the most important partial pressure is H2S and the pH value of water. Thus, for example, at low concentrations of H2S (partial pressure 6.3 • 10-5 to 7 • 10-3 bar), the

sulphide film is essentially pyrite FeS2 and triolite FeS, and rarely pirotitine Fe7S8 or canzit Fe9S8. When the partial pressure is above 7 • 10-3 bar, the prevailing film is a canzite.
The pH of the water is also have influence on the type of sulphide film. When the pH value is 3-4 or greater than 9, pyrite prevails; When the pH value is 4-6.3 or 8.8-10, the film is a mixture of cansite, pyrite and troilite, and when the pH value in the region of 6.6-8.4, the film is generally canzite.
Fex Sy settles on the surface of the wall as a black powder or deposit, creating a film that is protected under the condition that it is uniform and unbroken throughout the surface. Otherwise, this deposit, powder or sludge residue becomes a cathode on the steel, and the result is a deep pitting corrosion of the anode, i.e. Exposed metal surfaces. From reaction (8) it follows that the reaction product is not only FeS but also atomic hydrogen. This form of hydrogen has a pickling characteristic in the surface of the metal wall surface, which can never be perfectly flat, enters the structure of the metal grid and causes brittleness or fragility. This type of corrosion is very dangerous, and it can take place very quickly. It is also called SSC (corrosion), because, due to tightening stress and weakening of the structure of the metal grid, there is a breakdown. This type of corrosion is of local character and occurs most often in seams and around them. According to NACE standard MR-01-75, SSC corrosion occurs in all systems where partial pressure H2S is greater than 0.0035 bar.
There is another type of corrosion damage that can be caused by the presence of hydrogen. Namely, atomic hydrogen, collected in the metal wall bores, turns into a molecular one. In the continuous process, this increases the volume, as well as the pressure, which is reflected by the appearance of bubbles and cracks. This type of corrosion is called HIC (hydrogen-induced cracking) corrosion. The solution of the problem shown should be sought in a smooth tube, with no irregularities, which occur due to inclusions during the construction of the pipe. Steel, in its chemical composition rich in manganese sulfide (MnS), is most prone to creating inclusions. It is advantageous if it contains as much calcium as can, in order to during the manufacture of pipes, in the metal would not get segregation. In selection of metal resistant to H2S, its hardness is also important. Namely, there is material resistance, but provided the hardness does not exceed 22 HRC. Very hard steels are more susceptible to hydrogen corrosion than less rigid. In their selection, the hardness of the metal and the values of their load should be considered, ie. hardness of metal and the H2S concentration, Figures 5 and 6.

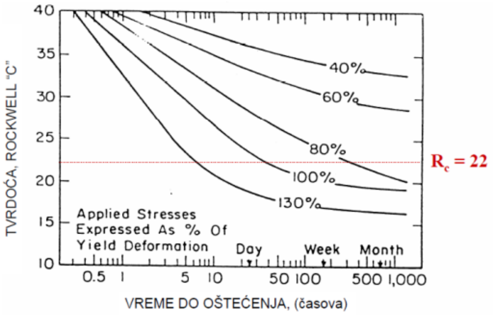


Figure 5. The impact of stress on time of material fracture, due to H2S corrosion for different hardness ("Rockwell").

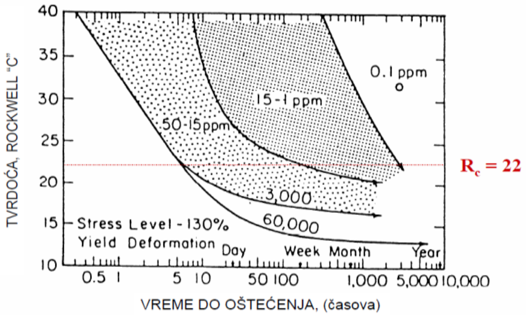


Figure 6. The influence of the H2S concentration at the time of fracture of materials for different hardnesses ("Rockwell")

In addition to the occurrence of H2S, it should be noted that microorganisms can accelerate corrosion if there are conditions for their development, such as moisture, basic minerals, organic matter as a source of energy and a suitable pH value. Microorganisms, such as Desulfovobrio (sulphate-reducing), use hydrogen created by electrochemical corrosion for their growth and reduce sulfates to H2S, resulting in anaerobic corrosion.

Oxygen corrosion

Of the three listed gas that can be dissolved in water when transporting oil and gas fluids, oxygen is by far the most harmful. Oxygen is a strong oxidant and reacts very quickly with metal. As a depolarizer and electronic acceptor in cathodic reactions, oxygen accelerates anodic destruction of metals [19]. It can cause strong corrosion at very low concentrations (<1.0 ppm) [20], and drastically increase the corrosivity of CO2 and H2S [21]. In pipelines and production equipment may be injected with water or inhibitors [22]. Oxygen is not present in groundwater, but can come through contact with the air through accidental cracks or planned exposure to the atmosphere. Waters from the lake, the ocean or the river are mostly saturated with oxygen, and water from shallow sources can contain some oxygen. Oxygen solubility in water depends on the pressure, temperature and content of chloride. Less is soluble in salt than in pure water. Accelerates corrosion because it is a strong oxidizing agent and mainly causes pitting corrosion. If the water contains enough O2, oxidation of Fe2 + to Fe3 + can occur, before Fe2 + ions are diffused from the surface of the metal to the solution. In this case, protective Fe (OH) 3 is formed on the surface. However, if a sufficient amount of chloride ions is present, they participate in the formation of the layer and the rate of corrosion continues to increase by increasing the concentration of O2 [21]. Figure 7 shows the corrosion of pipes due to the action of oxygen.

Figure 7. Corrosion of pipes due to the action of oxygen

Galvanic corrosion

This type of corrosion occurs when two metallic materials with different electrochemical potentials are in contact and are exposed to the electrolytic environment. In such a situation, a metal with a smaller negative potential becomes anode and begins corroding [13, 23]. Anode loses metal ion to balance the flow of electrons. Because metals are composed of crystals, many of these cells are set up, causing intergranular corrosion. Problems are most serious when the surface area difference between the anode and the cathode is large (the surface of the anode is smaller than the surface of the cathode) Figure 8. Figure 9 shows the galvanic corrosion of the pipes and parts of the equipment used for the production of oil and gas.

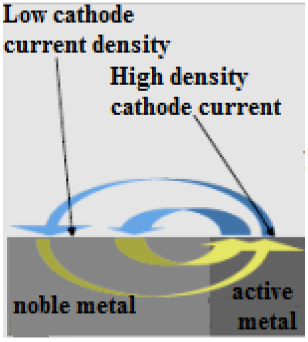


Figure 8. Anode surface smaller than the cathode

Figure 9. Galvanic corrosion

Corrosion in gaps

Corrosion in gaps is usually a local corrosion that takes place in narrow slits or a part of the metal surface in a protected or restricted environment compared to the rest of the metal, usually begins with the creation of a differentiation aeration article - due to the corrosion occurance, the oxygen is consumed in the small volume of the electrolyte in the gap, on the open surface the pressure of oxygen is undisturbed [1], Fig. 10.

Into gaps disrupts the passivity and increases the concentration of dissolved metal cations which attract negatively charged ions of Cl- from solution. Due to the high concentration of metal cations and chloride anions, the reaction occurs:

$$MeCl2 + 2H_2O \rightarrow Me(OH)_2 + 2HCl \qquad (9)$$

As a result of the reaction in the gap, the pH is significantly lowered (it can have values of 1 to 4), which increases the dissolution rate of the metal while the external electrolyte is neutral.

The high concentration of the solution in the gap causes even less solubility of the oxygen, which contributes to the condition of the deaerated gap. The mechanism of corrosion propagation in the openings is autocatalytic, since its unfolding creates even more favorable conditions for the continuation of the process.

The oxygen dissolved in the drilling fluid causes corrosion in the gaps of the rubber-drilling tool [24]. Figure 11 shows the corrosion damage of the pipes due to corrosion in the gap.

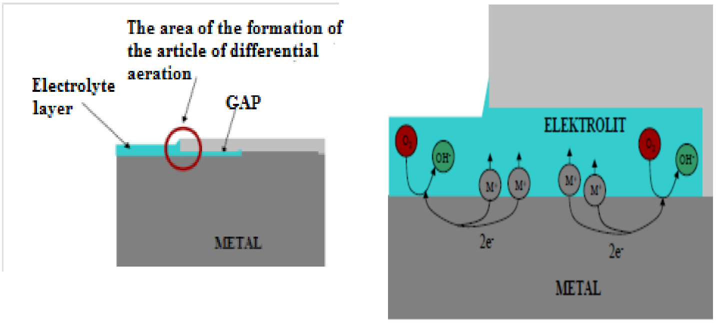


Figure 10. Corrosion in gaps, initiation and propagation of corrosion

Figure 11 Corrosion damage caused by corrosion in gaps

Erosion corrosion

The erosion corrosion mechanism increases the speed of the corrosion reaction by continuously removing the passive layer of corrosion products from the pipe wall. The passive layer represents a thin layer of corrosion product which actually serves to stabilize the corrosion reaction and slows it down. As a result of turbulent fluid flow and high pressure in the pipeline, this passive layer can be removed, which leads to an increase in the corrosion rate [25]. Erosion corrosion occurs when there is a turbulent fluid flow that causes a significantly higher rate of corrosion [26] and depends on the velocity of fluid flow and density and the morphology of solids present in the liquid [13]. The high speed and the presence of abrasive materials and corrosive gases in the produced liquids in the wells contribute to this destructive process. This form of corrosion is often neglected or recognized as wear on the surface of the pipe [27].

Microbiological induced corrosion

This type of corrosion is caused by bacterial activity. Bacteria produce waste products such as CO2, H2S and organic acids that increase corrosion of pipelines [28]. Microbes tend to form colonies in a hospitable environment and allow for increased corrosion under the colony. The formation of these colonies is supported by neutral water, especially when it stagnates [13]. Numerous reports have been published about the presence of microbes in reservoirs [29, 30, 31]. Lazar et al. [30] found rich microbiological flora Bacillus, Pseudomonas, Micrococcus, Micobacterium, Clostridium and Escherichia in the waters of formed oil fields. Utvrđeno je da Escherichia sadrži hidrogenazu, enzim koji koristi molekularni vodonik i može biti povezan sa depolarizacijom katodne vodonične kiseline, što dovodi do korozije čeličnih spojnica i cevi u naftnim bušotima [32]. It has been found that Escherichia contains a hydrogenase, an enzyme that uses molecular hydrogen and can be associated with the depolarization of cathodic hydrogenic acid, which leads to corrosion of steel joints and tubes in oil drills [32]. Bacteria that produce some forms of polysaccharides, such as Achromobacter sp., Flavobacterium sp., And Desulfuricans sp., Adhere to one another, forming a large mass on the walls of the tube, causing major problems with injection well connections [31]. Microbiologically-induced corrosion (MIC) is identified by the appearance of black slurry waste material or nodes on the surface of the pipe, as well as the cracking of the pipe walls below these deposits. Figure 12 represents the corrosion of the pipeline under the influence of corrosion MIC, [33].

Figure 12. Microbiological induced corrosion

Stress corrosion

Stress corrosion cracking (SCC) is probably the most complex form of corrosion because it involves several independent factors, and as a result often results in catastrophic fractures and large damage. Stress corrosion and refraction caused by stress corrosion are most often due to simultaneous action by tightening the static stress (external or internal) and local corrosion [34]. Forms of external corrosion often represent the beginning of crack formation, although the crack can already be present due to mechanical damage to the surface. Therefore, the prevention of the occurrence of these three forms of corrosion is often the prevention of stress corrosion. The most obvious identification characteristic of SCC in the pipelines is the high pH of the surrounding environment, the appearance of fractures or colonies of parallel cracks on the outer surface of the tube [35]. Figure 13 shows the pipeline after pipe stress corrosion cracking.

Figure 13. Fracture of pipes due to stress corrosion

Reducing corrosion in the oil and gas industry

The challenges of corrosion of oil fields are not static phenomena. Fluid characteristics change over time, resulting in systems becoming less responsive to corrosion-reduction programs [3]. In the sphere of control and prevention of corrosion in the oil and gas industry, there are technical options such as cathode and anode protection, material selection, chemical dosing and application of indoor and outdoor coatings. It is widely known in the oil and gas industry that effective corrosion management contributes to maintaining property integrity and optimizing the costs of monitoring and inspection [36]. Methods for reducing corrosion effects can be classified as follows [13]:

- Choosing suitable materials
- Use of inhibitors
- Use of protective coatings
- Adequate monitoring of corrosion and inspections
- Cathodic protection technology

When existing construction materials are not corrosion-resistant, materials that meet certain requirements in terms of corrosion resistance are selected [13]. Stainless steel covers a wide range of alloys, each of which has a certain combination of resistance to corrosion and mechanical properties. When used in the exploration of oil and gas, many of these stainless steels are used depending on the requirements of the exploitation conditions. Applicable corrosion-resistant alloys in the oil and gas industry proposed by Smith [37] include Cr and Ni, duplex and stainless steel. Johansson and associates [38] proposed special stainless steels for solving the problem of corrosion in the oil and gas industry.

Nalli [13] presented some of the most frequently used materials in the oil and gas industry, based on detailed research of the process and conditions of work. Mannan et al. [39] introduced a new alloy of 945, the nominal composition Fe, 47Ni, 20.5Cr, 3Mo, 2Cu, 3Nb, 1.5Ti resistant to corrosion when applied to the oil and gas industry. Craig [40] introduced some alloys (shown in Table 1) whose applications in the oil and gas industry are higher in the absence of oxygen.

Table 1. Chemical composition of recommended materials in the oil and gas industry

Alloy	**Nominal composition**							**Application of oil and gas**
	Cr	**Ni**	**Mo**	**Fe**	**Mn**	**C**	**N**	
13 Cr	13	-	-	Balanced	0.8	0.2	-	Resistance to corrosion in CO2 / NaCl concentrations in the absence of O2 and H2S
316	17	12	2.5	Balanced	1.0	0.04	-	It is often used on oil fields with complete absence of O2
22 Cr	22	5	3	Balanced	1.0	0.1	0.1	Subject to localized corrosion in the presence of small amounts of O2 and H2S
25 Cr	25	7	4	Balanced	1.0	0.1	0.3	Resistant to corrosion in H2S / CO2 environments in the absence of elemental sulfur

Use of inhibitors

The corrosion inhibitor is a chemical that, when added to the solution in very small amounts, significantly increases the resistance of the material to corrosion. A good inhibitor is non-toxic for the environment, economical for application and effective in very low concentrations [41]. In the production, transport and processing of oil and gas, internal corrosion control is achieved to the greatest degree with the use of corrosion inhibitors [42]. The corrosion inhibitor can operate in several ways: it can limit the speed of the anode process or the cathode process by simply blocking active locations on the surface of the metal. Alternatively, the increasing potential of the metal surface can act, so that the metal enters the passivation area where a natural oxide film is formed. Further action of some inhibitors is that the inhibitory compound contributes to the formation of a thin layer on the surface that prevents the corrosion process [43].

Factors considered before using corrosion inhibitors in the oil and gas industry include toxicity, environmental safety, availability and costs. Organic corrosion inhibitors are more efficient than inorganic to protect steel from acid corrosion [42]. Miksic et al. [44] estimated several types of corrosion inhibitors for the petroleum industry in different flow conditions. Inhibitors were tested at a concentration range of 50 to 200 ppm in electrolytic and electrolyte / hydrocarbon mixtures in the presence of CO2 and H2S in static and dynamic conditions. Unlike conventional methods, such as amine-based corrosion inhibitors, the injection of easily volatile corrosion inhibitors (VpCI) into any part of the system immediately creates a mono-molecular protective layer that is supplemented [45]. VpCI technology is an environmentally safe and economical option to protect against corrosion. VpCI forms a physical bond on the surface of the metal and creates a protective layer that protects against aggressive ions. It can be used in pipelines, oil and gas wells and refineries. In addition, these anti-corrosive additives based on VpCI are designed to function well in multiphase flow systems. A graph showing world consumption of corrosion inhibitors based on value is given in Figure 14 [46].

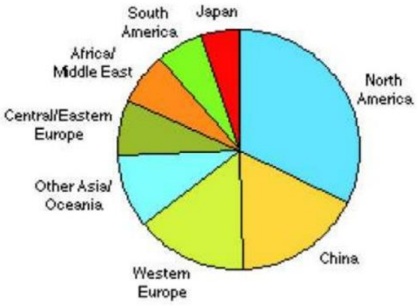


Figure 14. World consumption of corrosion inhibitors

Use of protective coatings

The metal protective layer is used to avoid direct contact with process media in order to extend the life of the equipment. The protective layer can be paints, coatings, metal or non-metallic coatings. Non-metallic coatings such as fiber glass, epoxy and rubber, are used on equipment such as separators, impact drums and storage tanks. Sometimes, on certain components, such as flanges and screws, nickel, zinc and cadmium coatings are preferred [13]. The Phillips Ecofisk wells with low H2S content, 90 lb and.-2 CO2 and up to 30,000 ppm chloride were implanted with N-80 protective tubes, which lasted only 19 months and despite the application of inhibitors so coating application [47] was applied. Where no inhibitor is injected, the coated tubes continue to last only 19 months, however, with the use of inhibitors every 30 days, the life span of protective tubes for up to 7 years has been prolonged [48].

Fuzioni epoxide (FBE) and three-layer polyolefin (3LPO) (polyethylene or polypropylene (PP)) are currently the most commonly used external corrosion protection systems [49]. The one-tier FBE is most applicable in North America, Saudi Arabia, and the United Kingdom; Double-layer FBE in Australia; And 3LPO coatings dominate the rest of the world market for tubular coatings [50]. Bredero Shav, as world leader in pipe coating solutions, presented several unique advanced and proven technologies for coating pipelines. This includes a composite coating system (HPCC) with one powder coating, consisting of a basic coating of the FBE, a medium density polyethylene layer and a layer containing a chemically modified polyethylene adhesive. Coating technology for high-strength steel used for the construction of oil and gas pipes, in areas of extremely low temperatures, because they allow for reduction in the thickness of the pipe wall, high flexibility and hardness. The coating on high-strength steel tubes should be resistant to impact at -40 ° C / -50 ° C. The application technology of a multilayer polypropylene composite FBE on steel tubes used in high-temperature wells. The method provides a fixed outer diameter and a homogeneous foam structure without the inclusion of air [51]

Technology of cathodic protection

Cathodic protection is a method of reducing corrosion by minimizing the potential difference between the anode and the cathode. This is achieved by applying the current to a structure to be protected (such as a pipeline) from a source. When sufficient current is applied, the whole structure will be in one potential, in this way, the anode and cathode locations will not exist [52]. Usually used in combination with coatings and can be considered as a secondary control of corrosion. The cathodic protection system can be designed to prevent both corrosion and microbiologically controlled corrosion [53]. Two methods of applying cathodic protection include [54]:

- Sacrifice (or galvanic) anodic-cathodic protection (SACP)
- Impressive instantaneous cathodic protection (ICCP)

The main difference between these two is that the ICCP uses an external source of power supply with inert anodes, and SACP uses the naturally present electrochemical potential difference between the various metal elements to provide protection.

Sacred anodic-cathodic protection

In this type of application, the natural electrochemical potentials of different metals are used to provide protection. The sacrificial anodes are connected to the structure under protection and conventional current flows from anode to the structure as long as the anode is more active than the structure. As a stream of currents, all corrosion occurs on the anode that is sacrificed to provide protection against corrosion to the structure. Figure 15 is a diagram representing the cathodic protection of sacrificial anodes [1].

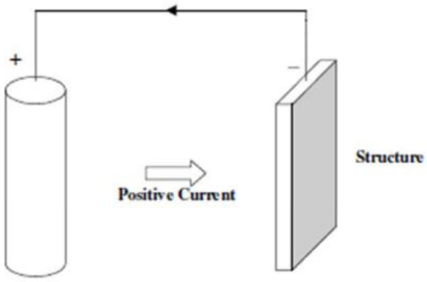


Figure 15. Cathodic protection with sacrificial anode

Impressed current cathodic protection (ICCP)

In impressed instantaneous cathodic protection, the current is impressed or applied by powering. The energy source must be able to deliver direct current, and examples are transformer rectifier units, units for the production of solar energy or thermoelectric generators. The anodes are inert or have low power consumption and high efficiency which reduces costs. Typical anodes are titan coated with mixed metal oxide or platinum, silicon iron, graphite and magnetite. Laoun et al. [55] applied an impressed instantaneous cathodic protection to a dig in pipeline using a solar photovoltaic generator as an energy source, the output current being high enough to protect the pipeline at low cost applications. Figure 16 represents the ICCP scheme used [55].

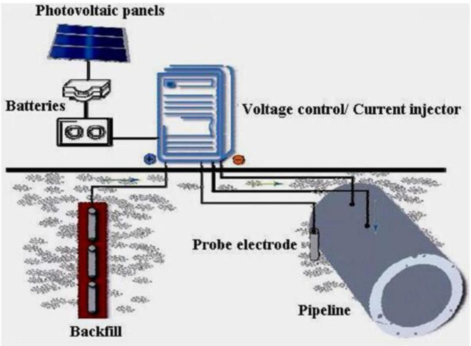


Figure 16. Schematic representation of the ICCP.

Adequate monitoring of corrosion and inspections

Corrosion monitoring is a practice of measuring the corrosivity of the process conditions by using probes (mechanical, electrical or electrochemical devices) that are inserted into the process stream and continuously exposed to the flow process conditions. Only corrosion monitoring techniques allow direct and online measurement of metal / corrosion losses in petroleum and process systems [56]. One of the methods is the periodic measurement of wall thickness of tubes at fixed and endangered locations for the purpose of corrosion assessment [56]. Corrosion is also monitored by placing electronic probes into the pipelines and measuring the change in electrical resistance in the probe. The transport pipelines are checked by intelligent pigs to determine the state of the inner surfaces of the pipeline due to corrosion and measure the thickness of the pipe wall [13].

Based on an assessment of material conditions, a corrective measure for material change or replacement of equipment or sometimes temporary repair work is initiated before replacement is made. In practice, it is observed that physical control is the best way to track corrosion and assess material conditions. Other areas in which corrosion monitoring and inspections in the oil and gas industry are required include drilling, digester, rinsing, drainage, conduit, drainage and acid water systems [3].

Discussion

To alleviate the effects of corrosion in the oil and gas industry, solutions for the various types of corrosion discussed in this paper are outlined. Stainless steels are widely used in the oil and gas industry because they are resistant to acid-induced corrosion by H2S. Materials presented by Nalli [13] have different applications in various equipment of the oil and gas industry with high content of H2S and high temperatures. Materials (13 Cr, 316, 22 Cr and 25 Cr) recommended by Craig [40] are applicable to the solution of corrosion in the oil and gas industry, but are only active in the absence of oxygen, H2S, and elementarn sulfur. The alloy (13 Cr) is resistant to corrosion in CO2 / NaCl concentrations in the absence of O2 and H2S, while 25 Cr is resistant to corrosion in H2S / CO2 environments in the absence of elemental sulfur. The inhibitors have been shown to be one of the main tools for the suppression of corrosion in the oil and gas industry. They protect metal surfaces by reacting with impurities in the environment that can cause pollution. Most inhibitors have been shown to be the main tools for suppressing oxygen corrosion [46] by removing oxygen from the fluid, thereby improving the chances of material resistance to corrosion in contact [13].

Corrosion control by inhibitors is not recommended for low-H2S boreholes, since this option has high implications for operating costs throughout the life of the field thanks to the operating costs of injecting the inhibitor and the higher frequency of workers. Nevertheless, there is concern regarding the efficacy of inhibitors in the control of sulphide stress in carbon tightening [37]. However, the impressed current cathodic protection method presented is a better way to solve these problems because the process has wide potential protection and the system can be adapted.

Literature

1. Roberge PR: *Handbook of corrosion engineering*. New York: McGraw-Hill; 2000.Google Scholar
2. Kermani MB, Smith LM: *CO2 corrosion control in oil and gas production: design considerations*. London: The Institute of Materials, European Federation of Corrosion Publications; 1997.Google Scholar
3. Champion Technologies: *Corrosion mitigation for complex environments*. Houston: Champion Technologies; 2012.Google Scholar
4. Corbin D, Willson E: *New technology for real-time corrosion detection*. USA: Tri-service corrosion conference; 2007.Google Scholar

5. Lusk D, Gupta M, Boinapally K, Cao Y: Armoured against corrosion. *Hydrocarb Eng*2008, 13:115–118. 10.1061/(ASCE)1084-0699(2008)13:3(115)CrossRefGoogle Scholar
6. Oyelami BO, Asere AA: *Mathematical modelling: An application to corrosion in a petroleum industry*. *NMC Proceedings Workshop on Environment*. Abuja, Nigeria: National Mathematical Centre;Google Scholar
7. Uhlig HH: The cost of corrosion in the United States. *Chem and Engng News* 1949, 27:2764. 10.1021/cen-v027n039.p2764CrossRefGoogle Scholar
8. Simons MR: *Report of offshore technology conference (OTC) presentation*. NACE International oil and gas production; 2008.Google Scholar
9. Tuttle RN: Corrosion in oil and gas production. *J of Petrol Technol* 1987, 39:756–762.CrossRefGoogle Scholar
10. http://www.touchbriefings.com/pdf/30/exp032_p_12Nyborg.pdf
11. Dean F, Powell S: *Hydrogen flux and high temperature acid corrosion*. 06436 edition. NACExpo 2006 conference; 2006.Google Scholar
12. Kermani MB, Harrop D: *The impact of corrosion on the oil and gas industry*. 11: SPE Production Facilities; 1996:186–190.Google Scholar
13. Nalli K An overview. In *Corrosion and its mitigation in the oil and gas industry*. PM-Pipeliner Report; 2010.Google Scholar
14. Dugstad A: *The importance of* $FeCO_3$ *supersaturation on the* CO_2 *corrosion of carbon steels, corrosion "92, paper 14*. Houston: NACE; 1992.Google Scholar
15. Gatzky LK, Hausler RH: A novel correlation of tubing corrosion rates and gas production rates. *Adv in* CO_2 *Corro* 1984, 1: 87.Google Scholar
16. Schmitt G: *Fundamental aspects of* CO_2 *corrosion*. 1st edition. Houston: NACE; 1984:10.Google Scholar
17. Dunlop A, Hassel HL, Rhodes PR: *Fundamental considerations in sweet gas well corrosion*. 1st edition. Houston: NACE; 1984:52.Google Scholar
18. Ray JD, Randall BV, Parker JC: *Use of reactive iron oxide to remove* H_2S *from drilling fluid*. Houston: 53rd Annu. Fall Tech. Conf. of AIME; 1978.Google Scholar
19. Weeter RF: Desorption of oxygen from water using natural gas for counter-current stripping. *J Petrol Technol* 1965, 17(5):51.CrossRefGoogle Scholar
20. Snavely ES: Chemical removal of oxygen from natural waters. *J Petrol Technol* 1971, 23(4):443–446.CrossRefGoogle Scholar
21. TPC Publication 5: *Corrosion Control in Petroleum Production*, NACE, Houston,TX, 1979, 7-9
22. D. A. Lopez, T. Perez, S. N. Simison: *Materials and Design* 24 (2003) 561-575
23. Martin RL: *Use of electrochemical methods to evaluate corrosion inhibitors under laboratory and field condition*. Manchester: UMIST conference of electrochemical techniques; 1982.Google Scholar
24. Hudgins CM: A review of corrosion problems in the petroleum industry. *Mater Prot* 1969, 8(1):41–47.Google Scholar
25. Hassani S, Roberts KP, Shirazi SA, Shadley JR, Rybicki EF, Joia C: Flow loop study of NaCl concentration effect on erosion corrosion of carbon steel in CO_2 saturated systems. *CORRO* 2012, 68: 2.Google Scholar
26. Sami AA, Mohammed AA: Study synergy effect on erosion-corrosion in oil and gas pipelines. *Engng and Technol* 2008, 26: 9.Google Scholar
27. Bertness TA: Reduction of failures caused by corrosion in pumping wells. *API Dril Prod Pract* 1957, 37: 129–135.Google Scholar
28. Ossai CI: Advances in asset management techniques: an overview of corrosion mechanisms and mitigation strategies for oil and gas pipelines. *ISRN Corro* 2012, 570143.Google Scholar
29. Crawford PB: *Possible reservoir damage from MEOR*. Edited by: Donaldson EC, Clark JB. Springfield, VA: Proceedings of 1982 international conference on microbial enhancement of oil recovery, Afton, OK, May 16–21; 1983:76–79. NTIS NTISGoogle Scholar
30. Lazar I, Constantinescu P: Field trials results of microbial enhanced oil recovery. In *Microbes and oil recovery*. Edited by: Zajic JE, Donaldson EC. El Paso: Bioresources Publications; 1985:122–143.Google Scholar

31. Singer ME: Microbial biosurfactants. In *Microbes and oil recovery*. Edited by: Zajic JE, Donaldson EC. El Paso: Bioresources Publications; 1985:19–38.Google Scholar
32. Gates GPL, Parent CF: Water quality control presents challenge in giant Wilmington Field. *Oil Gas J* 1976, 74(33):115–126.Google Scholar
33. http://www.lbl.gov/Publications/Currents/Archive/Apr-30-2004.html
34. Wilhelm SM, Kane RD: Status report: corrosion resistant alloys. *Petrol Engng Int* 1987, 3641.Google Scholar
35. Baker MJ: *Stress corrosion cracking study*. 2004. http://www.polyguardproducts.com/products/pipeline/TechReference/SCCReport-Final Report with Database.pdf Google Scholar
36. Energy Institute: *Guidance for corrosion management in oil and gas production and processing*. London: Annual Report; 2008.Google Scholar
37. Smith L: Control of corrosion in oil and gas production tubing. *British Corro J* 1999, 34(4):247. 10.1179/000705999101500905 Cross Ref Google Scholar
38. Johansson E, Pettersson R, Alfonsson E, Weisang-Hoinard F: Specialty stainless for solving corrosion problems in the oil and gas industry. *Offshore World* 2010., 40:Google Scholar
39. Mannan S, Patel S: *A new high strength corrosion resistant alloy for oil and gas applications*. New Orleans: Paper presented at NACE Corrosion; 2008. Google Scholar
40. Craig BD: Selection guidelines for corrosion resistant alloys in the oil and gas industry. *NiDI Tech Series* 1995, 10073: 1–8.Google Scholar
41. I.L. Rozenfel′d, Corrosion inhibitors, McGraw-Hill Companies, 1981
42. Rajeev P, Surendranathan AO, Murthy CSN: Corrosion mitigation of the oil well steels using organic inhibitors – a review. *J Mater Environ Sci* 2012,3(5):856–869. Google Scholar
43. Graeme W: *Corrosion protection of metals in marine environment*. J. Metal Corrosion Protection, Chemistry Department, University of Auckland; 2010.Google Scholar
44. Miksic BM, Kharshan MA, Furman AY Proceeding of 10th European Symposium of Corrosion and scale inhibitors; 2005.Google Scholar
45. Kharshan M, Furman A: *Incorporating vapor corrosion inhibitors (VCI) in oil and gas pipeline additive formulations*. NACE, Corrosion 98(236); 1998.Google Scholar
46. Muller S, Syed QA, Yokose K, Yang W, Jackel M: *Corrosion inhibitors*. SCUP Home; 2009.Google Scholar
47. Houghton CJ, Westermark RV: *J Pet Technol*. 1983, 239.Google Scholar
48. Hovsepian PE, Lewis DB, Munz WD, Lyon SB, Tomlinson M: Combined cathodic arc/unbalanced magnetron growth CrN/NbN super lattice coatings for corrosion resistant applications. *Surf Coat Tech* 1999, 120(121):535–541.CrossRefGoogle Scholar
49. http://www.europipe.co
50. Westood J: *Macro factors driving the global oil and gas industry and the subsea pipelines sector*. Toronto; 2011.Google Scholar
51. Shiwei WG, Gritis N, Jackson A, Singh P: *Advanced onshore and offshore pipeline coating technologies*. Shangai, China: 2005 China international oil and gas technology conference and expo; 2005.Google Scholar
52. Guyer JP: *An introduction to cathodic protection*. New York: Continuing Education and Development Inc.; 2009.Google Scholar
53. Lazzari L, Pedeferri P: *Cathodic protection*. 1st edition. New York: McGraw Hill; 2006.Google Scholar
54. Baeckmann WV: *Handbook of cathodic corrosion protection*. 3rd edition. New York: McGraw Hill; 1997.Google Scholar
55. Laoun B, Niboucha K, Serir L: Cathodic protection of a buried pipeline by solar energy. *Revue des Energies Renouvelables* 2008, 12(1):99–104.Google Scholar
56. Canadian Association of Petroleum Producers Annual report. In *Best management practices for the mitigation of internal corrosion in oil effluent pipeline systems*. Calgary: Annual report. CAPP; 2009.Google Scholar

Synthesis of modern nanomaterials used for antibacterial and industrial applications

Dragica Chamovska[1], Andrzej Kowal [2,3]

[1] Ss. Cyril and Methodious University, Faculty of Technology and Metallurgy, Skopje, R. Macedonia

[2] Institute of Non-ferrous Metals, CLAiO, Poznan, Poland

[3] ELCATAK, Krakow, Poland

Abstract

Nanotechnology allows fabrication of materials with diameters in the range between 1 to 100 nm. These nanomaterials can be used not only in industry but also in medicine and biology. Nanoparticles of Ag, Cu and Re can be interesting alternative as antibacterial materials and for industrial applications. Antibacterial properties of Ag nanoparticles are well described. New methods of antibacterial Ag nanoparticles synthesis are cheap and interesting. Cu and CuO nanoparticles can be applied as nanofluids in heat transfer systems, as nanocomponents for gas sensors, as nanocatalysts in the synthesis of alcohols, selective adsorbents of electromagnetic radiation and as antibacterial materials. Ag, Cu, CuO and Re nanoparticles were synthesized using wet chemical method. Physicochemical parameters of synthesized materials were analyzed using Scanning Electron Microscopy, Scanning Probe Microscopy, HRTEM, DLS (PCS) and XRD techniques. Using wet chemical method Ag, Cu and CuO nanoparticles of diameter in the range 3 – 41 nm can be produced. Rhenium is added to super alloys used for the production of monocrystalline jet engine blades, elements in power station turbines and screen for space vehicles. Petrochemical industry utilizes rhenium as catalyst in the production of fuels. Rhenium nanopowders were synthesized with polyol and boric acid method. The sizes of produced Re nanograins were determined by DLS (Photon Correlation Spectroscopy) as about 2-4 nm.

Key words: *Synthesis, modern nanomaterials, antibacterial properties, industrial applications*

Introduction

Nanotechnology is a rapidly growing field of science. This area has become an integral part of modern technology. Nanotechnology is said to be a “key technology of the 21st century”, which is the result of its interdisciplinary nature.

Nanomaterials are increasingly becoming a part of our daily lives. They are characterized by new properties that do not accompany to their counterparts existing at the macro scale. Therefore, nanomaterials are used in innovative products and processes.

The vast majority of manufactured nanomaterials are available in different shapes and sizes. It is expected that their use will significantly increase in the next decade.

Nanotechnology allows fabrication of materials with diameters in the range between 1 to 100 nm [1, 2]. These nanomaterials can be used not only in industry but also in medicine and biology. Nanoparticles of Ag [3], Cu [4] and Re [5] can be interesting alternative as antibacterial materials and for industrial applications. Antibacterial properties of Ag nanoparticles are well described. New methods of antibacterial Ag nanoparticles synthesis are interesting [6].

Cu and CuO nanoparticles can be applied as nanofluids in heat transfer systems, as nanocomponets for gas sensors, as nanocatalyst in the synthesis of alcohols, as selective adsorbents of electromagnetic radiation and as antibacterial materials.

Rhenium belongs to the most rare, heave and as well as most expensive metals in the world. The application of rhenium has been limited for long time, but now it is the subject of great interest due to the development of new industrial branches, especially, advanced technologies in aviation and petrochemistry. Rhenium is added to super alloys used for the production of monocrystalline jet engine blades, elements in power station turbines and screen for space vehicles. Petrochemical industry utilizes rhenium as catalyst in the production of fuels.

Experimental

Antibacterial Ag nanoparticles were synthesized using new methods [6].
Cu and CuO nanoparticles were synthesized using wet chemical method [7] and the size of nanoparticles were analyzed using Scanning Electron Microscopy, Scanning Probe Microscopy, HRTEM, DLS and XRD techniques.
Rhenium nanopowders were synthesized with boric acid and polyol method [8]. The sizes of nanograins were determined by DSL (Photon Correlation Spectroscopy).

Results

Nanoparticles of Ag, Cu and CuO of diameter in the range 3 – 41 nm were effectively produced. The sizes of Re nanograins determined by Photon Correlation Spectroscopy as about 2-4 nm (Table 1).

Table 1. Ranges of Ag, Cu and CuO crystallite sizes calculated with the Scherrer equation (based on the half width of the peaks of the diffractogramms) and for Re nanoparticles using DLS (PCS) technique.

Sample	Crystallite size (nm)
Ag (polyol method)	3 – 12
Cu (polyol method)	5 – 13
CuO (polyol method)	6 – 41
Re (boric acid method)	2 – 4

Conclusion

- Nanoparticles of important metals, with diameters in the range between 2 to 50 nm, can be produced using cheap, colloide chemistry methods.
- For nanoparticles applications further study must devolope new methods of metal and oxide nanoparticles deposition on metal and plastics surface.
- Nanoparticles of Cu and CuO can be interesting alternative as antibacterial materials.
- Re nanocomposite can be promising material for industrial applications.

References

1. M. A. Dobrovolskaia, S. E. McNeil, *Nat. Nanotechnol.*, 2007, 2, 469.
2. Y. Xia, X. Xia, H. C. Peng, *J. Am. Chem. Soc.*, 2015, 137, 7947.
3. Q. H. Tran, V. Q. Nguyen , A. T. Le, *Adv. Nat. Sci. Nanosci. Nanotechnol.*, 2013, 9, 33001.
4. Laura Tamayo, Manuel Azócar, Marcelo Kogan, Ana Riveros, Maritza Páez, *Materials Science and Engineering: C*, 2016, 69, 1391–1409

5. A. D. Dobrzańska - Danikiewicz, W. Wolany, *Archives of materials science and engineering*, 2016, 82, 2, 70-78
6. M. Parlinska-Wojtan, M. Kus-Liskiewicz, J. Depciuch, O. Sadik, *Bioprocess and Biosystems Engineering*, 2016, 39, 8, 1213-1223.
7. M. Kaminska, M. Woch, E. Bielanska, A. Kowal, *3rd International Symposium on Surface Imaging/Spectroscopy at the Solid/Liquid Interface*, Krakow, 2012, p. 106.
8. A. Kowal, M. Tomic, D. Chamovska, M. Woch, *3rd International Symposium on Surface Imaging/Spectroscopy at the Solid/Liquid Interface*, Krakow, 2012, p. 111.

Design miniaturized tensile testing machine

Fabler Hamid

HITEC University Taxila Cantt., Pakistan

Abstract

The tensile properties of materials, such as the ultimate tensile strength, yield strength, elongation and elastic modulus, are very important factors for engineering designs. However, it is not easy for students to understand and evaluate the tensile properties of materials. In this study, a small and handy tensile testing machine was designed to help students conduct tensile tests in class using a miniature tensile specimen. The tensile testing machine consists of a stepping motor as an actuator, a load-cell, a load- cell amplifier, a data acquisition system and the testing machine frame. The detected load signal is amplified by the amplifier and is sent to the data acquisition (DAQ) system. The DAQ system with LabVIEW software receives the signals from the load-cell and displacement gauge. Using this testing machine, it is possible to conduct tensile tests on miniature tensile specimens at speeds of 0.001~1.0 mm/s.

Keywords: *Portable tensile testing machine, miniature specimen, heat treatment, stress-strain curve*

Introduction

In engineering design and analysis, tensile stress-strain relationships are frequently needed. From the relationships of the material, various mechanical properties, such as the ultimate tensile and yield strengths, Young's modulus, Poisson's ratio, the elongation, and reductions in area can be obtained. Also, the true stress-strain properties, strain hardening and tensile toughness can be calculated by means of conversion using special equations from the stress-strain curve.

To conduct a tensile test, it is first necessary to consider the tensile testing equipment and specimens. The most widely used tensile testing machines are screw-driven testing machines with a moving crosshead and a closed-loop servo- hydraulic testing machine with a hydraulic actuator. However, testing machines are relatively heavy and are typically installed in a laboratory. Conventional test methods for evaluating mechanical properties require a massive testing machine and relatively large material samples.

Miniature tensile testing techniques to obtain the mechanical properties of materials have been an interest of many researchers [1-5]. Partheepan et al proposed a simple miniature disc-type tensile specimen and fixtures to hold specimens with the help of a rigid pin to predict the mechanical properties of materials [1]. They verified the feasibility of the sample geometry using finite element method (FEM) analysis.

A miniforce tester driven by a DC-servomotor with a ball-screw guide-way was newly developed for a solder ball joint shear test by Chao and Liu [2]. The full-scale displacement and maximum applied load were 100 mm and 100 kgf, respectively. The displacement resolution of the stage was maintained at 1 micron using a precision digital displacement gage closed-loop control module. LaVan developed a tensile testing system to perform tensile tests onmicrosamples 3.1 mm long with a gauge cross-section of 0.2 mm^2 [3]. They conducted a tensile test of samples cut from weld metal to investigate the local mechanical properties of the weld joint.

A novel tensile device compatible with a scanning electron microscope (SEM) was designed and built by Ma et al.

They integrated a servo-motor and a three-stage reducer for a quasistatic loading mode with a loading speed of 10 nm/s. They adopted a small lead precise ball screw with left- and right-hand threads to keep the centre of the specimen stationary during the tensile test.

Hou and Chen developed a new uniaxial tensile testing system, consisting of a closed-loop piezo-electric (PZT) actuator, a load cell, and two grippers to hold the specimen in order to investigate the mechanical behaviour of thin films [5]. However, these systems are complicated and/or much more expensive than conventional tensile testing methods.

Acquiring new instructional laboratory apparatuses and preparing samples are a challenge due to typical budgetary limitations. In addition, sophisticated skills are required to operate the testing machine, especially the servo-hydraulic testing machine. Therefore, a new approach for an easy-to-handle and inexpensive tensile testing system is necessary for undergraduate students in mechanical, civil and materials engineering, so that they may conduct tension tests easily by themselves.

In this article, a miniaturised tensile testing system involving the use of a specially designed miniature tensile specimen is proposed. The system developed was designed to convert the rotation motion of a ball screw into the linear motion of specimen grips that apply a tensile load to the specimen. The frame contains an aligned linear motion guide for the movement of the specimen grips, ensuring the co-linearity of the travel axes. One side of the specimen is connected to a ball-screw block and the other side is connected to a load-cell to detect the load magnitude. It was concluded that such an apparatus can be designed, developed and constructed in house within a manageable budget. This can be accomplished by taking advantage of the capstone senior design project.

Design of the tensile testing machine specifications

The performance requirements of the machine were established for breaking using a 6061 aluminium alloy plate specimen with a thickness of 1 mm. In terms of the loading capacity of the testing machine, the specimen preparation and handling processes, thin miniaturised specimens are suitable. The functional requirements of the machine are as follows:

- Sample size: 1 mm thick, gauge cross-section area of 4 mm2, and gauge length of 8 mm.
- Maximum stroke: 20 mm.
- Maximum tensile force: 2.0 kN

Design concept

The machine is designed to pull one end of the sample, while the other end of the sample is attached to the load cell to monitor the applied load. The maximum tensile load to break the aluminium 6061 sample with a cross section area of 4 mm^2 and an ultimate tensile strength of at most 300 MPa was determined to be 1.2 kN. Thus, the maximum tensile force requirement of the machine was set to 2.0 kN. The load is measured with load cells with 0.5% of the maximum rated load.

In order to pull the sample without torsion, a ball screw converts the stepping motor rotation into linear motion. A ball screw with a diameter of 10 mm and pitch of 2 mm positioned in line with the specimen provides the tensile force. A chain is used to couple the stepping motor to the ball screw because a collinear arrangement would have made the system too long. A stepping motor with a capacity of 40 N-cm generates a full rotation in 200 steps and can be driven by the control system in 1/5 steps. A linear motion guide is adopted for precise alignment of the specimen without any distortion during gripping and tensile loading. Figure 1 shows the overall structure of the miniaturised tensile testing machine.

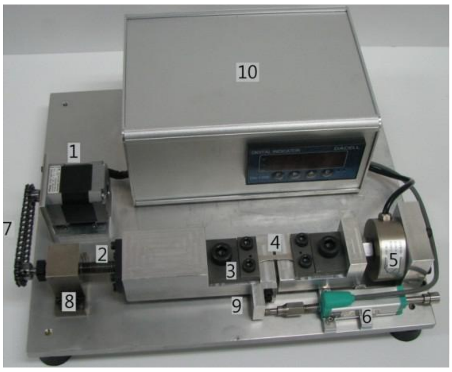


Figure 1: Photo of the miniature tensile testing machine with a size of 330 x 280 x 155 mm: 1) stepping motor; 2) ball screw block; 3) specimen holders; 4) miniature tensile specimen; 5) load-cell; 6) displacement gage; 7) chain; 8) bearing holder; 9) linear motion guide; and 10) control box.

A special specimen holder was designed to carry out the tensile test. The specimen holder consists of two fixtures made of die steel, as shown in Figure 2. The specimen fits into a cut-out in the specimen holder. The cut-out is machined into the same shape and dimension of the grip section of the specimen, 0.97 mm deep on the holder, for easy fixing of the specimen. The fixture is provided in the form of a hole that is 10.5 mm in diameter to hold the specimen with the help of a loading pin with a diameter of 10 mm. The test specimen experiences the tensile load through the loading pin. The specimen is attached at both ends by fixing the specimen holders. The prepared test specimen fixed in, then, gripped with the help of the loading pin. The test was carried out in the present case with a speed of 0.15 mm/min. A preload of 1 N is applied to nullify the effect of any initial nonlinearity in the output of the miniature test.

A National Instruments USB-6009 data acquisition card is used to create the square- wave signal that drives the stepper motor and to acquire the analogue signals from the load cell indicator as well as the displacement gage. The application software of the system is written in LabVIEW, a graphical programming language provided by National Instruments. The graphical user interface (GUI) provides the user with complete control over all aspects of the tensile testing machine, as shown in Figure 3. When first powered up, the GUI guides the user through all of the steps necessary to conduct the measurements. Geometrical details such as the length, width and thickness of the test specimen are supplied to the software. All data gathered throughout the experiments can be exported to a text file for further processing using a spreadsheet tool.

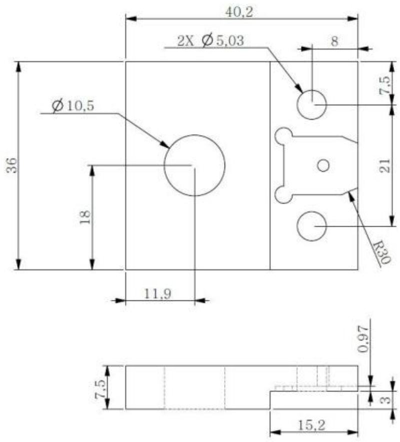
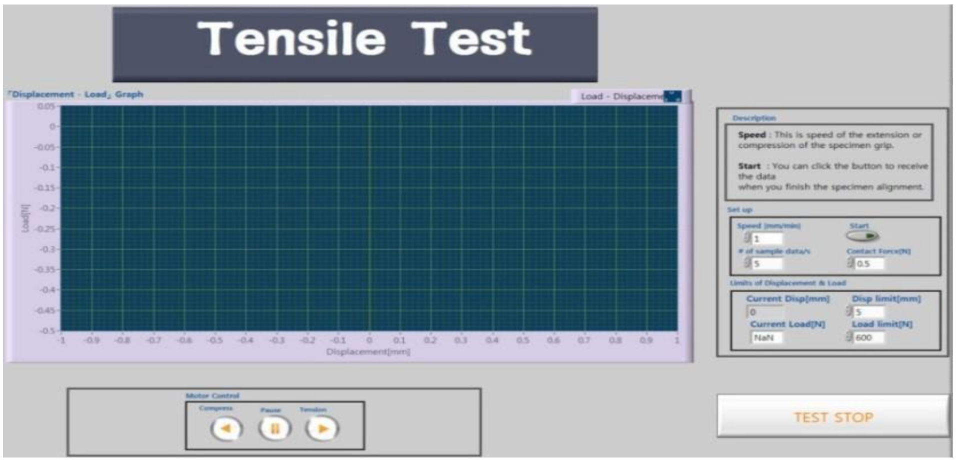


Figure 2: Dimensions of the specimen holder (all dimensions in mm).



Speed : This is speed of the extension or compression of the specimen grip.

Start : You can click the button to receive the data
when you finish the specimen alignment.

Speed [mm/min] 1
\# of sample data/s 5
Contact Force[N] 0.5
Current Disp[mm] 0
Disp limit[mm] 5
Current Load[N] NaN
Load limit[N] 600

Figure 3: The user interface written in LabVIEW. The interface includes a real-time plot of the applied load against displacement. Also included are setup routines for the sample setup process.

Specimen testing

In this study, a miniature specimen is designed, as shown in Figure 4. The size and dimensions of the specimen were miniaturised, based on a conventional standard tensile specimen. A finite element analysis of the miniature tensile test was carried out using the commercially available OptiStruct code in order to verify the specimen geometry without stress concentration. An elastic analysis of this test was carried out with the specimen geometry using various radii (from 5 mm to 40 mm) of gauge section of the specimen. Figure 5 shows the longitudinal stress distribution at an applied load of 500 N. The nominal stress of the gauge section with a cross-section area of 4 mm^2 is 125 MPa, as expected. The stress distribution result verifies that there is no stress concentration on the gauge section of the specimen geometry with a radius of 30 mm, as shown in Figure 5.
In order to make many specimens inexpensively for students, a punching process was adopted. The punch and die were made of SKD11 die steel. A die in the same shape as the specimen is punched on a thin plate with a thickness of 1 mm, as shown in Figure 6. The procedure for making this specimen is much easier compared with those of conventional tensile test specimens, which require a number of machining operations.

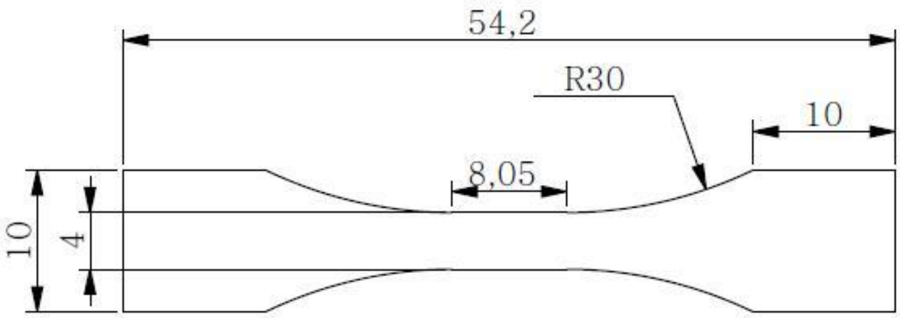


Figure 4: Dimensions of the miniature tensile specimen.

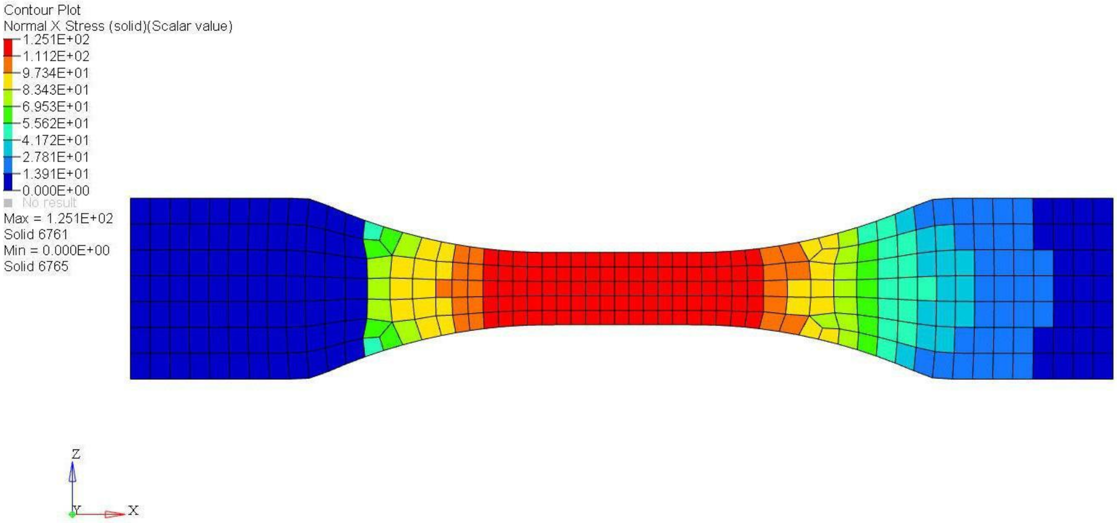


Figure 5: Finite element result of the miniature specimen to check the stress conntration.

Figure 6: Photo of the specimen using a blanking process and a blanked-out plate.

Tensile testing and results

Different types of heat treatment are generally utilised to achieve a good combination of strength and ductility. Therefore, in order to help students understand the effects of heat treatments on mechanical properties, five specimens were provided to acquire the optimal heat treatment condition with respect to the ultimate tensile strength. The students were supposed to conduct tensile tests of specimens, which had been heat-treated under different conditions. In order to understand the influence of a heat treatment on the mechanical behaviour, heat-treatable aluminium 6061 alloy was adopted.

The students were supposed to find the optimal ageing time for the highest tensile strength of the 6061 alloy within an aging time range. The specimens were solid-solution-treated at 803 K for 1 hour, quenched in room-temperature water and, then, underwent aging treatments within an aging range of 0 to 300 minutes. The students had to choose an arbitrary aging time from between 0 and 300 minutes, because the maximum ultimate tensile strength was found near 120 minutes according to our previous experimental results. The students were asked to provide the stress-strain curve of the tested samples and determine the optimum aging time for the highest ultimate tensile strength in a laboratory class. They also had to summarise the test results, as shown in Table 1.

Table 1: Summarised tensile test results on various aging time.

Ageing time (min.)	YS (MPa)	UTS (MPa)	Elongation (%)
0	81.1	169.5	42.3
10	150.8	258.7	27.3
30	254.2	298.5	17.5
60	276.1	302.3	12.8
120	287.8	309.9	13.3
180	274.2	297.6	13.5
210	275.2	303.7	13.7
240	245.1	282.4	15.2
300	243.2	283.8	13.9

Figure 7 presents the engineering stress-strain curves of the aluminium 6061 alloy at various aging times. Regarding the solid-solution treated sample, the ultimate tensile strength (UTS) and yield strength (YS) were 81.1 MPa and 169.5 MPa, respectively. Figure 8 shows the UTS and YS values against aging times for the solid-solution-treated aluminium 6061 alloy samples. According to this figure, the UTS and YS increased continuously up to 120 minutes and, then, decreased with increasing ageing time.

The maximum UTS of the aged treatment of aluminium 6061 alloy was 309.9 MPa, which is close to that of aluminium 6061 T6 tempered alloy [6]. Therefore, from Figure 7, the optimal aging time for obtaining the highest UTS was found to be close to 120 minutes. Compared to the solid-solution-treated sample, the UTS and YS of the aged sample with an aging time of 120 minutes both increased dramatically by 83.9% and 254.9%, respectively. However, the degree of elongation decreased from 42.3% to 13.3%. The difference in the strength and ductility is attributed to the precipitation strengthening effect from the heat treatment. From these experiments, students could understand the effect of a heat treatment on mechanical properties and could learn how to acquire the UTS, YS and elongation of materials from tensile tests.

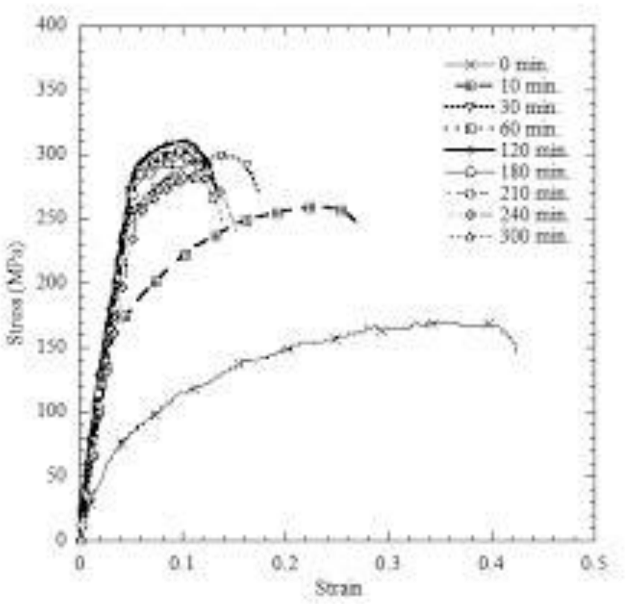


Figure 7.

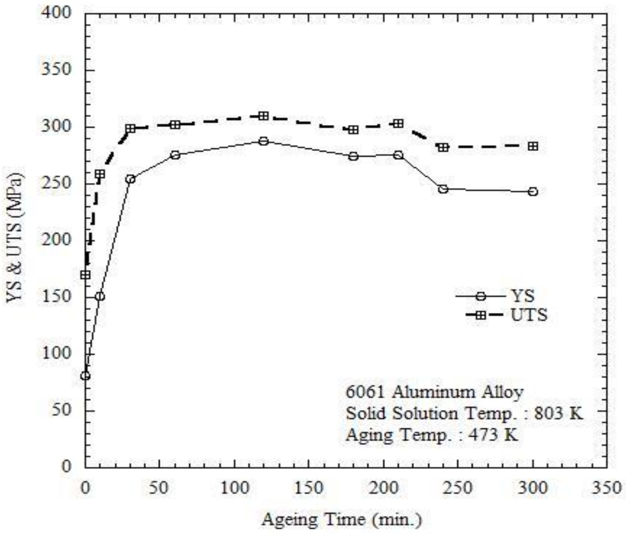


Figure 8.

Conclusions

This article described a method to evaluate material properties using a miniature tensile testing machine with a miniature specimen through a simple experimental setup. A portable miniaturised tensile testing apparatus was designed and developed. The newly designed specimen is small in size and easy to prepare. Finally, the developed testing system can be used as an instructional experimental apparatus to assist students in their efforts to understand the basic mechanical properties of materials.

References

1. Partheepan, G., Sehgal, D.K. and Pandey, R.K., Design and usage of a simple miniature specimen test setup for the evaluation of mechanical properties. *Inter. J. Microstructure and Materials Properties*, 1, **1**, 38-50 (2005).
2. Chao, Y.C. and Liu, D.S., Gold wire and solder joint microforce testing using microforce tester. *Experimental Techniques*, 25, **5**, 37-40 (2003).
3. LaVan, D.A., Microtensile properties of weld metal. *Experimental Mechanics*, 23, **3**, 31-34 (1999).
4. Ma, Z., Zhao, H., Huang, H., Zhang, L., Wang, K. and Zhou, X., A novel tensile device for in situ scanning electron microscope mechanical testing. *Experimental Techniques*, November, 1-9 (2002).
5. Hou, P.H. and Chen, T.Y., An automatic tensile test measurement system for miniature specimens. *Experimental Mechanics*, 29, **4**, 32-36 (2005).
6. Kaufman, J.G., *Properties of Aluminum Alloys*. Materials Park, Ohio: The Aluminum Association, Inc. ASM Inter., 162-170 (1999).

Proposed treatment of waste water from the galvanization process

Predlog tretmana otpadnih voda iz procesa galvanizacije

Nemanja Tošković, Danijela Rajić, Dragan Tošković, Ljubica Vasiljević
[1]University of East Sarajevo. Faculty of Technology Zvornik, Karakaj, 75400 Zvornik, B&H
[1]Univerzitet u Istočnom Sarajevu, Tehnološki fakultet Zvornik, Karakaj bb, 75400 Zvornik, BIH

Abstract

The galvanization process of metallic objects is, according to its properties, quantitatively and qualitatively one of the largest waste water pollutants. A large number of pollutants such as metaliones, acids, bases, organic solvents, oils and fats, and surface-active substances over drainage waters and as an main part of the galvanizing solution come into waste water. In this paper, one of the possible methods of treatment of wastewater from the galvanization process in industrial capacities is proposed.

Izvod

Proces galvansko-hemisjke zaštite metalnih predmeta je prema svojim karakteristikama, kako kvantitativnim tako i kvalitativnim jedan od najvećih zagađivača otpadnih voda. Veliki broj zagađujućih materija kao što su joni metala, kiseline, baze, organski rastvarači, masti i ulja i površinski aktivne materije preko ispirnih voda i kao sastavni dio rastvora za galvanizaciju dolaze u otpadne vode. U ovom radu je predložen jedan od mogućih postupaka tretmana otpadnih voda iz procesa galvanizacije u industrijskim kapacitetima.

Uvod

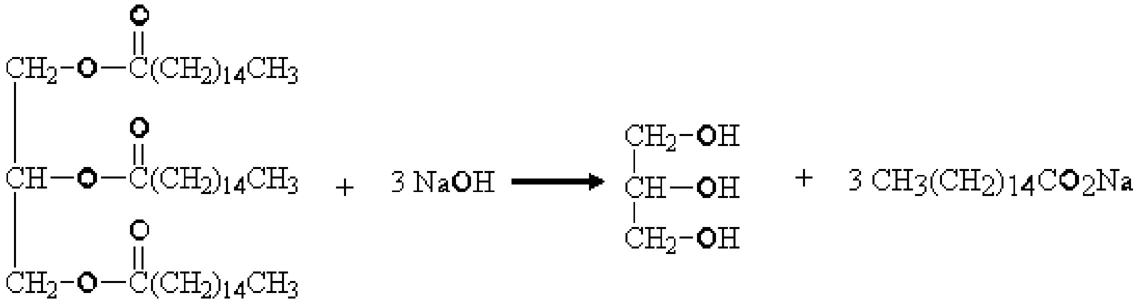
Proces galvanizacije zahtjeva potapanje predmeta raznih oblika i dimenzija u rastvore elektrolita različitog sastava gdje se odvijaju procesi hemijske i elektrohemisjke depozicije metala. Nakon svakog prenošenja predmeta iz kade sa jednim osobinama rastvora elektrolita u drugu vrši se ispiranje i tako dolazi do stvaranja određenih količina otpadnih voda [1]. Da bi se smanjilo onečišćenje svakog sledećeg rastvora, posle svakog koraka bitno je dobro isprati predmet. Pored otpadnih voda iz samog procesa(koncentrovane vode), ispirne vode predstavljaju značajnu količinu vode kojoj je potreban tretman i mogu sadržati jone metala (Cu, Ni, Cr, Zn, Pb, Fe), kiseline, baze, rastvarače, površinski aktivne materije i niz organskih zagađivača[1-3].
Nanošenje metalnih prevlaka najčešće se vrši u kiselim elektrolitima i pri ispiranju dolazi do kontaminacije voda hidratisanim solima metala. Takođe, za povećanje provodljivosti metala koriste se kiseline, za bakar i hrom, sumporna a za nikl i kadmijum borna kiselina. U sastav ovih elektrolita ulaze i površinski aktivne materije koje poboljšavaju kvalitet proizvoda a takođe utiču na sastav otpadnih voda [2]. Zakonski okviri su veoma oštri po pitanju sadržaja ispuštenih štetnih materija u površinske tokove pa se zbog toga razmatraju različiti načini prečišćavanja otpadnih voda iz procesa galvanizacije [4-6].
Otpadne vode koje nastaju u procesu galvanizacijepo svom karakteru su veoma toksične i agresivne. Toksičnost ovih voda je vezana za prisustvo hromnih jona, jona teških metala a agresivnost od prisustva mineralnih kiselina i baza[7].
Sve otpadne vode nastale u procesu galvanizacije mogu se podjeliti na:
1. koncentrovane kisele
2. razblažene kisele
3. koncentrovane alkalne

4. razblažene alkalne
5. koncentrovane hromne[2,4].

Kisele vode potiču iz procesa hemijskog čišćenja-dekapiranja i elektrohemisjkog čišćenja (bipolarni sistem). Razblažene kisele vode nastaju u procesu ispiranaja nakon:dekapiranja (1)hromiranja, niklovanja,bakarisanja, pocinčavanja. Koncentrovane kisele vode nastaju pri zameni i korekciji elektrolita.

$$Fe_2O_3 + 3H_2SO_4 \rightarrow Fe_2(SO_4)_3 + 3H_2O \qquad (1)$$

Alkalne vode potiču iz procesa alkalnog čišćenje. Alkalno čišćenje i odmašćivanje daje razblažene alkalne vode- reakcija saponifikacije (2). Koncentrovane alkalne vode nastaju pri zameni i korekciji elektrolita.



(2)

Hromne vode-razblažene potiču od procesa ispiranja nakon hromiranja i prikupljaju se zajedno sa razblaženi kiselim vodama; koncentrovane hromne vode nastaju pri zamjeni i korekciji elektrolita.

Eksperimentalni dio

Za prečićavanje otpadnih voda iz postrojenja galvanizacije mogu se primjenjivati sljedeće metode: hemijske (tretiranje hemijskim reagensima i jonska izmjena)

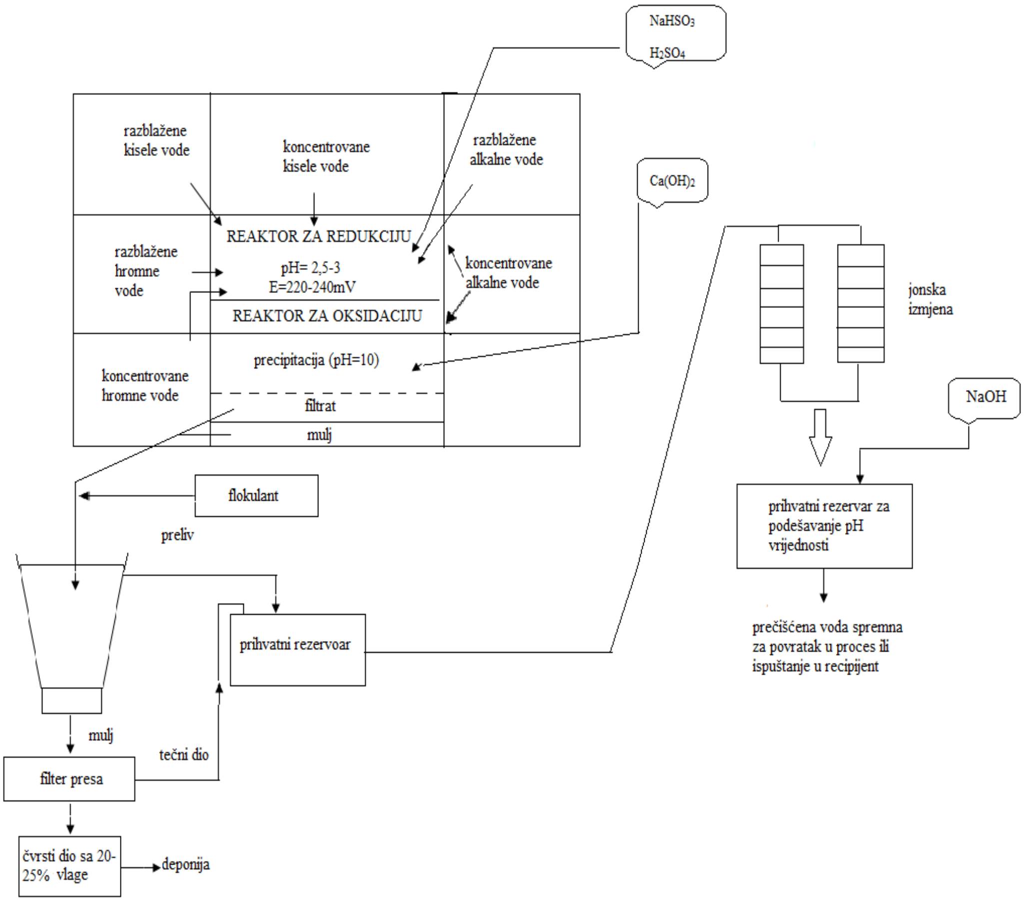
- elektrohemijske
- termičke
- adsorpcione
- reversna osmoza.

Postupak tretmana hemijskim reagensima čiji je predlog dat u ovom radu zasniva se na reakcijama oksidacije i redukcije, neutralizacije kiselina i baza i taloženja hidroksida metala.

U Tabeli 1 dat je pregled tipa industrijskih otpadnih voda i mjesta u procesu galvanizacije u kojima nastaju, kao i opšti način uklanjanja.

Tabela 1. Pregled tipa i načina uklanjanja otpadnih voda iz procesa galvanizacije

vrsta vode	izvor nastajanja	način uklanjanja
Kisela	Dekapiranje dezoksidacija pocinčavanje niklovanje,bakarisanje	Reagens za regulisanje pH vrednosti u reaktoru za redukciju
Alkalna	odmašćivanje (saponifikacija)	Reagens u reaktoru za redukciju ili procesu precipitacije
Hromatna	Hromiranje	redukcija Cr^{6+} u Cr^{3+}



Slika 1. Šema predloga tretmana otpadnih voda iz procesa galvanizacije

Tretman otpadnihhromnih voda

Obrada homnih voda vrši se u bazenu-reaktoru za redukciju gdje se dodaju sve kisele vode od ispiranja. One dolaze u prihvatni bazen sa pH vrijednošću 4-5, što nije dovoljno za redukciju Cr^{6+} u Cr^{3+}. U reaktoru za redukciju zapremine $5m^3$ pH vrijednost se kreće u granicama 2,5-3,0 i E^0=220-240mV što omogućava redukciju Cr^{6+} u Cr^{3+}. $NaHSO_3$ je redukciono sredstvo a podešavanje pH vrijednosti se vrši dodatkom sumporne kiseline ili dodatkom alkalnih otpadnih voda. Za automatsko vodjenje reakcije redukcije Cr^{6+}koristi se redoks mVelektroda sa rasponom potencijala 220-240 mV i pH-elekroda. Redukcija hromatase odvija u kiseloj sredini sledećom reakcijom:

$$4CrO_{3(s)} + 6NaHSO_{3(s)} + 3H_2SO_{4(aq)} \rightarrow 3Na_2SO_{4(aq)} + 2Cr_2(SO_4)_{3(aq)} + 6H_2O_{(l)} \qquad (3)$$

Taloženje i obrada taloga precipitacija

Nakon procesa redukcije tretirana voda je kisela pH=3,5 (sastoji se od sulfata Cu,Ni,Zn,Cr,Fe) prelazi u bazen za oksidaciju sa vazduhom i precipitaciju sa$Ca(OH)_2$ gdje se održava pH vrijednost od 9-10 na kojoj se istalože svi prisutni hiroksidi(4-7). U precipitator su smještene plastične cijevi za aeraciju kroz koje su uduvava vazduh radi poboljšane oksidacije i miješanja. Talog i mulj se pumpama uz dodatak flokulanta-polielektrolitprebacuju u taložnik zapremine $80m^3$ iz koga tečni dio preliva u prihvatni rezervoar a istaloženi mulj ide na filter presu. Nakon filter prese čvrsti dio se odlaže na deponiju a tečni vraća u prihvatni rezervoar i zajedno sa prelivom iz taložnika šalje na jonoizmjenjivačke filtere(anjonske i katjonske) i nakon podešavanja pH vrijednosti (pH=7) dodatkom NaOH ponovo vraća u proces ili ispušta u vodotok.

Taloženje i obrada taloga-precipitacija:

$$Fe_2(SO_4)_3 + 3Ca(OH)_{2(aq)} \rightarrow 2Fe(OH)_{3(s)} + 3CaSO_{4(aq)} \tag{4}$$

$$NiSO_{4(aq)} + Ca(OH)_{2(aq)} \rightarrow Ni(OH)_{2\,(s)} + CaSO_{4(aq)} \tag{5}$$

$$Cr_2(SO_4)_{3(aq)} + 3Ca(OH)_{2(aq)} \rightarrow 2Cr(OH)_{3(s)} + 3CaSO_{4(aq)} \tag{6}$$

$$4CuSO_{4(aq)} + Ca(OH)_{2(aq)} \rightarrow Cu(OH)_{2(s)} + CaSO_{4(aq)} \tag{7}$$

Rezultati i diskusija

Sve industrijske otpadne vode nakon procesa prečišćavanja moraju zadovoljiti zakonske odredbe kako bi bile ispuštene u kanalizacioni sistem ili jedan dio vraćen ponovo u proces. U Tabeli 2 date su prosječne i maksimalne koncentracije pojedinih komponenti koje se nalaze u ispirnim vodama. Zakonom propisani kvalitet odnosi se na prirodni kolektor u koji se onečićena voda ispušta a to je definisano Zakonom o vodama RS i BiH [8-10]. Utvrđeni su uslovi ispuštanja, granične vrijednosti štetnih i opasnih materija koje se smiju ispuštati u površinske vode kao i način utvrđivanja saglasnosti izmjerenih sa dozvoljenim vrijednostima.U Tabeli 3 je dat sadrzaj metala u otpadnoj vodi iz procesa galvanizacije nakon predloženog hemijskog tretmana -prečićavanja.

Tabela 2. Sadržaj metala u ispirnim vodama procesa galvanizacije

Komponenta	**prosječna koncentracija mg/dm^3**	**maksimalna koncentracija mg/dm^3**
Fe	25	100
H_2SO_4	75	450
Cr^{n+}	30	100
Cu	20	150
Ni	25	150
Zn	3	85
Pb	2	40
Cd	5	30
Ag	10	60

Tabela 3. Sadržaj metala u opadnoj vodi iz procesa galvanizacije nakon hemijskog tretmana-prečićavanja

broj	**komponenta**	**II klasa vodotoka (mg/dm^3)**	**koncentracije prečićene vode (mg/dm^3)**
1.	Cu^{2+}	0,1	0,97
2.	Fe^{2+}	0,3	0,2
3.	Cd^{2+}	0,005	0,0045
4.	Ni^{2+}	0,05	0,04
5.	Pb^{2+}	0,05	0,008
6.	Ag^{+}	0,1	0,08
7.	Cr^{6+}	0,1	0,06
8.	Cr^{3+}	0,1	0,02
9.	Zn^{2+}	0,2	0,06

Zaključak

Predloženim postupkom je moguće kvalitetno izvršiti tretman otpadnih voda nastalih u procesima galvanizacije u industrijskim uslovima i obezbjediti zakonom propisani kvalitet otpadne vode koji se odnosi na prirodni kolektor u koji se ispušta.Takodje,ovako tretirana otpadna voda se može ponovo vraćati i koristiti u procesima ispiranja. Čvrsti dio prečišćavanja se odlaže na bezbedne deponije amože se koristiti nakon termičkog tretmana za drenaže putne podloge.

Regulisanje ispuštanja opasnih i štetnih supstanci u prirodne vode mora biti u saglasnosti sa Zakonima područja na kojima se vode nalaze kao i sa Uredbom o klasifikaciji voda i kategorizaciji vodotoka, kao i svim drugim propisima za zaštitu okoline, propisima za otpadne vode i postrojenjima za prečišavanje pri čemu lokalni uslovi u recipijentu treba da budu uzeti u obzir u tehnološkom, ekonomskom i ekološkom smislu. Zbog svega ovoga predloženi tretman ima značajnu ulogu u djelotvornom prečišavanju voda iz postrojenja za galvanizaciju.

Literatura

1. Krstić, I.,Stanisavljević, M., Lazarević, V., Takić, Lj., Redesigning wastewater treatment of the technological process of galvanization, *Journal Materials Protection, 2011, 52, No 3*
2. Arsnenović, B., Ivanović, B., Quality of wastewater and waste air of technological process of galvanization, *Journal Materials Protection,* Vol 8, No 1, 2016
3. Stanisavljević, P.M., Tehnologije prerade otpadnih voda i industrijskog opasnog otpada, Visoka tehnička škola strukovnih studija Požarevac, 2010, pp. 322-330
4. Todorović, G., Fizičko-hemijski tretman otpadnih voda iz procesa galvanizacije, Diplomski rad, Tehnološki fakultet Zvornik, 2010
5. Berradi, M., El Harfi, A., Optimization the treatment of the wastewater industrial from the hot-dip galvanizing of steel by the method of eperiment desing, Mor. J. Chem, (3) No 1, 2015, pp. 142-145
6. Berradi, M. et all, *J. Mater. Environ. Sci.* 5, (2) 2014, pp. 360-365
7. Plattes, M. et all *J. Hazard. Mater.* 148, 2007, pp. 613-615
8. Pravilnik o uslovima ispuštanja otpadnih voda u površinske vode, Službeni Glasnik Republike Srpske 11/94
9. Zakon o vodama Republike Srpske, Službeni Glasnik Republike Srpske 10/98
10. Uredba o uslovima ispuštanja otpadnih voda u okoliš i sisteme javne kanalizacije, član 55 Stav 1 Zakona o vodama BiH 70/06

Application of pollution indices in the assessment of the potential contamination with heavy metals in urban parks of Pančevo, Obrenovac, Smederevo and Belgrade

Procena potencijalnog zagađenja zemljišta teškim metalima u urbanim parkovima Pančeva, Smedereva, Obrenovca i Beograda na osnovu indeksa zagađenja zemljišta

Dragana Pavlović, Marija Pavlović, Zorana Mataruga, Veljko Perović, Gordana Gajić, Snežana Jarić, Miroslava Mitrović, Pavle Pavlović

Department of Ecology, Institute for Biological Research "Siniša Stanković", University of Belgrade, Bulevar despota Stefana 142, 11000 Belgrade, Serbia

Odeljenje za ekologiju, Institut za biološka istraživanja "Siniša Stanković", Univerzitet u Beogradu, Bulevar despota Stefana 142, 11000 Beograd, Srbija

Abstract

In this study, concentrations of selected elements (Cr, Ni, Pb and Zn) in soil samples taken from five urban parks in Pančevo, Smederevo, Obrenovac and Belgrade (Serbia) affected by different anthropogenic activities were determined. Soil samples were digested in nitric acid, while element concentrations were determined using the ICP-OES method. Enrichment factor (EF), Pollution index (PI), Ecological risk (Ei) and Potential ecological risk index (RI) were also evaluated. The obtained results revealed that concentrations of some elements exceeded the maximum allowed concentration (MAC) in soils, as well as background values. Pearson correlation coefficient (p) and the results of Principal Component analysis (PCA) indicate a natural origin of Cr and Ni (soil parent material), while Pb and Zn presumably originate from anthropogenic inputs (traffic). Based on the obtained enrichment factor (EF) and pollution index (PI), the overall soil status was classified from slight to moderate pollution. In the view of the potential ecological risk index (RI), all investigated soils showed low potential ecological risk.

Keywords: *Urban soils, Heavy metals, Soil pollution, Ecological risk*

Izvod

U ovoj studiji su određene koncentracije odabranih elemenata (Cr, Ni, Pb i Zn) u uzorcima zemljišta uzorkovanih u pet urbanih parkova u Pančevu, Smederevu, Obrenovcu i Beogradu (Srbija) koji su pod uticajem različitih antropogenih aktivnosti. Uzorci zemljišta su pripremljeni vlažnom digestijom pomoću azotne kiseline, a koncentracije hemijskih elemenata su određivane korišćenjem ICP-OES metode. Takođe su i izračunati Faktor obogaćenja (EF), Indeks zagađenja (PI), Faktor rizika i Potencijalni ekološki indeks rizika (RI). Rezultati su pokazali da koncentracije nekih elemenata prekoračuju maksimalno dozvoljene koncentracije (MDK) elemenata u zemljištu kao i background vrednosti. Pirsonov korelacioni koeficijent (p) i Analiza glavnih komponenti (PCA) su pokazale da Cr i Ni imaju prirodno poreklo (iz matičnog supstrata), dok se poreklo Pb i Zn vezuje za antropogene izvore (dominantno iz saobraćaja). Na osnovu dobijenih Faktora obogaćenja (EF) i Indeksa zagađenja (PI) status zagađenja zemljišta je klasifikovan u opsegu neznatno do umereno zagađenog. U pogledu Potencijalnog ekološkog indeksa rizika (RI) sva ispitivana zemljišta pokazuju nizak potencijalni ekološki rizik.

Ključne reči: *Urbana zemljišta, Teški metali, Zagađenje zemljišta, Ekološki rizik*

Uvod

Zemljište predstavlja složeni heterogeni matriks koji nastaje hemijskim i fizičkim promenama geološkog supstrata, pod uticajem živih organizama i različitih klimatskih faktora [1]. Kvalitet zemljišta je od presudne važnosti za životnu sredinu koja je u urbanim i industrijalizovanim sredinama narušena usled oslobađanja različitih zagađujućih materija. Teški metali se prirodno nalaze u zemljištu i vode poreklo od matičnog supstrata na kojem je zemljište formirano i na koje čovek ne može bitno da utiče [2]. Međutim, u površinskim slojevima zemljišta često se mogu naći i teški metali koji vode poreklo iz različitih antropogenih izvora kao što su industrijska postrojenja, saobraćaj, gradske toplane, deponije komunalnog i industrijskog otpada i sl. [3]. Smatraju se jednim od važnih zagađivača zemljišta, a osnovni razlog za to je njihovo kompleksno ponašanje, toksičnost i nemogućnost biološke razgradnje. Kada jednom dospeju u zemljište, ostaju dugo vremena i putem apsorpcije od strane biljaka ulaze u lanac ishrane. Neki od njih (Cr, Zn, Cu, Mn i dr.) su esencijalni za više organizme i njihovo prisustvo je neophodno u niskim koncentracijama [4], dok u većim količinama mogu imati toksični efekat [3]. U urbanim sredinama ljudi mogu doći u kontakt sa teškim metalima putem kože, udisanjem i gutanjem [5-7]. U poređenju sa odraslima deca su nesumnjivo pod većim uticajem zagađivača iz zemljišta, a razlog su njihove još nedovoljno razvijene higijenske navike i neposredni kontakt sa površinskim slojem zemljišta tokom igranja [5]. Poslednjih nekoliko decenija posebna pažnja je posvećena problemu zagađenja urbanih zemljišta teškim metalima. Pristup problemu je multidisciplinaran i često je pored utvrđivanja osnovnih fizičko-hemijskih karakteristika i ukupnog sadržaja teških metala u zemljištu neophodno i utvrđivanje njihovog porekla, mobilnosti i biodostupnosti. Izračunavanjem različitih faktora i indeksa dobijaju se dodatne informacije o obogaćenju zemljišta ispitivanim elementima i njihovom potencijalnom riziku po životnu sredinu [8-12].

Istraživanje u ovom radu je sprovedeno sa ciljem da se: utvrdi sadržaj Cr, Ni, Pb i Zn u uzorcima zemljišta iz gradskih parkova u Pančevu, Smederevu, Obrenovcu i Beogradu, i primenom statističkih metoda utvrde njihovi potencijani izvori i proceni statusa zagađenja ispitivanih zemljišta.

Eksperimentalni deo

Lokaliteti istraživanja

Uzorci zemljišta su sakupljeni u urbanim parkovima izloženim različitim izvorima zagađenja u Pančevu, Smederevu, Obrenovcu i Beogradu kao i na kontrolnom staništu u Arboretumu Šumarskog fakulteta, Univerziteta u Beogradu.

Uzorkovanje zemljišta u Pančevu je obavljeno u parku Narodna bašta. To je najveći i najstariji gradski park u Pančevu, koji je pozicioniran na 44°51'54" severne geografske širine i 20°39'23" istočne geografske dužine, na nadmorskoj visini od 77 m. Prostire se na 14 ha. Od centra grada je udaljen 1.3 km. Nalazi se severozapadno od industrijskih izvora zagađenja: od fabrike azotnih đubriva (HIP-Azotara d.o.o.) 2.69 km, od petrohemijske industrije (HIP-Petrohemije) 3.50 km i od Rafinerije nafte Pančevo (NIS-RNP) 4.43 km.

Lokalitet na kome je izvršeno uzorkovanje u Smederevu se nalazi u centralnom gradskom jezgru koje je pozicionirano na 44°39'54" severne geografske širine i 20°55'37" istočne geografske dužine, na nadmorskoj visini od 73 m. Industrijska zona je locirana 7 km jugoistočno od grada, a glavni izvor zagađenja je železara „Hesteel Serbia Iron & Steel d.o.o. Beograd“, Smederevo.

Lokalitet za istraživanje u Obrenovcu je bio Gradski trg Obrenovac - Trg dr Zorana Đinđića koji je okružen ulicama opterećenim saobraćajem. Park je pozicioniran na 44°39'17" severne geografske širine i 20°12'3" istočne geografske dužine, na nadmorskoj visini od 78 m. Od dominantnih izvora zagađenja, koje predstavljaju dve termoelektrane „Nikola Tesla-A“ i „Nikola Tesla-B“ i dve deponije pepela i šljake nastalih sagorevanjem uglja, ukupne površine oko 1000 ha, trg dr Zorana Đinđića je udaljen oko 4 km.

Istraživanje u Beogradu je obuhvatalo dva lokaliteta od kojih je jedan izložen direktnim izvorima zagađenja poreklom iz saobraćaja (Park kod hale Pionir) i drugi koji je izolovan od direktnog izvora zagađenja (Arboretum Šumarskog fakulteta Univerziteta u Beogradu). Zelene površine oko hale Pionir zauzimaju površinu oko 50 000 m^2. Park je pozicioniran na 44°48'53" severne geografske širine i 20°29'7" istočne geografske dužine, na nadmorskoj visini od 104.44 m. Od centra grada je udaljen oko 2 km. Nalazi se u neposrednoj blizini nekoliko velikih saobraćajnica, a od najbliže industrijske zone u opštini Palilula oko 1 km. Saobraćaj i blizina industrijske zone predstavljaju najveće izvore zagađenja. Zelene površine su u značajnoj meri fragmentisane betonskim površinama.

Arboretum Šumarskog fakulteta Univerziteta u Beogradu predstavlja zelenu površinu sa specifičnom namenom i izuzetnu botaničku i pejzažno-arhitektonsku vrednost. Smešten je na severozapadnoj padini Košutnjaka, iznad leve obale Topčiderske reke na 44°00'48" istočne geofrafske dužine i 20° 00' 28" severne geografske širine i nadmorskoj visini od 110-125 m. Zauzima površinu oko 3 ha.

Uzorkovanje i analiza zemljišta

Uzorkovanje je izvršeno tokom 2012. godine u urbanim parkovima gore pomenutih gradova, pomoću pedološke sonde od nerđajućeg čelika, sa dubine od 0-10 cm. Na svakoj od navedenih parkovskih površina je izvršeno uzorkovanje na tri mesta (Pančevo-P1, P2, P3; Smederevo-S1, S2, S3; Obrenovac-O1, O2, O3; Beograd-B1, B-2, B-3 i Kontrola-K-1, K-2 i K-3) i to tako što je na svakom mestu uzeto po 5 uzoraka od kojih je formiran kompozitni uzorak (ukupno 15 uzoraka). Uzorci zemljišta su pakovani u obeležene polietilenske kese i dopremljeni u laboratoriju gde su sušeni do konstantne težine, usitnjeni i samleveni pomoću laboratorijskog mlina sa nerđajućim noževima, a zatim prosejani kroz sito od 1.5 mm. Ovako pripremljeni uzorci su korišćeni za određivanje sadržaja Cr, Ni, Pb i Zn.

Za određivanje ukupnog sadržaja hemijskih elemenata, uzorci zemljišta (0.3 g) su razarani u mikrotalasnoj peći (CEM, 39 MDS-2000), korišćenjem metode USEPA 3052 (1996) [13]. Svi uzorci su pripremani u pet ponavljanja. Koncentracije hemijskih elemenata u zemljištu su merene metodom optičke emisione spektrometrije za simultanu multielementarnu analizu (ICP - OES, Spectro Genesis). Sadržaj hemijskih elemenata izražen je u mg kg^{-1} suvog uzorka. Analitička procedura je validirana korišćenjem standardnog referentnog materijala (Loam soil - ERM - CC141), koji je prošao kroz standardni postupak digestije radi kontrole kvaliteta laboratorijskog protokola, i dobijena je tačnost od 100 ± 15 %. Referentni materijal je dobijen od Instituta za Referentne Materijale i Merenja (IRMM, Institute for Reference Materials and Measurements, Geel, Belgium), a odobrila ga je i sertifikovala Evropska komisija (EC - JRC, European Commision - Joint Research Centre).

Pokazatelji zagađenja zemljišta metalima

Faktor obogaćenja (EF)

Faktor obogaćenja (EF) je izračunat sa ciljem da se odredi stepen zagađenja zemljišta teškim metalima u odnosu na background vrednost datog elementa u zemljištu ispitivanog područja. Za izračunavanje EF korišćena je jednačina 1:

$$\mathrm{EF} = \frac{C_i/C_{Fe}}{B_i/B_{Fe}} \quad (1)$$

gde je: EF – faktor obogaćenja, Ci – izmerena koncentracija ispitivanog elementa u uzorku zemljišta, C_{Fe} –koncentracija referentnog elementa (Fe) u uzorku zemljišta, Bi – background koncentracija ispitivanog elementa i B_{Fe} - background koncentracija referentnog metala (Fe).

Predložena je sledeća klasifikaciju zagađenja na osnovu vrednosti EF [14]: EF <2 neznatna do niska zagađenost, EF=2-5 umerena zagađenost, EF=5-20 značajna zagađenost, EF=20-40 veoma visoka zagađenost i EF > 40 ekstremno visoka zagađenost.

Indeks zagađenja (PI)

Indeks zagađenja (PI) je izračunat sa ciljem da se odredi stepen zagađenja ispitivanog zemljišta u odnosu na graničnu vrednost konkretnog elementa definisanog zakonskom uredbom [15]. Za izračunavanje PI korišćena je jednačina 2 [16]:

$$\mathrm{PI} = \frac{\mathrm{C_i}}{\mathrm{S_i}} \tag{2}$$

gde je: C_i izmerena koncentracija ispitivanog elementa u uzorku zemljišta i S_i referentna (granična) vrednost tog elementa. Stepen zagađenja prema ovom indeksu je podeljen u pet kategorija [17]: PI < 1 bez zagađenja (čisto, bezbedno), PI=1-2 neznatno zagađenje, PI=2-4 umereno zagađenje, PI=4-6 jako zagađenje i PI > 6.0 ekstremno zagađenje.

Faktor rizika (Ei)

Faktor rizika (Ei) [16] pojedinačnog elementa predstavlja odnos koncentracije datog elementa i njegove background vrednost, a izračunava se prema jednačini 3:

$$\mathrm{Ei} = \mathrm{Ti}\frac{\mathrm{C_i}}{\mathrm{B_i}} \tag{3}$$

gde je: Ti - faktor toksičnosti za dati element (Cr-2, Ni-5, Pb-5 i Zn-1) [18], C_i izmerena koncentracija ispitivanog elementa u uzorku zemljišta i Bi – background koncentracija tog elementa. Stepen rizika prema ovom faktoru je klasifikovan na sledeći način: Ei < 40 nizak rizik, Ei=40-80 umeren rizik, Ei=80-160 značajan rizik, Ei=160-320 visok rizik i > 320 veoma visok rizik[18].

Potencijalni ekološki indeks rizika (RI)

Potencijalni ekološki indeks rizika (RI) je izračunat kao suma faktora rizika (Ei) hemijskih elemenata prema jednačini 4:

$$\mathrm{RI} = \sum \mathrm{Ei} \tag{4}$$

Stepen rizika prema ovom indeksu je klasifikovan na sledeći način: RI < 150 nizak ekološki rizik, RI=150-300 umeren ekološki rizik, RI=300-600 značajan ekološki rizik i >600 veoma visok rizik [18].

Statistička obrada podataka

Deskriptivna statistička analiza je urađena korišćenjem Microsoft Office Excel 2010. Rezultati su prikazani tabelarno i grafički. Pirsonov koeficijent korelacije (p) i analiza glavnih komponenti (PCA - Principal Component Analysis) su urađeni sa ciljem da se utvrde međusobni odnosi između elemenata u zemljištu i utvrdi njihovo potencijalno poreklo korišćenjem softverskog paketa SPSS 17.0. Da bi se dobila jasnija slika odnosa ispitivanih varijabli, osnovne komponente su rotirane upotrebom Varimax merode rotacije faktora sa Kajzerovom normalizacijom [19].

Rezultati i diskusija

Koncentracije teških metala u zemljištu

Koncentracije Cr, Ni, Pb i Zn u ispitivanim zemljištima urbanih područja Pančeva, Smedereva, Obrenovca, Beograda i kontrolnog staništa i osnovni statistički parametri su prikazani u Tabeli 1, zajedno sa opsegom prosečnih koncentracijama ispitivanih elemenata opisanih za dva osnovna tipa svetskih zemljišta [20] i maksimalno dozvoljenim koncentracijama (MDK) datih elemenata

definisanih zakonskom regulativom Republike Srbije [21]. Lokalne background vrednosti su dobijene aritmetičkim izračunavanjem pomoću medijane (Median+2MAD metod) [22], (Tabela 2).
Ukupan sadržaj Cr u uzorcima zemljišta se kretao od 53.05 mg kg^{-1} u Pančevu do 126.59 mg kg^{-1} u Smederevu (Tabela 1), pri čemu su koncentracije Cr na svim lokalitetima bile više od prosečnih vrednosti opisanih za dva osnovna tipa svetskih zemljišta [20], i više od backgraund vrednosti za ispitivana područja [2, 22].Ustanovljeno je da količina Cr u zemljištu varira u širokom opsegu i da na pojedinim lokalitetima sadržaj Cr prevazilazi MDK propisane zakonskom regulativom za ispitivana područja [21]. Hrom u zemljištu može dospeti nekontrolisanim odlaganjem i izlivanjem otpadnih sirovina iz hemijske i metalurške industrije, sagorevanjem uglja, kao i prekomernom upotrebom sredstava koja se koriste u poljoprivredi [20]. Međutim, razlog za povišen sadržaj Cr u Pančevu, Smederevu i Obrenovcu ne mora nužno da bude njegovo antropogeno poreklo, imajući u vidu činjenicu da ispitivana zemljišta odlikuju veće količine Cr koje su prirodnog (geološkog) porekla. Mrvić i saradnici [2] su pokazali da se visoke koncentracije Cr nalaze u nekim aluvijalnim zemljištima i to najčešće na istim lokalitetima koje karakteriše veći sadržaj Ni. Slične ili nešto više koncentracije Cr u zemljištu urbanih parkova Beograda su izmerene i u prethodnim studijama [8, 9].
U svetskim zemljištima za prosečan sadržaj Ni se smatra opseg od 13-26 mg kg^{-1} [20], dok je utvrđeni sadržaj Ni u ovoj studiji veoma varijabilan i na nekim lokalitetima višetruko premašuje navedeni opseg vrednosti (od 21.51 mg kg^{-1} u Pančevu do 134.73 mg kg^{-1}u Smederevu). Ustanovljeno je da prosečna količina Ni na svim lokalitetima viša od MDK [21], kao i da je u Pančevu neznatno viša od lokalnih background vrednosti [2, 22]. Koncentracije Ni utvrđene u ovom istraživanju su nešto niže od ranije opisanih za urbana područja Beograda [8, 9, 12], ali i dalje značajno više od količine nađene u zemljištima nekoliko Evropskih gradova [23-25], što se može dovesti u vezu sa njegovim geološkim poreklom [2]. Naime, Mrvić i saradnici [2] su pokazali da oko 80 % uzoraka naših zemljišta nije zagađeno Ni, a da se povećane koncentracije javljaju u zemljištima koja nastaju od matičnih supstrata koja obiluju Ni (ultrabazične, bazične, sedimentne i metamorfne stene), Međutim, pored geološkog porekla, Ni u zemljištu može dospeti i njegovim oslobađanjem u različitim procesima u industriji metala, pri sagorevanju fosilnih goriva i dr. [10].
Prosečni sadržaj Pb za svetska zemljišta se kreće u opsegu od 22-28 mg kg^{-1}[20]. Slično kao kod Ni i sadržaj Pb je u ispitivanim zemljištima višestruko veći, i kreće se u rasponu od 43.76 mg kg^{-1} u Pančevu do 100.80 mg kg^{-1} u Smederevu. Prosečne vrednosti Pb u ispitivanim zemljištima su takođe više od background vrednosti za ispitivana područja [2, 22], ali ne premašuju MDK [21]. Razlog za povećani sadržaj Pb u ispitivanim zemljištima, posebno u Beogradu (mesto uzorkovanja B2) može da bude rezultat oslobađanja izduvnih gasova poreklom iz saobraćaja, s obzirom da je u Srbiji olovni benzin bio u upotrebi sve do 2010. godine [26]. Prethodna istraživanja Gržetić i saradnika, 2008 godine [8], su pokazala značajno više koncentracije Pb u zemljištima urbanih zona Beograda, dok su 2016.godine Andrejić i saradnici [12] ustanovili značajno niži sadržaj Pb koji je sličan ili nešto viši od vrednosti dobijenih u ovom istraživanju.
Prosečan sadržaj Zn definisan za svetska zemljišta se kreće od 45 mg kg^{-1} do 60 mg kg^{-1}, dok se sadržaj Zn na ispitivanim područjima kretao od 45.68 mg kg^{-1} u Obrenovcu do čak 248.02 mg kg^{-1}u Beogradu. Prosečan sadržaj Zn u uzorcima iz Smedereva i Beograda je viši od opisanih background vrednosti za ispitivana područja [2, 22], ali ne prelazi MDK [21]. Visoke koncentracije Zn u urbanim zemljištima na teritoriji Beograda su utvrđene i ranijim istraživanjima [9, 12, 27]. U Beogradu i Smederevu potencijalni izvori Zn bi mogla da bude emisija poreklom iz saobraćaja [10], dok u parku u Smederevu dodatni izvor Zn se može dovesti u vezu sa emisijom suspendovanih čestica poreklom iz topionice rude gvožđa [28].

Tabela 1. Prosečan sadržaj Cr, Ni, Pb i Zn (mg kg^{-1} s.m.) u uzorcima zemljišta sakupljenim u urbanim parkovima Pančeva, Smedereva, Obrenovca, Beograda i Kontrolnog staništa. Vrednosti su prikazane kao srednja vrednost ± standardna devijacija (n=5)

Lokalitet	**Cr**	**Ni**	**Pb**	**Zn**
Pančevo 1	122.462±7.448	67.928±0.989	76.608±3.931	56.895±0.677
Pančevo 2	91.000±21.127	73.602±0.955	62.318±1.871	51.708±1.922
Pančevo 3	53.052±1.019	21.515±0.379	43.760±1.768	61.965±3.215
Srednja vrednost	88.838±34.755	54.348±28. 757	60.895±16.470	56.856±5.129
Smederevo 1	72.105±1.288	72.318±0.912	47.320±0.415	206.060±0.688
Smederevo 2	115.998±3.641	100.382±1.828	100.805±5.119	152.985±2.527
Smederevo 3	126.592±1.185	134.732±1.132	70.380±1.044	119.560±1.568
Srednja vrednost	104.898±28.890	102.395±31.269	72.835±26.827	159.535±43.620
Obrenovac 1	115.610±0.422	97.988±0.712	92.052±0.910	80.025±2.044
Obrenovac 2	113.742±14.826	88.172±0.700	68.870±1.325	62.768±1.226
Obrenovac 3	85.435±18.600	60.515±0.495	45.215±4.634	45.680±4.879
Srednja vrednost	104.929±16.908	82.225±19.431	68.712±23.419	62.824±17.127
Beograd 1	78.488±6.139	38.532±0.290	79.002±0.685	80.192±2.259
Beograd 2	72.488±7.180	37.585±0.122	128.795±1.870	248.015±2.095
Beograd 3	71.472±9.136	35.378±0.554	72.292±3.191	134.530±0.668
Srednja vrednost	74.216±3.749	37.165±1.619	93.363±30.868	154.246±85.631
Kontrola 1	97.155±1.897	48.648±0.557	71.742±6.109	51.895±0.217
Kontrola 2	75.760±16.649	38.595±0.686	78.725±3.095	57.512±2.902
Kontrola 3	80.278±1.406	34.708±0.310	80.078±0.312	54.835±0.351
Srednja vrednost	84.398±11.277	40.650±7.194	76.848±4.473	54.748±2.810
Opseg srednjih vrednosti za svetska zemljišta[a]	47 - 51	13 - 26	22 - 28	45 - 60
MDK	100	50	100	300

[a] Opseg srednjih vrednosti hemijskih elemenata za dva osnovna tipa svetskih zemljišta [20]

[b] Maksimalno dozvoljene koncentracije hemijskih elemenata [21]

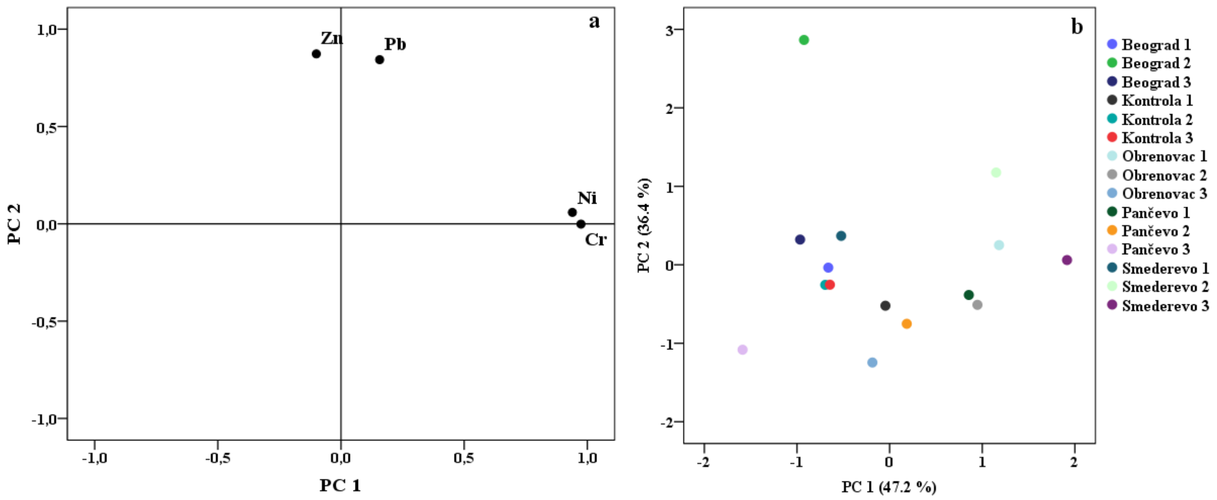
Tabela 2. Background vrednosti Cr, Ni, Pb i Zn (mg kg-1, s.m.) u lokalnom zemljištu [22]

Lokalitet	Cr	Ni	Pb	Zn
Pančevo	47.508	49.315	25.114	96.450
Smederevo	69.000	103.000	53.500	115.000
Obrenovac	79.000	131.000	35.123	74.000
Beograd	61.000	72.000	37.000	68.000

Određivanje odnosa i porekla teških metala

Da bi se utvrdio međusobni odnos između ispitivanih elemenata u zemljištu, kao i njihovi potencijalni izvori, korišćen je Pirsonov koeficijent korelacije (p) i analiza glavnih komponenti (PCA-Principal Component Analysis). Rezultati korelacione analize su pokazali značajnu pozitivnu korelaciju samo između Ni i Cr (p=0.843**), ukazujući na njihovo zajedničko poreklo. PCA analizom su dobijene dve glavne komponente sa svojstvenim vrednostima većim od 1, koje zajedno opisuju 83.6 % ukupne varijabilnosti. Prva komponenta objašnjava 47.2 % varijabilnosti i pokazuje značajnu pozitivnu korelaciju Cr i Ni, potvrđujući njihovo zajedničko prirodno-geološko poreklo dok druga komponenta objašnjava 36.4 % ukupne varijabilnosti i ukazuje na antropogeno poreklo

Pb i Zn (Slika 1a). Prostorni uticaj Pb i Zn je najviše izražen u Beogradu i to posebno na mestu uzorkovanja B2, ali delimično i u Smederevu. Uticaj Cr i Ni je najizraženiji u Smederevu, a delimično se prenosi i na uzorke iz Obrenovca i Pančeva (Slika 1b).



Slika 1. Rezultati analize glavnih komponenti (PCA): a) grafik loadinga i b) grafik skorova ispitivanih elemenata u uzorcima zemljišta

Pokazatelji zagađenja zemljišta teškim metalima

Radi boljeg shvatanja uticaja pojedinih elemenata na nivoe zagađenja zemljišta na ispitivanim lokalitetima, njihovih izvora kao i procene njihovog ekološkog rizika izračunati su: Faktor obogaćenja (EF), Indeks zagađenja (PI), Faktor rizika (Ei) i Potencijalni ekološki indeks rizika (RI). Za njihovo izračunavanje je potrebno uzeti u obzir background vrednosti za određeni element koje su dobijene aritmetičkim izračunavanjem na osnovu medijane [22] za istraživani lokalitet, kao i granične vrednosti propisane zakonskom uredbom za ispitivano područje [15].

Faktor obogaćenja(EF)

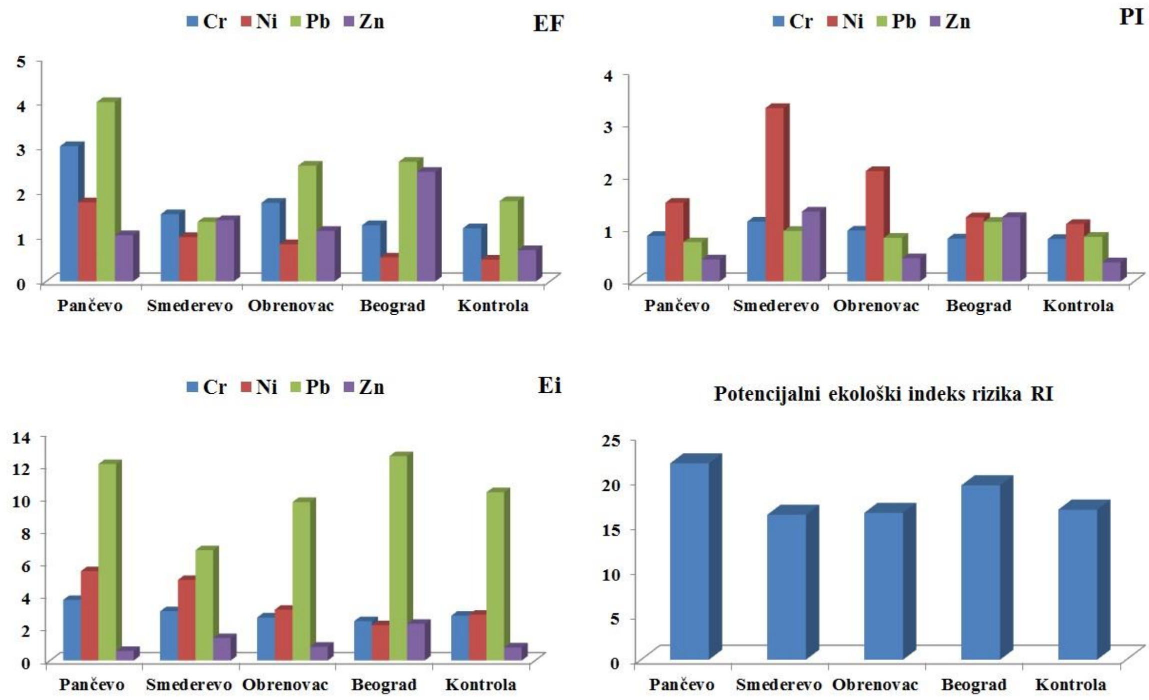
Na osnovu srednjih vrednosti EF (Slika 2) na ispitivanim lokalitetima uočeno je neznatno obogaćenje zemljišta ispitivanim elementima. Za sledeće elemente je utvrđen umeren faktor obogaćenja – Pančevo za Cr i Pb, Obrenovac za Pb i Beogradu za Pb i Zn. Pored njegovog prirodnog porekla, umereno obogaćenje zemljišta u Pančevu hromom bi mogao da bude rezultat i upotrebe sredstava koja se koriste za održavanje parkovskih površina [20], dok obogaćenje Pb Pančevu, Obrenovcu i Beogradu i Zn u Beogradu može biti uslovljeno emisijom poreklom iz saobraćaja i upotrebom olovnog benzina [26].

Indeks zagađenja (PI)

Na osnovu srednjih vrednosti koje su dobijene izračunavanjem PI utvrđeno je da nema zagađenja ispitivanim elementima na većini lokaliteta. Međutim, u Pančevu je ustanovljeno neznatno zagađenje Ni, u Smederevu Cr i Zn, u Beogradu Ni, Pb i Zn i na kontrolnom staništu Ni. Takođe je utvrđeno i umereno zagađenje Ni u Smederevu i Obrenovcu (Slika 2). Umereno zagađenje u Smederevu i Obrenovcu verovatno nije posledica antropogenog zagađenja, već prirode supstrata u gradskim parkovima koji se formiraju na aluvijumima koja prirodno mogu sadržati nešto veće količine Ni [2].

Faktor rizika (Ei) i Potencijalni ekološki indeks rizika (RI)

Prema kategorizaciji faktora rizika (Ei) i potencijalnog ekološkog indeksa rizika (RI), zemljišta na ispitivanim lokalitetima se mogu svrstati u grupu zemljišta niskog potencijalnog ekološkog rizika (Slika 2).



Slika 2.Grafički prikaz Faktora obogaćenja (EF), Indeksa zagađenja (PI), Faktora rizika (Ei) i Potencijalnog ekološkog indeksa rizika (RI) za ispitivana zemljišta

Zaključak

Na osnovu rezultata analize zemljišta ispitivanih urbanih parkova u Srbiji koji su izloženi različitim izvorima zagađenja može se zaključiti sledeće:

Ukupan sadržaj svih analiziranih elemenata je veoma varijabilan i u većini uzoraka viši od prosečnih koncentracija utvrđenih za svetska zemljišta.

Izmerene koncentracije Cr i Pb u svim analiziranim uzorcima su bile više od ustanovljenih lokalnih background vrednosti, ali uglavnom niže od MDK. Za Ni i Zn su utvrđena pojedinačna prekoračenja background i MDK vrednosti.

Statističke analize su pokazale visoku pozitivnu korelaciju između Ni i Cr koji formiraju poseban klaster i pripadaju prvoj glavnoj komponenti, sugerišući da je njihov sadržaj uslovljen geološkim poreklom. Zn i Pb pripadaju drugoj glavnoj komponenti, a njihov sadržaj je uslovljen antropogenim izvorima koji ne predstavljaju ugrožavajući faktor i svode se na tačkasta zagađenja.

Na osnovu vrednosti faktora i indeksa (EF, PI, Ei, RI) može se zaključiti da na istraživanim lokalitetima postoji neznatno i/ili umereno obogaćenje i zagađenje zemljišta ispitivanim elementima, ali da ne predstavlja potencijalni ekološki rizik za životnu sredinu.

Vrednosti EF, PI, Ei, RI ispitivanih elemenata treba posmatrati kao indikativne, a potpuna procena njihovog potencijalnog štetnog efekta može da se postigne frakcionom analizom njihovih dostupnih formi.

Zahvalnost.

Ovaj rad je podržan od strane Ministarstva prosvete, nauke i tehnološkog razvoja Republike Srbije projektom OI 173018.

Literatura

1. Alloway, B. J., Trace Metals in Soil, Chapman & Hall, London, 1995, p368.
2. Mrvić, V., Antonović, G., Martinović,Lj., Plodnost i sadržaj opasnih i štetnih materija u zemljištima Centralne Srbije, Institut za zemljište, Beograd, 2009, pp 75-144.
3. Wei, B., Yang, L., A review of heavy metal contaminations in urban soils, urban road dusts and agricultural soils from China, *Microchm. J.* 2010, 94, 99-107
4. Adriano, D.C., Trace Elements in Terrestrial Environments: Biogeochemistry, Bioavailability and Risks of Metals, Springer, New York, 2001, p 867.
5. Manta, S.D., Angelone, M., Bellanca, A., Neri, R., Sprovieri, M., Heavy metals in urban soils: a case study from the city of Palermo (Sicily), Italy. *Sci. Total Environ.*2002, 300, 229-243
6. Cheng, H., Li, M., Zhao, C., Li, K., Peng, M., Qin, A., Cheng, X., Overview of trace metals in the urban soil of 31 metropolises in China, *J. Geochem. Explor*. 2014, 139, 31-52
7. Wu, S., Peng, S., Zhang, X., Wu, D., Luo, W., Zhang, T., Zhou, S., Yang, G., Wan, H., Wu, L., Levels and health risk assessments of heavy metals in urban soils in Dongguan, China, *J. Geochem. Explor*. 2015, 71-78
8. Gržetić, I., Ghariani, R.H.A., Potential health risk assessment for soil heavy metal contamination in the central zone of Belgrade (Serbia), *J. Serb. Chem. Soc.* 2008, 73,923-934
9. Kuzmanoski, M.M., Todorović, M.N., Aničić-Urošević, M.P., Rajšić, S.F., Heavy metal content of soil in urban parks of Belgrade. *Hem. Ind.* 2014, 68, 643-651
10. Akan, J.C., Audu, S.I., Mohammed, Z., Ogugbuaja V.O., Assessment of Heavy Metals, pH, Organic Matter and Organic Carbon in Roadside Soils in Makurdi Metropolis, Benue State, Nigeria. *J. Environ. Prot.* 2013, 4, 618-628
11. Hu, Y., Liu, X., Bai, J., Shih, K., Zeng, E. Y., Cheng, H., Assessing heavy metal pollution in the surface soils of a region that have had undergone three decades of intense industrialization and urbanization. *Environ. Sci. Pollut. R.* 2013, 20, 6150-6159
12. Andrejić, G., Rakić, T., Šinnžar-Sekulić, J., Mihailović, N., Grubin, J., Stevanović, B., Tomović, G., Assessment of heavy metal pollution of topsoils and plants in the City of Belgrade, *J. Sreb. Chem. Soc.* 2016, 81,447-458
13. US Environmental Protection Agency (USEPA), Microwave Assisted Acid Digestion of Siliceous and Organically Based Matrices 3052 (A 20), SW-846 Ch 3.2, method code 10136206. USEPA, Washington, DC, 1996.
14. Sutherland, R.A., Bed Sediment-Associated Trace Metals in an Urban Stream, Oahu, Hawaii. *Environ. Geol.* 2000, 39, 611-627
15. Službeni glasnik Republike Srbije., Uredba o programu sistematskog praćenja kvaliteta zemljišta, indikatorima za ocenu rizika od degradacije zemljišta i metodologiji za izradu remedijacionih programa, Službeni glasnik Republike Srbije, 2010, 88/10.
16. Hu, Y., Liu, X., Bai, J., Shih, K., Zeng, E. Y., Cheng, H., Assessing heavy metal pollution in the surface soils of a region that have had undergone three decades of intense industrialization and urbanization, *Environ. Sci. Pollut. R.* 2013, 20, 6150-6159
17. Yang, Z., Lu, W., Long, Y., Bao, X., Yang, Q., Assessment of heavy metals contamination in urban topsoil from Changchun City, China, *J. Geochem. Explor.* 2011, 108, 27-38
18. Hakanson, L., An ecological risk index for aquatic pollution control. A sedimentological approach, *Water Res*. 1980, 14, 975-1001
19. Mihailović, A., Budinski-Petković, Lj.,Popov, S., Ninkov, J., Vasin, J., Ralević, N. M., Vučinić-Vasić, M., Spatial distribution of metals in urban soil of Novi Sad, Serbia: GIS based approach. *J. Geochem. Explor.*2015, 150, 104-114

20. Kabata-Pendias, A., Pendias, H., Trace Elements in Soils and Plants, CRC Press, London, DC, 2001, p 331.
21. Službeni glasnik Republike Srbije., Pravilniku o dozvoljenim količinama opasnih i štetnih materija u zemljištu, Službeni Glasnik Republike Srbije, 1994, 23/9.
22. Mrvić, V., Kostić-Kravljanac, Lj.,Čakmak, D., Sikirić, B., Brebanović, B., Perović, V., Nikoloski, M., Pedogeochemical mapping and background limit of trace elements in soils of Branicevo Province (Serbia). *J. Geochem. Explor*. 2011, 109, 18-25
23. Manta, S.D., Angelone, M., Bellanca. A., Neri, R., Sprovieri, M., Heavy metals in urban soils: a case study from the city of Palermo (Sicily), Italy, *Sci. Total. Environ*. 2002, 300, 229-243
24. Madrid, L., Dıáz-Barrientos, E., Madrid, F., Distribution of heavy metal contents of urban soils in parks of Seville, *Chemosphere*,2002,49, 1301-1308
25. Imperato, M., Adamo, P., Naimo, D., Arienzo, M., Stanzione, D., Violante, P., Spatial distribution of heavy metals in urban soils of Naples city (Italy), *Environ. Pollut*. 2003, 124, 247-256
26. Ghariani, R.H.A., Gržetić. I., Antić. M., Nikolić-Mandić. S., Distribution and availability of potentially toxic metals in soil in central area of Belgrade, Serbia. *Environ. Chem. Lett.* 2010, 8, 261-269
27. Marjanović, M.D., Vukčević, M.M., Antonović, D.G., Dimitrijević, S.I., Jovanović, Đ.M., Matavulj, M.N., Ristić, M.Đ., Heavy metals concentration in soils from parks and green areas in Belgrade, *J. Serb. Chem. Soc.* 2009, 74, 697–706
28. Dragović, R., Gajić, B., Dragović, S., Đorđević, M., Đorđević, M., Mihailović, N., Onjia, A., Assessment of the impact of geographical factors on the spatial distribution of heavy metals in soils around the steel production facility in Smederevo (Serbia), *J. Clean. Prod.* 2014, 84, 550-562

Treatment of leachate by electrocoagulation using aluminium electrode

Tretman deponijskih procjednih voda elektrokoagulacijom primjenom aluminijumskih elektroda

Borislav N. Malinović[1], Tijana Djuricic[1], Miomir G. Pavlović[2]

[1]University of Banja Luka, Faculty of Technology, Banja Luka, Bosnia and Herzegovina

[2]University of Eastern Sarajevo, Faculty of Technology, Zvornik, Bosnia and Herzegovina

[1]Univerzitet u Banjoj Luci, Tehnološki fakultet, Banja Luka, Bosna i Hercegovina

[2]Univerzitet u Istočnom Sarajevu, Tehnološki fakultet, Zvornik, Bosna i Hercegovina

Apstract

In this study was investigated the effect of aluminium as anode material on the turbidity, chemical oxigen demand (COD) and total dissolved solids (TDS) removal efficiency by the electrocoagulation of landfill leachate. The treatment was performed in a batch electrochemical reactor of 0,25 dm^3 capacity with distance between electrodes 1,5 cm. The sample of leachate was supplied from regional sanitary landfill "Ramici", Banja Luka. Effects of process parameters such as current density and electrolysis duration are investigated on removal efficiencies of turbidity, COD and TDS. The maximum turbidity and TDS removal efficiency is achieved in 120 minutes of treatment (86,8%; 60,2%), but maximum COD removal efficiency is achieved in 90 minutes of treatment (54,5%), at the current density j=25 mA/cm^2 and the concentration of supporting electrolyte γ_{NaCl}=1 g/L.

Key words: *electrochemical treatment, landfill, TDS, COD, turbidity.*

Izvod

U radu je istraživan uticaj aluminijuma kao anodnog materijala na efikasnost uklanjanja mutnoće, hemijske potrošnje kiseonika (HPK) i ukupno rastvorenih čvrstih čestica (TDS) procesom elektrokoagulacije deponijskih procjednih voda. Tretman je izveden u šaržnom elektrohemijskom reaktoru zapremine 0,25 dm^3 sa međusobnim rastojanjem elektroda 1,5 cm. Uzorak procjednih voda je uzet sa regionalne sanitarne deponije „Ramići" Banja Luka. Ispitivan je uticaj procesnih parametara na mutnoću, HPK i TDS. Maksimalna efikasnost uklanjanja mutnoće i TDS je postignuta za 120 minuta tretmana (86,8%; 60,2%), a maksimalna efikasnost uklanjanja HPK je postignuta za 90 minuta tretamana (54,5%), *pri gustini struje j=25 mA/cm^2 i koncentraciji pomoćnog elektrolita γ_{NaCl}=1 g/L.*

Ključne riječi: *elektrohemijski tretman, deponija, TDS, HPK, mutnoća.*

INTRODUCTION

Leachate is one of the basic problems of waste management, but because of its huge pollution require special attention and treatment because of the enormous impact on the quality of the environment. Leachate is formed when rainwater penetrates through the waste in a landfill and carries some forms of pollutants. The sanitary landfill is the most common method of disposal of urban solid waste [1]. In areas that have enough available land, sanitary landfills used for the disposal of municipal solid waste. However, even with numerous economic benefits, the sanitary landfill methods poses a number of environmental shortcomings, such as the generation of landfill leachate [2].

This paper represents a case study for the Ramici regional landfill in Banja Luka, Bosnia and Herzegovina. Banjaluka is the second largest city in B&H and the largest city of the Republika Srpska entity. By estimation this region has 400000 inhabitants and the level of services for collecting and transporting waste is about 70%. Waste management in the Banjaluka region is currently based on landfilling. The landfill is located near the City of Banja Luka and municipal, industrial (non-hazardous) and clinical wastes are dumped without being separated [3]. Leachate composition depends on different factors, such as the kind of waste, site hydrology, age, type, and landfill operation [4]. The leachate from Banjaluka landfill contains heavy metals, organic and inorganic compounds in its composition [5].

Young landfill leachates are generally easier to treat compared with old ones [6]. Leachate from the old landfills contain less organic biodegradable matter and more toxic components, so the purification of the water should be used a combination of several different processes. Many studies have investigated different physical-chemical methods to treat landfill leachate and wastewater [7-10]. Biological treatment, including anaerobic and aerobic process is very efficient for leachate at an early stage with a high BPK_5/HPK relations. However it is not effective in the leachate with a fairly low BPK_5/HPK relations, or in high concentrations of toxic metals. Therefore, the physical-chemical processes commonly used for pre-treatment or treatment of these landfill water. Adsorption and membrane filtration are major physical leachate treatment methods [11-13]. Coagulation-flocculation, chemical precipitation, chemical and electrochemical oxidation methods are the most common chemical methods used for landfill leachate treatment [14-17].

In addition to the electrochemical oxidation, for treatment or pre-treatment of leachate is increasingly being used electrocoagulation methods. The electrocoagulation process involves the *in situ* generation of coagulants through the electro-dissolution of a sacrificial anode, which is usually made of iron or aluminium. The main electrochemical reactions are the oxidation of the metallic anode (Fe or Al) and the reduction of water [18]. The electrochemical reactions that occur in this process, including the formation of bubbles of gas (H_2 and O_2) to the electrodes. The bubbles of gas assist flotation, and thus promote the process itself. Compared to conventional chemical coagulation, electrocoagulation basic advantages are a smaller amount needed coagulate ions, the greater pollutants removal efficiency, there is no use of chemicals thus reducing the possibility of secondary pollution and reduces the quantity of sludge, less reaction time and consequently less, simple and easy handling equipment [19]. Ilhan *et al.* used electrocoagulation treatment of landfill leachate for reducing the COD values by using Fe and Al electrodes. They concluded that electrocoagulation is better method than chemical coagulation because electrocoagulation achieves greater efficiency to reduce COD and the reduction of sulphate. Al electrode is more preferred because of its high removal efficiency and low and stable sludge capacity for leachate [20]. Similar research of landfill leachate treatment by electrocoagulation conducted Kabuki *et al.* They found that the optimum operating conditions for the reduction of COD and removal of suspended solids and organic carbon are at the current density j=20 mA/cm^2, electrolysis duration t=60 min and pH=8. The optimum operating conditions for the removal of Kjeldahl nitrogen and NH_3-N are at the current density j=30 mA/cm^2, electrolysis time t=60 min and pH=8 [21]. The process of electrocoagulation also use Xiangdong *et al.* for landfill leachate treatment. In this study, Fe and Al electrode were compered. Iron anodes give better COD and NH_3-N removal performance than the aluminium anodes at 2,98 mA/cm^2 current density, 50 min electrolysis time and pH=6,5 [22]. Mahmad *et al.* carried out the removal of total chromium, colour and turbidity from leachate by electrochemical coagulation with two type of electrodes (aluminium and stainless steel). Based on the result, can be concluded that aluminium electrodes are best for removal of turbidity and colour but stainless steel electrodes is better for removal total chromium [23].

MATERIAL AND METHODS

The experimental part of the research consisted for treating landfill leachate by using electrocoagulation. The sample of leachate was taken from the tank in which the leachate coming from the drainage pipes (Figure 1).

Figure 1. Drainage pipe and landfill leachate tanks (regional sanitary landfill Ramici)

Experimental setup is shown on the Figure 2. The batch electrochemical reactor of 250 cm^3 capacity made from polypropylene with constant mixing (400 rpm) was used, combined with two electrodes of the same area surface. The dimensions of the electrodes are 40x40x1 mm. The total effective area of one electrode is 37,3 cm^2, and the distance between 2 cm. Electrodes were connected to electrical power source (Atten, APS3005SI; 30V, 5A).

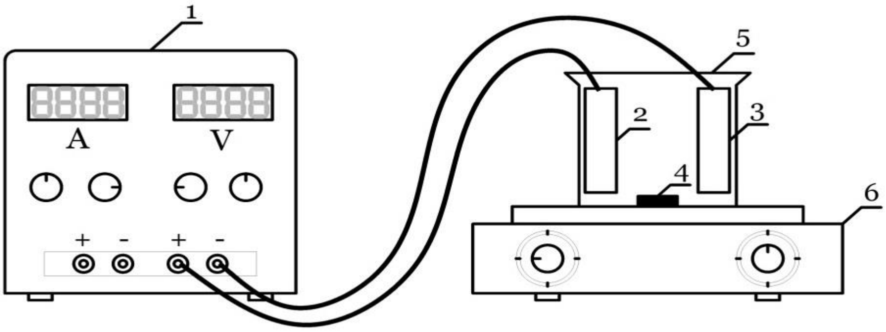


Figure 2. Schematic view of electrochemical reactor
1 – source of electric power; 2 – anode; 3 – cathode; 4 – magnetic stir bar; 5 – electrochemical cell; 6 – magnetic stirrer)

All the experiments were performed at an ambient temperature, with the wastewater volume of 200 cm^3. Before each treatment electrodes were cleaned and degreased. As an electrode material was used aluminum (Al 99.5/ENAW-1050 A; max. 0.25% Si, max. 0.40% Fe, max. 0.05% Cu, max. 0.05% Mn, max. 0.05% Mg, max. 0.05% Ti, max. 0.07% Zn, min. 99.50% Al). All the used chemicals are of *p.a*. For the purpose of experiment were used the following commercially available chemicals: 99,5% sodium chloride (Lachner, Czech Republic), 97% sodium hydroxide (Zorka

Sabac, Serbia), 36% hydrochloric acid (Lachner, Czech Republic), Acetone (Lachner, Czech Republic).

The values of parameters before treatment are given in the following table.

Table 1. The results of analysis of sample landfill leachate

Rb.	Parameter	Measuring unit	Result
1.	pH	-	7,98
2.	TDS	g/L	12,5
3.	Conductivity	mS/cm	19,5
4.	Electrolyte resistivity	Ωcm	51
5.	Salinity	SAL	13,2
6.	Turbidity	NTU	104
7.	COD	mgO_2/L	7010

Treated landfill leachate after each treatment was adjusted pH=11 (using NaOH), and the formed precipitate was filtered through filter paper, Filtres Fioroni, France (Ref.:0015A00007; size: 125 mm, qty.: 1000). The samples of landfill leachate before and after treatment were analyzed on the following parameters: turbidity, total dissolved substances (TDS), chemical oxygen demand (COD), pH, electrolyte resistivity (ρ), conductivity (κ) and salinity *(SAL)*. TDS, ρ, κ and *SAL* are determined on the multimeter (Consort C861), and a turbidity on the turbidimeter (LP 2000, HANNA instruments). COD was measured by the closed spectrophotometric method on COD Reactor (Hach, USA), colorimeter (COD CheckItDirect, Lovibond, Germany) by standard cuvette (Test Tube MR, Lovibond, Germany). Prepared sample wastewater before and after treatment were analyzed in accordance with standard methods [24].

RESULTS AND DISCUSION

Results of the electrochemical treatment of landfill leachate are shown through removal efficiency of TDS, COD and removal efficiency of turbidity, *Eu* (%), whose ratio could be described by following equation:

$$E_U = \frac{\gamma_i - \gamma_f}{\gamma_i} \times 100[\%] \qquad (1)$$

where are γ_i and γ_f the initial and the final value of parameter which efficiency is determined.

Examined the influence of current density on the efficiency of removing TDS, COD and turbidity. In this experiment was used current densities of 10, 25 i 50 mA/cm^2. Figure 3 shows that the higher removal efficiency of TDS, COD and turbidity is achieved at a current density of j=50 mA/cm^2 (25,76%; 32,3%; 28,85%). However, these are slightly higher values (except for turbidity) than for j=25 mA/cm^2. Although the difference in the achieved efficiency at high current density is not negligible, for further experiments used the current density j=25 mA/cm^2, considering that lower density reduces investment costs.

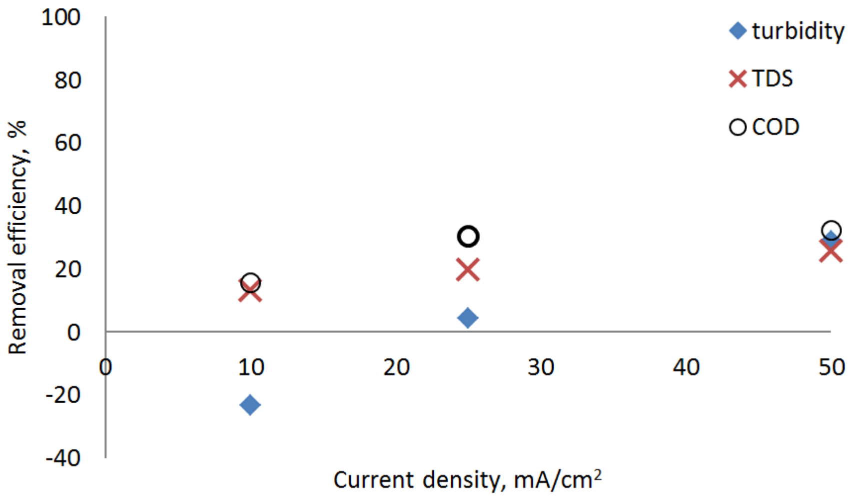


Figure 3. TDS, COD and turbidity removal efficiency at different current densities (t=30 min, stirring 400 rpm)

Figures 4, 5 and 6 shows the impact of electrolysis time (15; 30; 60; 90 and 120 min) on TDS, COD and turbidity removal efficiency.

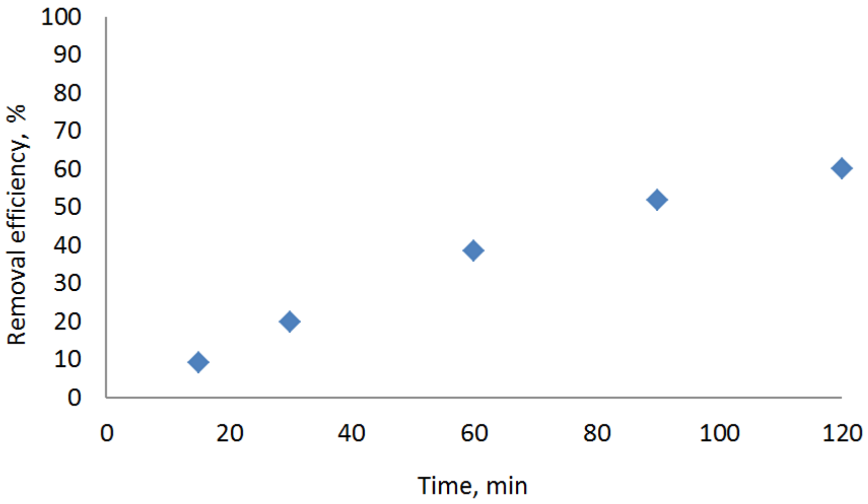


Figure 4. The impact of electrolysis duration on the removal of TDS (j=25 mA/cm^2, stirring 400 rpm)

The highest removal efficiency of TDS is achieved at the electrolysis duration of 120 minutes and amounts 60,2% (Figure 4).

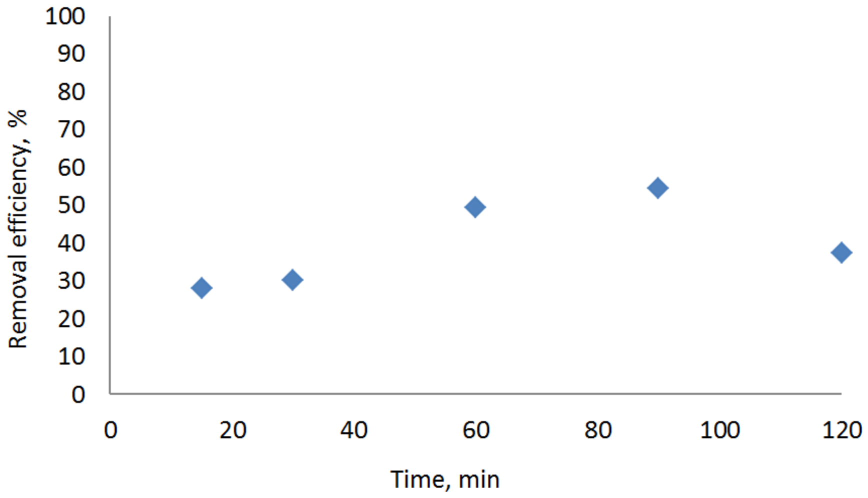


Figure 5. The impact of electrolysis duration on the removal of COD
(j=25 mA/cm^2, stirring 400 rpm)

The highest removal efficiency of COD is achieved at the electrolysis duration of 90 minutes and amounts 54,5 % (Figure 5). After 90 minutes of treatment the removal efficiency of COD decreases.

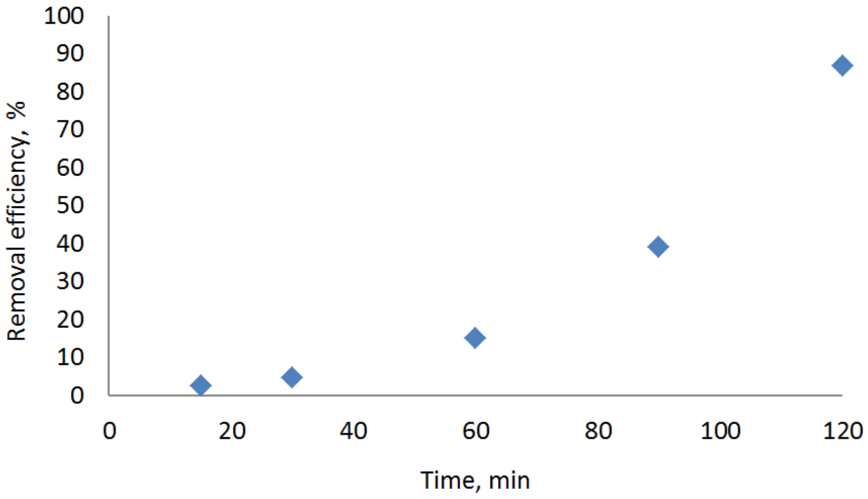


Figure 6. The impact of electrolysis duration on the removal of turbidity
(j=25 mA/cm^2, stirring 400 rpm)

Figures 6 shows the impact of electrolysis duration (15; 30; 60; 90 and 120 min) on turbidity removal efficiency. Maximum efficiency is achieved in 120 minutes (86,8 %).

CONCLUSION

Based on the presented results it can be conclude that the electrocoagulation process is an alternative to other methods of treatment of landfill leachate wastewater. By increasing the duration of electrocoagulation increases the removal efficiency of total dissolved solids and turbidity.

Acknowledgements

This work was supported in part by the Ministry of Science and Technology of the Republic of Srpska under Project 19/6-020/961-19/15.

REFERENCES

1. Mojiri, A., Aziz, H., Zaman, N., Aziz, S., & Zahed, M. Powdered ZELIAC augmented sequencing batch reactors (SBR) process for co-treatment of landfill leachate and domestic wastewater. Journal of Environmental Management, **139** (2014), 1-14.
2. Aziz, S. Q., Aziz, H. A., Mojiri, A., Bashir, M., Salem, S., Amr, A. Landfil Leachate Treatment Using Sequencing Batch Reactor (SBR) Process: Limitation of Operational Parameterts and Performance. International Journal of Scientific Research in Knowlwdge, **1**(3) (2013), 34-43.
3. Bjelic D., Stevanovic Carapina H., Neskovic Markic D., Sobot Pesic Z., Mihajlov A., Vukic Lj. Environmental Assessment Of Waste Management In Banjaluka Region With Focus On Landfilling. Environ Eng Manag J, 14(4), (2015) 1455-1463.
4. Foul, A.A., Aziz, H.A., Isa, M.H., Hung, Y.T. Primary treatment of anaerobic landfill leachate using activated carbon and limestone: batch and columnstudies. Inter. J. Environ. Waste Management, **4** (2009), 282-290.
5. Neskovic Markic D., Bjelic D., Zugic Drakulic N., Stevanovic Carapina H., Sobot Pesic Z. Assessment Of The Impact Of Banjaluka Landfill On Groundwater Quality. Carapth J Earth Env, 10(2), (2015) 271-280.
6. Kargi, F. & Pamukoglu, M. Adsorbent supplemented biological treatment of pre-treated landfill leachate by fed-batch operation. Bioresource Technology, **94**(3) (2004), 285-291.
7. Mojiri, A. Review on Membrane Bioreactor, Ion Exchange and adsorption Methods for Landfill Leachate Treatment. Australian Journal of Basic and Applied Sciences 5, **5**(12) (2011), 1365-1370.
8. Bashir, M., Aziz, H., Yusoff, M., Aziz, S., Mohajeri, S. Stabilized Sanitary Landfill Leachate Treatment Using Anionic Resin: Treatment optimization by Response Surface Methodology. Journal of Hazardous Materials, **182**(1-3) (2010), 115-122.
9. Foo, H. & Hameed, B. An overview of landfill leachate treatment via activated carbon adsorption process. Journal of Hazardous Materials, **171**(1-3) (2009), 54-60.
10. Dhas, J. Removal of COD and Colour from Textile Wastewater Using Limestone and Activated Carbon. MSc thesis. University Sains Malaysia, Cagliary, Italy: IWWG- International waste working group, 2008.
11. Kiliç, M., Kestioglu, K., Yonar, T. Landfill Leachate treatment by the combination of physicochemical methods with adsorption process. Journal of Biodiversity and Environmental Sciences, **1**(1) (2007), 37-43.
12. Bohdziewicz, J., Bodzek, M., Gorska, J. Aplication of pressure-driven membrane techniques to biological treatment of landfill leachate. Process Biochemistry, **36**(7) (2001), 641-646.
13. Trebouet, D., Schlumpf, J., Jaounen, P., Quemeneuer, F. Stabilized landfill leachate treatment by combined physicochemical-nanofiltation process. Water Research, **35**(12) (2001), 2935-2942.
14. Ahn, D., Yun-Chul, C., Won-Seok, C. Use of coagulation and zeolite to enhance the biological treatment efficiency of high ammonia leachate. Journal of Environmental Science and Health, **37**(2) (2002), 163-173.
15. Marttinen, S., Kettunen, R., Somunen, K., Soimasuo, R., Rintala, J. Screening of physical-chemical methods for removal of organic material, nitrogen and toxicity from low strength landfill leachates. Chemosphere, **46**(6) (2002), 851-858.
16. Chiang, L. & Chang, C. Electrochemical oxidation combined with physical-chemical pretreatment processes for the treatment of refractory landfill leachate. Environmental Engineering Science, **18**(6) (2001), 369-378.
17. Lin, S. & Chang, C. Treatment of landfill leachate by combined electro-fenton oxidation and sequencing batch reactor method. Water Research, **34**(17) (2000), 4243-4249.

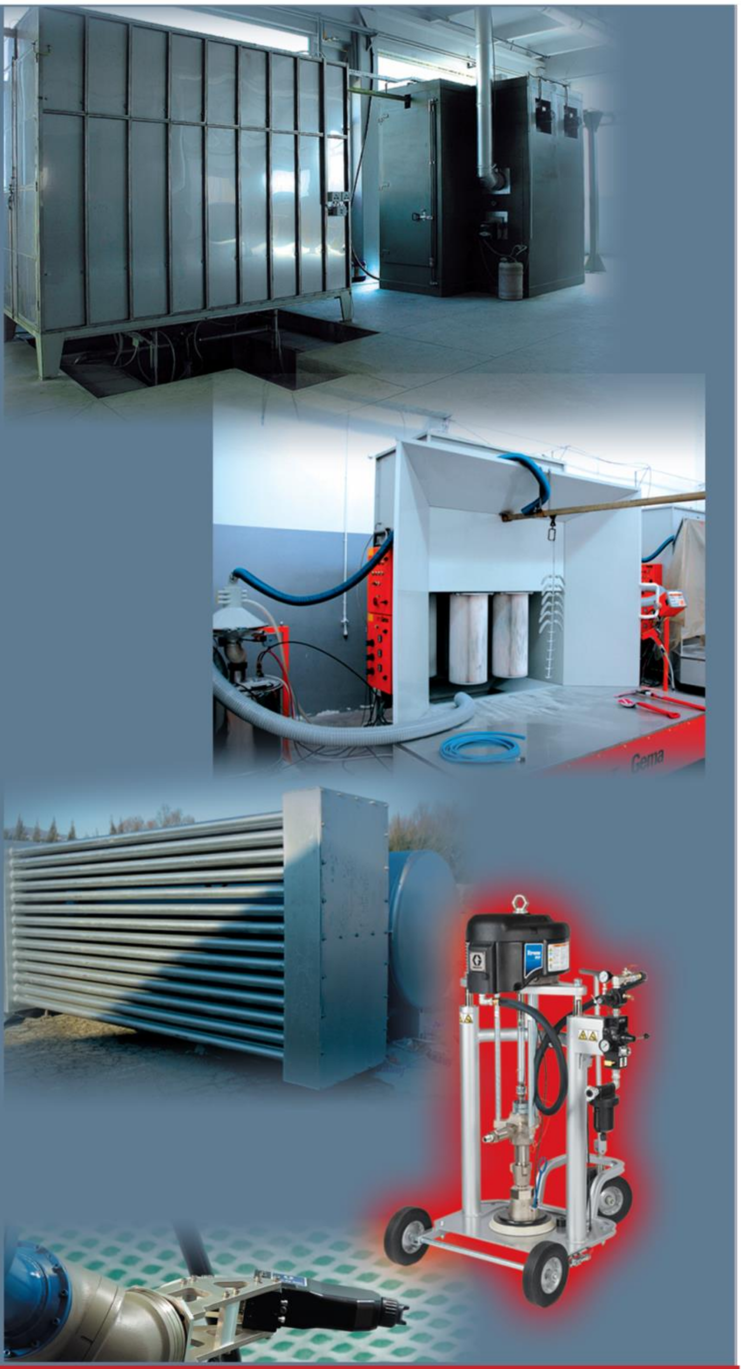
18. Lacasa, E., Canizares, P., Saez, C., Fernandez, F. J., Rodrigo, M. A. Electrochemical phosphates removal using iron and aluminium electrodes. Chemical Engineering Journal, **172**(1) (2011), 137-143.
19. Malinovic, B.N., Malinovic, T., Bunic, S.: Treatment of cyanides in a flow electrochemical reactor, XXIV International Conference “Ecological Truth”, Eco-Ist’16, Vrnjacka Banja, 12-15 june 2016, 398-407
20. Ilhan, F., Kurt, U., Apaydin, O., Talha Gonullu, M. Treatment of leachate by electrocoagulation using aluminum and iron electrodes. Journal of Hazardous Materials, **154**(1-3) (2008), 381-389.
21. Kabuk, H. A., Ilhan, F., Avsar, Y., Kurt, U., Gonullu, M. T. Investigation of Leachate treatment with Electrocoagulation and Optimization by Response Surface Methodology. Clean-Soil, Air, Water, **41** (2013), 1-7.
22. Xiangdong Li, Junke Song, Jiandong Guo, Zhichao Wang, Qiyan Feng. Landfill leachate treatment using electrocoagulation. Procedia Environmental Sciences, 10 (2011) 1159 – 1164.
23. Mahmad M. K. N., Rozainy M. R., Abustan I., Baharun N.. Electrocoagulation Process by Using Aluminium and Stainless Steel Electrodes to Treat Total Chromium, Colour and Turbidity. Procedia Chemistry 19 (2016) 681 – 686.
24. American Public Health Association (APHA). Standard Methods of Water and Wastewater. 18th ed. American Public Health Association, American Water Works Association, Water Environment Federation publication. APHA, Washington D.C. (1992).

INDEKS AUTORA

AUTHOR INDEX

SPONZORI

SPONSORS




INTERNATIONAL SOCIETY OF ELECTROCHEMISTRY
ISE

PITURA®

HEMIPRODUKT BOJE I LAKOVI

G-CERTi SYSTEM SERVICE ISO 9001:2008 Cert No: GKSR-0156-QC
G-CERTi SYSTEM SERVICE ISO 14001:2004 Cert No: GKSR-0156-EC

Hemiprodukt doo Novi Sad
Masarikova br 1 , tel:+381 21 2998-420
PIB 101653108
e-mail:hemiboje@gmail.com
www.hemiprodukt.co.rs

“**Hemiprodukt**” osnovan je 1991. godine u Begeču kao samaostalna zanatska radnja za proizvodnju hemijskih proizvoda. 1992 godine je osnovano preduzeće “Hemiprodukt” d.o.o, za proizvodnju boja i lakova, spoljnju i unutrašnju trgovinu, konsalting i zastupanje, koje se aktivira 1996. godine. Zbog povećanja obima poslovanja “Hemiprodukt” d.o.o. u toku 1997 i 1998 godine preuzima proizvodnju boja, lakova i razredjivača od SZR “Hemiprodukta”. Početkom 2002. godine sedište “Hemiprodukta” d.o.o. se seli u Novi Sad, ulica Masarikova 1, radi bolje komunikacije sa poslovnim partnerima.

Osnovni cilj firme “Hemiprodukt” je da pruži tržištu kvalitetne boje i lakove uz maksimalnu fleksibilnost i efikasnost u pogledu zadovoljavanja specijalnih zahteva kupaca.

Organizacija firme

- Sedište firme i veleprodaja: **Novi Sad,** Masarikova 1
- P.J. proizvodnja, veleprodaja i maloprodaja: **Begeč**, Nikole Tesle 35
- P.J. veleprodaja**: Beograd**, Zrenjaninski put 94

Proizvodni program

Sistemi za antikorozionu zaštitu metala premazima

Alkidni
Modifikovani alkidni-brzosušivi
Nitro
Epoksidni
Poliuretanski
Vinil-akrilni
Premazi za visoke temperature-silikonski

Industrijski podovi

Akrilni premaz
Epoksi premaz i samorazlivajući pod
Poliuretanski premaz i samorazlivajući pod

Premazi za drvo

Alkidni
Nitro
Poliuretanski
Vodorazredivi akrilni i poliuretanski

Specijalni proizvodi za građevinarstvo i široku potrošnju

HEMIPRODUKT
BOJE I LAKOVI

G-CERTi SYSTEM SERVICE
ISO 9001:2008
Cert No: GKSR-0156-QC

G-CERTi SYSTEM SERVICE
ISO 14001:2004
Cert No: GKSR-0156-EC

Hemiprodukt doo Novi Sad
Masarikova br 1 , tel:+381 21 2998-420
PIB 101653108
e-mail:hemiboje@gmail.com
www.hemiprodukt.co.rs

Naši proizvodi za zaštitu metala su usaglašeni sa standardima, te navodimo izveštaje Instituta kojima to i potvrđujemo:

- Zaštitni sistem boja – Osnovna boja za metal , Colorton emajl univerzalni, SPRS ISO 12944 za kategoriju atmosferske korozivnosti C3 DUGI (H) vek trajanja (više od 15 godina).
- Zaštitni sistem boja – Osnovna boja za metal BS, Industrijski emajl BS, SPRS ISO 12944 za kategoriju atmosferske korozivnosti C3 DUGI (H) vek trajanja (više od 15 godina).
- Zaštitni sistem boja – Hemipoks ZN prajmer, Hemipoks katran epoksi, SPRS ISO 12944 za kategoriju atmosferske korozivnosti C4 DUGI vek trajanja (više od 15 godina).
- Zaštitni sistem boja – Hemipoks osnovna, Hemipoks filer, Hemidur M zavrsni (emajl), SPRS ISO 12944 za kategoriju atmosferske korozivnosti C4 DUGI vek trajanja (više od 15 godina).
- Zaštitni sistem boja – Hemipoks osnovna, Hemidur M zavrsni (emajl), slana komora 500 h.
- Zaštitni sistem boja – Vinil Akril osnovna, Vinil akril zavrsna, SPRS ISO 12944 za kategoriju atmosferske korozivnosti C3 DUGI vek trajanja (više od 15 godina).

Hemiprodukt – fabrika za proizvodnju industrijskih boja, nudi svojim kupcima sveobuhvatna rešenja i ceo program prmaza za antikorozionu zaštitu i dekoraciju metalnih površina. Ispunjavanje posebnih zahteva, brza proizvodnja i isporuka istih, tehnička podrška i dugogodišnje iskustvo naših stručnjaka , dovodi nas i naše proizvode do sve većeg broja zadovoljnih kupaca.

Кнеза Милоша 7
11000 Београд

Савез инжењера и техничара Србије

Union of Engineers and Technicians of Serbia


NOV HEM