UDC 622

ISSN 2334-8836 (Štampano izdanje)
ISSN 2406-1395 (Online)

Mining and Metallurgy Engineering Bor

3/2015

Published by: Mining and Metallurgy Institute Bor

MINING AND METALLURGY INSTITUTE BOR

MINING AND METALLURGY ENGINEERING BOR is a journal based on the rich tradition of expert and scientific work from the field of mining, underground and open-pit mining, mineral processing, geology, mineralogy, petrology, geomechanics, metallurgy, materials, technology, as well as related fields of science. Since 2001, published twice a year, and since 2011 four times a year.

Editor-in-chief

Academic Ph.D. Milenko Ljubojev, Principal Reasearch Fellow, Associate member of ESC
Mining and Metallurgy Institute Bor
E-mail: milenko.ljubojev@irmbor.co.rs
Phone: +38130/454-109, 435-164

Editor

Vesna Marjanović, B.Eng.

English Translation

Nevenka Vukašinović

Technical Editor

Suzana Cvetković

Preprinting

Vesna Simić

Printed in: Grafomedtrade Bor

Circulation: 200 copies

Web site

www.irmbor.co.rs

Journal is financially supported by

The Ministry of Education, Science and Technological Development of the Republic Serbia
Mining and Metallurgy Institute Bor

ISSN 2334-8836 (Printed edition)

ISSN 2406-1395 (Online)

Journal indexing in SCIndex and ISI.

All rights reserved.

Published by

Mining and Metallurgy Institute Bor
19210 Bor, Zeleni bulevar 35
E-mail: milenko.ljubojev@irmbor.co.rs
Phone: +38130/454-110

Scientific – Technical Cooperation with the Engineering Academy of Serbia

Editorial Board

Prof.Ph.D. Tajduš Antoni
The Stanislaw University of Mining and Metallurgy, Krakow, Poland
Prof.Ph.D. Mevludin Avdić
MGCF-University of Tuzla, B&H
Prof.Ph.D. Vladimir Bodarenko
National Mining University, Department of Deposit Mining, Ukraine
Ph.D. Mile Bugarin, Principal Research Fellow
Mining and Metallurgy Institute Bor
Prof.Ph.D. Ruža Čeliković
MGCF-University of Tuzla, B&H
Ph.D. Miroslav R.Ignjatović, Senior Research Associate
Chamber of Commerce and Industry Serbia
Prof.Ph.D. Vencislav Ivanov
Mining Faculty, University of Mining and Geology "St. Ivan Rilski" Sofia Bulgaria
Academic Prof.Ph.D. Jerzy Kicki
Gospodarkl Surowcami Mineralnymi i Energia, Krakow, Poland
Ph. D., PEng. Dragan Komljenović
Hydro-Quebec Research Institute Canada
Ph. D. Ana Kostov, Principal Research Fellow
Mining and Metallurgy Institute Bor
Prof. Ph. D. Nikola Lilić
Faculty of Mining and Geology Belgrade
Ph.D. Dragan Milanović, Research Associate
Mining and Metallurgy Institute Bor
Prof.Ph.D. Vitomir Milić
Technical Faculty Bor
Ph.D. Aleksandra Milosavljević, Research Associate
Mining and Metallurgy Institute Bor
Ph.D. Dragoslav Rakić
Faculty of Mining and Geology Belgrade
Prof.Ph.D. Rodoljub Stanojlović
Technical Faculty Bor
Academic Prof.Ph.D. Mladen Stjepanović
Engineering Academy of Serbia
Ph.D. Biserka Trumić, Senior Research Associate
Mining and Metallurgy Institute Bor
Prof.Ph.D. Nebojša Vidanović
Faculty of Mining and Geology Belgrade
Prof.Ph.D. Milivoj Vulić
University of Ljubljana, Slovenia
Prof.Ph.D. Nenad Vušović
Technical Faculty Bor

JOURNAL OF INTERNATIONAL IMPORTANCE, VERIFIED BY A SPECIAL DECISION OF THE MINISTRY OF EDUCATION, SCIENCE AND TECHNOLOGICAL DEVELOPMENT OF THE REPUBLIC SERBIA - M24

INSTITUT ZA RUDARSTVO I METALURGIJU BOR

MINING AND METALLURGY ENGINEERING BOR je časopis baziran na bogatoj tradiciji stručnog i naučnog rada u oblasti rudarstva, podzemne i površinske eksploatacije, pripreme mineralnih sirovina, geologije, mineralogije, petrologije, geomehanike, metalurgije, materijala, tehnologije i povezanih srodnih oblasti. Izlazi dva puta godišnje od 2001. godine, a od 2011. godine četiri puta godišnje.

Glavni i odgovorni urednik
Akademik dr Milenko Ljubojev, naučni savetnik
Institut za rudarstvo i metalurgiju Bor
E-mail: milenko.ljubojev@irmbor.co.rs
Tel. 030/454-109, 435-164

Urednik
Vesna Marjanović, dipl.inž.

Prevodilac
Nevenka Vukašinović, prof.

Tehnički urednik
Suzana Cvetković, teh.

Priprema za štampu
Vesna Simić, teh.

Štamparija: Grafomedtrade Bor

Tiraž: 200 primeraka

Internet adresa
www.irmbor.co.rs

Izdavanje časopisa finansijski podržavaju
Ministarstvo za prosvetu, nauku i tehnološki razvoj Republike Srbije
Institut za rudarstvo i metalurgiju Bor

ISSN 2334-8836 (Štampano izdanje)

ISSN 2406-1395 (Online)

Indeksiranje časopisa u SCIndeksu i u ISI.

Sva prava zadržana.

Izdavač
Institut za rudarstvo i metalurgiju Bor
19210 Bor, Zeleni bulevar 35
E-mail: milenko.ljubojev@irmbor.co.rs
Tel. 030/454-110

Naučno - tehnička saradnja sa
Inženjerskom Akademijom Srbije

Uređivački odbor
Prof. dr Tajduš Antoni
Stanislavov univerzitet za rudarstvo i metalurgiju, Krakov, Poljska
Prof. dr Mevludin Avdić
RGGF-Univerzitet u Tuzli, BiH
Prof. dr Vladimir Bodarenko
Nacionalni rudarski univerzitet,
Odeljenje za podzemno rudarstvo, Ukrajina
Dr Mile Bugarin, naučni savetnik
Institut za rudarstvo i metalurgiju Bor
Prof. dr Ruža Čeliković
RGGF-Univerzitet u Tuzli, BiH
Dr Miroslav R. Ignjatović, viši naučni saradnik
Privredna komora Srbije
Prof. dr Vencislav Ivanov
Rudarski fakultet Univerziteta za rudarstvo i geologiju "St. Ivan Rilski" Sofija Bugarska
Prof. dr Jerzy Kicki
Državni institut za mineralne sirovine i energiju, Krakov, Poljska
Dr Dragan Komljenović
Istraživački institut Hidro-Quebec, Kanada
Dr Ana Kostov, naučni savetnik
Institut za rudarstvo i metalurgiju Bor
Prof. Dr Nikola Lilić
Rudarsko geološki fakultet Beograd
Dr Dragan Milanović, naučni saradnik
Institut za rudarstvo i metalurgiju Bor
Prof. dr Vitomir Milić
Tehnički fakultet Bor
Dr Aleksandra Milosavljević, naučni saradnik
Institut za rudarstvo i metalurgiju Bor
Dr Dragoslav Rakić, docent
Rudarsko geološki fakultet Beograd
Prof. dr Rodoljub Stanojlović
Tehnički fakultet Bor
Akademik Prof. dr Mladen Stjepanović
Inženjerska akademija Srbije
Dr Biserka Trumić, viši naučni saradnik
Institut za rudarstvo i metalurgiju Bor
Prof. dr Nebojša Vidanović
Rudarsko geološki fakultet Beograd
Prof. dr Milivoj Vulić
Univerzitet u Ljubljani, Slovenija
Prof. dr Nenad Vušović
Tehnički fakultet Bor

ČASOPIS MEĐUNARODNOG ZNAČAJA VERIFIKOVAN POSEBNOM ODLUKOM
MINISTARSTVA ZA PROSVETU, NAUKU I TEHNOLOŠKI RAZVOJ
REPUBLIKE SRBIJE - M24

CONTENS
SADRŽAJ

MINING AND METALLURGY INSTITUTE BOR
UDK: 622
ISSN: 2334-8836 (Štampano izdanje)
ISSN: 2406-1395 (Online)

UDK: 622.271:504.06(045)=111
doi:10.5937/MMEB1503001M

Miomir Mikić[*], *Daniel Kržanović*[*], *Milenko Jovanović*[*], *Miroslava Maksimović*[*]

REVIEW OF THE OPEN PIT SOUTH MINING DISTRICT - MAJDANPEK IMPACT ON THE ENVIRONMENT AND PROTECTIVE MESUARES[**]

Abstract

There are more than 50 years of the copper surface mining in Majdanpek, Serbia. During this period, the impact of mining activities on the environment was multifaceted: degradation of the land - mostly forestS, air pollution, water and soil and others. This paper presents measures to protect the environment from the impact of the open pit South Mining District and reclamation of tailings.

Keywords: *mining, degraded areas, environmental protection, reclamation*

INTRODUCTION

The negative impact of surface mining in addition to a temporary (or long term) occupation and changes in land use, where the deposit is situated, is reflected also on: - occupation of additional agricultural land that is used for disposal of waste (external landfill); - drainage of the open pits has the effect on the level and regime of groundwater regime; - protection of the open pits from surface water changes the water flows and affects the ability of irrigation the surrounding parcels; - dust and air pollution adversely affects the population and agricultural crops in the vicinity of the open pits; - excavation of mineral raw material changes the relief of land, affecting the climate and displacement the existing facilities or building the new infrastructure for exploitation the mineral raw materials, thereby also reducing the area of agricultural land; - impairment the aesthetic value of the environment and occurrence of noise due to the mechanization operation.

In addition to degradation and transformation of land surfaces to another “lower” shape, the open pits may also affect the pollution of land closer to or further away from the open pit with heavy metals from dust immission created during deposit mining or technological operations at the open pits.

The concept of pollution means the imission of pollutants (dust, gases) in the atmosphere of the open pits. The air pollutions, carried by the wind streams from the open pits, threaten the space in a direction even out of the open pits or the environment around them. Chemical pollutants that occur in the atmosphere of the open pits are formed as the result of technological processes in order to obtain the ore and in case of mass blasting, loading, transport, crushing and at the effect of natural factors - winds [1]. The matters in the form of gases and dust get into atmosphere of the environment from the open pits. The major air pollutants arising from the open pit mining operations include total suspended particulate (TSP) matter and particles with an equivalent aerodynamic diameter less than 10 microns (PM10) [2].

---

[*] *Mining and Metallurgy Institute Bor, Serbia*

[**] *This work is the result of the Project TR33023 “Development of Technologies for Flotation Processing the Copper Ore and Precious Metals to Achieve Better Technological Results” funded by the Ministry of Education, Science and Technological Development of the Republic of Serbia*

Air pollution in the area of the open pit mines depends on the extent of annual production and intensity of pollutant emission, terrain configuration around the open pit mines and climatic parameters [3]. In this case, the entire area of open pit mine is a source of environmental pollution. Outside the open pit mines, the dust is spread by wind, usually in a direction of dominant winds and the air pollution dispersion plume is formed. [3]. The highest air pollution from the open pits is on their edge while moving away from the edge of pits in direction of winds blowing; the air pollution is reduced or diluted (dispersion) [1]. This rule is applied to dust because gases are mainly diffused. Imission of dust in the environment of the open pits depends on the size of dust particles that are dispersed from the open pits by the wind currents. The largest particles (greater than 10 mm) begin to deposit near the edges of the open pits, while the finer particles smaller than 10 mm (PM10, PM2.5) are transported by the wind energy in a direction of its blowing and deposited away from the edge. The finest particles, dispersed by the wind currents from the open pits are not deposited, but remain flying in the air.

The open pits are a line source of dust for immediate surroundings. Removal of dust from the open pits depends on natural ventilation scheme that can be: flow, recirculation, convective and inverse. The TSP and PM10 levels in the open pit mining regions reduce the air quality and can cause silicosis, black lung (CWP), and increased mortality. They also reduce the visibility and affect surrounding flora and fauna [4]. Particles in the air are also known to play a critical role on climate [5], human health [6] and multi-phase atmospheric processes [8,9].

Due to the complexity of mining activities on the floors of the open pit South Mining District and large amounts of water on the bottom of the open pit and specificity of the flotation tailing dump facilities and unpredictability of the exact time and place of possible emergence of an accident and size of accidents, it is necessary to formulate the protective measures of working and living environment in the expansion of the open pit South Mining District [7].

1 SITE OF THE OPEN PIT SOUTH MINING DISTRICT MAJDANPEK

Majdanpek is located Eastern Serbia, near the town of Bor. North of Majdanpek is the Danube river which also represents the border between Serbia and Romania (Figure 1).

The open pit South Mining District is located on the south side of Majdanpek in Serbia and it is surrounded on all sides by hills and high waste dumps (overburden), Figure 2.

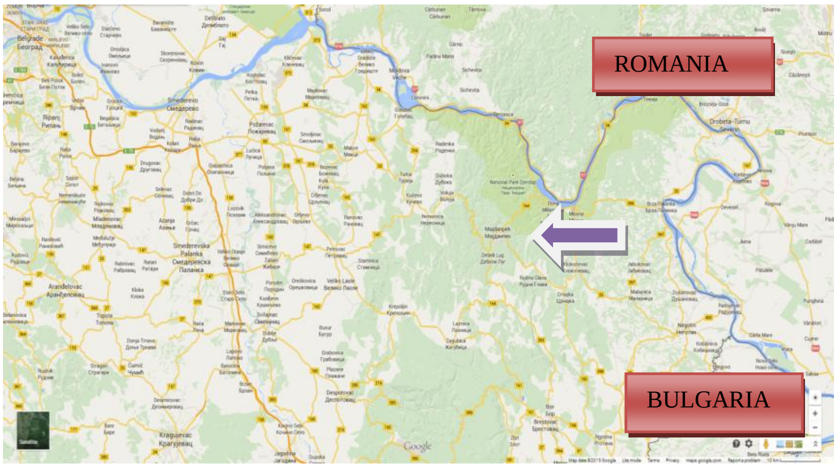


Figure 1 *Majdanpek with surroundings*

The only opening of the open pit is to the north or the town, Figure 1. All procedures at the open pit South Mining District are aimed to obtain copper ore by drilling and blasting operations and heavy loading and transport machines capable of contributing to the overall quality of the atmosphere at the open pit and beyond it.

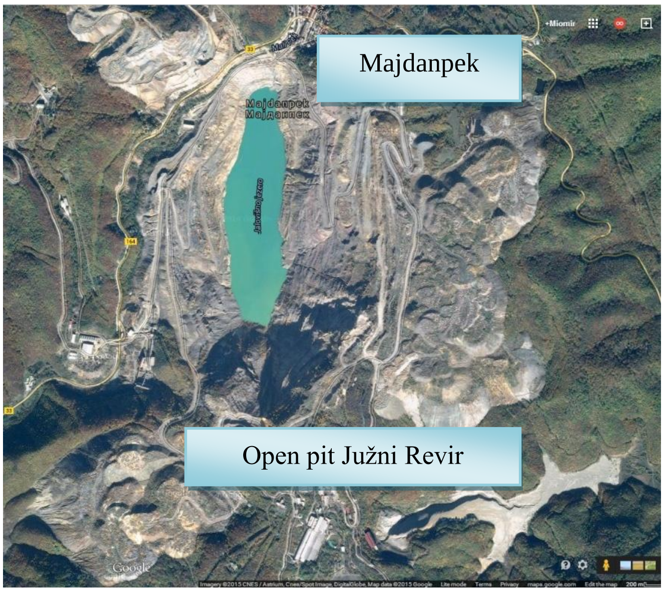


Figure 2 *Open pit South Mining District - Majdanpek*

Longer axis of the open pit is approximately 2,450m, while shorter axis is 1,600 m. The highest point of the open pit is approximately at the level of +588 m. The lowest point at the open pit is at 120.4 m. Height of floor is 15 m. This presents a potential threat to the environment because it can cause large-scale landslides at the open pit and endangering the regional asphalt road, the river bed of Mali Pek River and occurrence of cracks in buildings in the lower part of the town and endangering the occupants.

2 DATA ON EMISSION SOURCES OF POLLUTANTS

Expanding the open pit and operation of mining machinery create dust, which, due to the terrain configuration around the open pit, is dispersed by wind currents in the urban area.

Dust and gases are emitted by the mining equipment operation at the open pit dust and atmosphere of the open pit is polluted. In addition to the technological processes, the atmosphere quality at the open pit area is affected by natural factors - winds. All of pollution occurring at the open pit is dispersed by natural ventilation schemes and concentrated in the town. The air flow at the open pit occurs as the result of action the solar energy (insolation) and winds. The most common schemes of natural air movement at the open pit are: inverse and convective. The main sources of gas and dust emissions are machines that operate on technological phases of copper ore obtaining at the open pit South Mining District.

According to the previous measurements at the copper open pits in RTB Bor, the possible emission of dust were forecastted in copper ore obtaining per machine and they are shown in Table 1.

Table1 *Forecasted dust emissions at the open pit South Mining District*

Ord. No.	**Type of equipment**	**Concentration (mg/m^3)**	
	Period	**In summer**	**In winter**
1	Truck	3.77	1.05
2	Excavator	3.92	3.14
3	Drill	5.51	4.61
4	Loader	3.40	2.27
5	Bulldozer	8.66	3.10
6	Grader	7.20	2.10

Based on the number of machines in operation and known power of mobile machines that will work at the open pit as well as the composition of outlet gases from engines, the forecast emissions of exhaust gases that occur at the open pit by operation of mobile equipment is given in Table 2.

Table 2 *Forecasted gas emissions per one machine*

Type of equipment	**Engine power**	**Amount of exhaust gases**	**Total gas emissions (m^3/s) at their content in exhaust gas**				
	kW	**m^3/s**	**CO_2 =10%**	**CO =0.12**	**NO_4 =0.04**	**SO_2 =0.04**	**Aldehydes 0.002**
Truck KOMATSU HD785-7	875	0.6125	0.0611	0.00003	0.000245	0.000245	0.000001
Loader L-950	783	0.548	0.055	0.000657	0.0002192	0.0002192	0.000010
Bulldozer D8T	231	0.1615	0.016	0.00019	0.0000646	0.0000646	0.00000032
Grader	208	0.145	0.015	0.000174	0.000058	0.000058	0.0000029
Tank truck	450	0.315	0.032	0.000378	0.000126	0.000126	0.0000063

For combustion of 1 kg of oil, the amount of gas that is released during operation of internal combustion engines is between 13 and 15 m^3/kg. Concentration of gases at the open pit depends on the ratio of combustible components in the fuel, such as: carbon, hydrogen and sulfur as well as the proper chemical relations fuel-air. At the open pits in Majdanpek, the fuel D_2 is used where sulfur is from one weight percent, and it is 500 ppm of SO_2. The required amount of air for dilution the harmful components in exhaust gases of internal combustion engines depends on concentration of these components.

In liquid fuel D_2, the dominant factor which defines the required air amount for dispersion of gases from atmosphere of the open pit is taken as SO_2 due to its MDK value that is equal to 4 ppm. For dilution 1.0 m^3 SO_2 in the atmosphere of the open pits, 125 m^3 of air is required to reduce the harmful concentration in the air to MDK value.

3 MEANS AND METHODS FOR REDUCING THE ENVIRONMENTAL IMPACT

To protect the atmosphere in the mine and the town, it is needed to undertake the proposed complex measures of protection at the open pit.

Protective measures for drilling the boreholes

Protection measures to be taken at the open pit for air protection from dust and gases in drilling and blasting are the following:

- Dry and wet dedusting of boreholes,
- The explosive must have a positive oxygen balance which ensures a complete detonation,
- The stability conditions of explosives at least 3 months,
- Good homogenization of the components in the preparation of explosives,
- Organized and systematic testing of toxic gas in the laboratory conditions,
- Elimination of the paper - paraffin tread cartridge explosives and its replacement with shells that are suitable in terms of the balance of oxygen,
- Proper storage of explosives according to the instructions of the manufacturer and the use of the prescribed period,
- Setting the firing of the cartridge at the bottom of the borehole (increased efficiency of blasting, and small quantities of gases),
- The application of water stoppers made of plastic for clogging the boreholes during blasting or water balloons over the boreholes (volume of 50 l with a primer explosive 50 g/barrel),

Protective measures on loading

- Spraying of blasted material with water before loading by road tankers with installation and device for spraying (water displaces CO from cavities and associated nitrogen oxi-des).

Protective measures on transport

- Necessarily sprinkling (spraying) of transport routes during the dry season by road tankers with installation and device for spraying; 0.5 to 2.0 l/s is needed for 1.0 km of road.
- The use of diesel fuel of the constant elemental composition,
- Replacement of truck transport with the belt conveyor system.

Protective measures on disposal

- Spraying of level plateaus on the waste rock landfill
- Reclamation of the waste rock landfills according to the Project of remediation

3.1 Protective measures of the town on the dust from the open pit

The adequate protective measure is obtained by placing the PVC piping around the edges of the open pit toward the town with a device for creating a water curtain to overthrow dust. The pipeline can be connected to the system for dewatering from the open pit South Mining District.

The other measures include: the introduction of additional organizational-techni-cal measures and strict application of the machine manufacturer's instructions for efficient suppression of gas and dust in the operation of production machines at the open pit.

4 RECLAMATION OF DEGRADED AREAS OF THE WASTE ROCK LANDFILL OF THE OPEN PIT SOUTH MINING DISTRICT

In expanding the open pit South Mining District in stages from 1 to 6, the waste rock is excavated and formed four landfill sites, out of which three with finite boundaries and one with a space for storage under the new future projects. (Figure 3).

On the eastern side of the open pit is formed the landfill Kovej. On the western side of the open pit were formed the landfills Andesite Finger and Bugarski Stream. The disposal Ujevac is formed away from the open pits South and North Mining District and transport of waste rock is done by the belt conveyor system that can hold the waste rock from both open pits in Majdanpek and until now there are no final borders and it is not considered for reclamation.

The waste rock landfills are formed on already degraded areas and in the industrial zone. Due to the savings on transport costs, the waste rock is deposited from the final level to form the high slope inclinations of 31°.

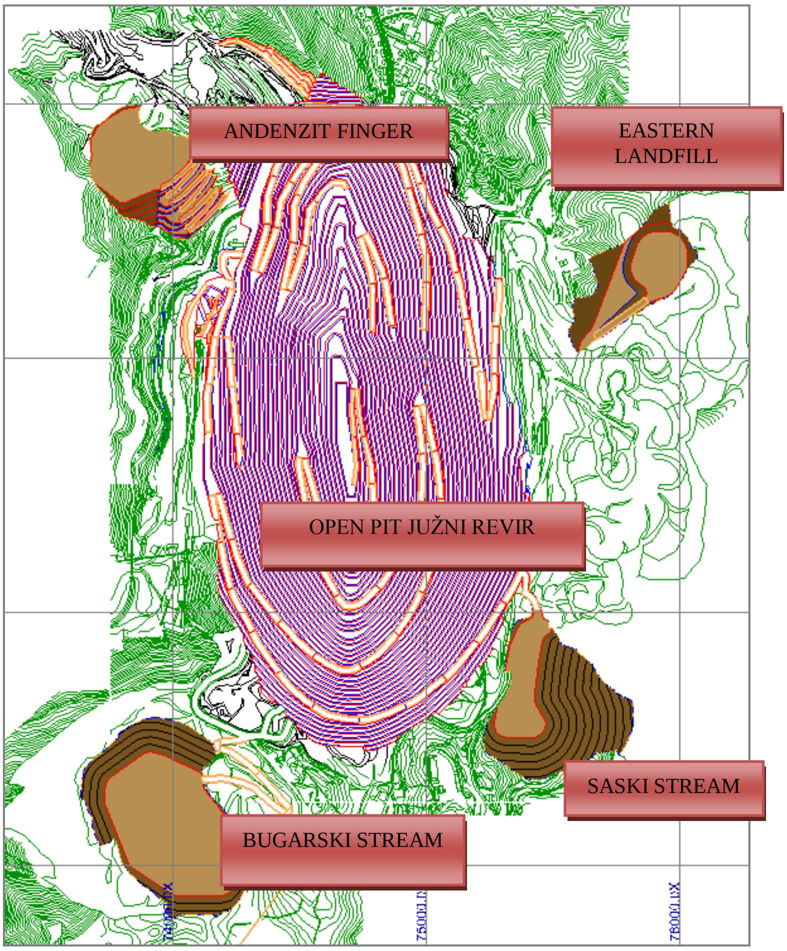


Figure 3 *2D view of the final condition of the open pit and landfill*

Remediation of degraded areas on the waste rock landfills Andesite Finger, Kovej, Bugarski Stream and Deponija includes the works aimed to the remediation of land. Since the soil of degraded areas does not contain enough nutrients for normal development of plants, the optimal form should be used with stages of agro-technical, technical and biological reclamation to the aim of remediation.

4.1 Data on structure and purpose of the land use

According to the physical and chemical properties of soil, geomorphology of the waste rock landfill, the exposure of areas to the south, climate and natural vegetation in the region, the optimal biological stage of remediation should be considered, including:

- Final planes of the waste rock landfills - afforestation,
- Final slopes of the waste rock landfills - afforestation.

Total degraded areas on the waste rock landfills of the open pit South Mining District South for remediation by locations are shown in Table 3.

Table 3 *Total degraded areas for reclamation*

Landfills	Level, m altitude	Flat surfaces, m^2	Level, m altitude	Inclined surfaces, m^2	Total surface, m^2
Andesite Finger (AP)	500	106 049	500/425	11 340	117 389
Kovej	596	48 659	596/575	15 033	63 692
Bugarski Stream	595	220 710	595/550	147 563	368 273
Landfill	580	64 564	580/415	173 332	237 896

4.2 Data on the selection of culture for remediation

Distribution of species on the surfaces of landfills during afforestation is given in Table 4 and it was carried out on the basis of micro-cellular conditions and research conducted in the period from 1988 to 1989 in Majdanpek at the landfill AP by the Institute of Forestry, Belgrade, Technical Faculty Bor and Copper Institute Bor and on the basis of the results obtained on remediation in Veliki Krivelj and Cerovo.

Table 4 *Structure of species by surfaces*

Waste dump	Surface structure	Structure of species	Surface, m^2
Andesite Finger(AP)	Final slope	Black pine	106 049.00
	Final slope	Birch + cilia	11 340.00
Kovej	Final slope	Red oak	48 659.00
	Final slope	Acacia	15 033.00
Bugarski Stream	Final slope	Brest	318 730.00
	Final slope	Acacia	203 240.00
Landfill	Final slope	Birch + cilia	64 564.00
	Final slope	Acacia	173 332.00

5 DESCRIPTION OF REMEDIATION METHODS OF DEGRADED AREAS

The aim of the revitalization of degraded areas at the waste rock landfills in Majdanpek is the protection of the environment. Degraded areas belong to the class of technogenic soil with insufficient proportion of nutrients making it necessary to apply the optimal re-cultivation of the stages of agro-technical, technical and biological reclamation [7].

1 **Stage of optimal agrotechnical remediation** represents the stage in which a series of measures are conducted aimed at establishing the productivity of the artificial creations - antroposalts. In the case of degraded areas in Majdanpek, it involves rehabilitation the existing access roads and subsequent planning area

on the final level (at the final disposal process to prevent the formation of lakes on flat surfaces to leave the vicious circle of waste piles).

2 **Technical stage of optimum remediation** includes: excavation, loading, transport and unloading of humus.

3 **Biological stage of optimum remediation** involves a complex of biotechnical and phytomeliorative measures for growing the forest plantations on waste rock landfills for the purpose of restoring the ecosystem.

5.1 Total costs of remediation

Total costs of remediation include the following costs of: agrotechnical phase (135,900 €), technical phase (11,291 €), biological phase (409,505 €), care and protection (87,447 €), unplanned costs (16,000 €). Total cost of remediation amounts to 660,143 €.

CONCLUSION

The Copper Mine Majdanpek is an important part of the system of Mining and Smelting Basin Bor. The extension of the open pits South Mining District and North Mining District in Majdanpek with the application of complex protective measures provides continuity in the production of copper ore which gives a **positive impact** on the social structure (national and ethnic) of population in terms of creation the new jobs and staying young to work and live in Majdanpek as well as the revival of villages in the surrounding municipalities.

An optimal form of remediation the degraded areas combined with auto rehabilitation and semi-remediation is a permanent solution for preservation the environment of the town of Majdanpek, provides better microclimate conditions as well as better appearance of the surroundings.

REFERENCES

[1] M. Mikić, D. Kržanović, M. Jovanović, Suppression of Creating and Raising the Dust with Dumper Transportation of Excavation at the Open Pits, Innovation and Development, 1/2009, 3-14;

[2] Sinha S., Banerjee S., Characterization of Haul Road Dust in an Indian Opencast Iron Mine, Atmos Environ 1997;31:2809–14;

[3] T. Apostolovski Trujić, M. Mikić, V. Tasić, Air Quality Control in the Area of Environmental Influence, The 46th International October Conference on Mining and Metallurgy - Proceedings, Serbia, 2014, 545-549;

[4] Wheeler AJ, Williams I, Beaumont RA, Manilton RS. Characterization of Particulate Matter Sampled During a study of Children's Personal Exposure to Airborne Particulate Matter in a UK Urban Environment, Environ Monit Assess 2000;65:69–77;

[5] Zhang R, Li G, Fan J, Wu D, Molina M., Intensification of Pacific Storm Track Linked to Asian Pollution, Proc Natl Acad Sci USA 2007;104:5295–9;

[6] Davidson C., Phalen R., Solomon P., Airborne Particle Matter and Human Health: A Review, Aerosol Sci Technol 2005;39:737–49;

[7] M. Mikić, R. Rajković, D. Kržanović, Recultivation of Degraded Area at the Open Pit South Mining District in Majdanpek, Mining 2012, OP Serbia, 491-499.

[8] Tie X., Madronich S., Walters S., Zhang R., Rasch P., Collins W., Effect of Clouds on Photolysis and Oxidants in the Troposphere, J. Geophys. Res 2003;108:4642–64;

[9] M. Mikić, D. Kržanović, R. Rajković, Effect of Exploitation at Social Community, and Other Public Facilities in Zone of the Open Pit South Mining District in Majdanpek, Mining 2012, Chamber of Commerce of Serbia, 397-402;

[10] M. Mikić, R. Rajković, D. Kržanović. Recultivation of degraded area at open pit Južni revir in Majdanpek, Mining 2012, Chamber of Commerce of Serbia, 491-499.

INSTITUT ZA RUDARSTVO I METALURGIJU BOR
UDK: 622

ISSN: 2334-8836 (Štampano izdanje)
ISSN: 2406-1395 (Online)

UDK: 622.271:504.06(045)=163.41

doi:10.5937/MMEB1503001M

Miomir Mikić[*], *Daniel Kržanović*[*], *Milenko Jovanović*[*], *Miroslava Maksimović*[*]

PRIKAZ UTICAJA POVRŠINSKOG KOPA JUŽNI REVIR - MAJDANPEK NA ŽIVOTNU SREDINU I ZAŠTITNIH MERA[**]

Izvod

Više od 50 godina se obavlja površinska eksploatacija bakra u Majdanpeku, u Srbiji. Tokom ovog perioda, uticaj rudarskih aktivnosti na životnu sredinu je bio višestruki: degradacija zemljišta-uglavnom šume, zagađenja vazduha, vode i zemljišta i dr. Ovaj rad predstavlja mere za zaštitu životne sredine od uticaja površinskog kopa Južni Revir i rekultivaciju jalovišta.

Ključne reči: *rudarstvo, degradirane površine, rekultivacija, zaštitne mere*

UVOD

Negativan uticaj površinske eksploatacije, pored privremenog (ali dugotrajnijeg) zauzimanja i izmene namene zemljišta, gde se nalazi ležište, odražava se još i na: – zauzimanje dodatnog poljoprivrednog zemljišta koje se angažuje za smeštaj jalovine (spoljašnje odlagalište); – odvodnjavanjem površinskih kopova vrši se uticaj na nivo i režim podzemnih voda; – zaštitom površinskih kopova od površinskih voda menjaju se vodni tokovi i utiče na mogućnost navodnjavanja okolnih parcela; – zagađenje vazduha prašinom utiče negativno na stanovništvo i poljoprivredne kulture u blizini kopova; – otkopavanjem mineralne sirovine menja se reljef zemljišta, utiče na klimu, izmeštaju se postojeći objekti infrastrukture ili grade novi koji služe eksploataciji mineralne sirovine ili objektima pripreme, čime se takođe smanjuju površine poljoprivrednog zemljišta; – narušavaju se estetske vrednosti okoline i dolazi pojave buke usled rada mehanizacije.

Pored degradiranja i transformisanja zemljišnih površina u drugi „niži'' oblik, površinski kopovi mogu da utiču i na zagađivanje zemljišta bliže ili dalje od kopa teškim metalima iz imisijom prašine koja nastaje pri eksploataciji ležišta, odnosno tehnološkim operacijama na kopovima. Površinski kopovi ruda metala su značajni zagađivači atmisfere.

Pod pojmom zagađenja podrazumeva se emisija zagađujućih materija (prašine, gasova) u atmosferu površinskih kopova. Nošena vetrenim strujama iz kopova, aerozagađenja ugrožavaju prostor na pravcu vetrova i izvan kopova, odnosno životnu okolinu oko njih. Hemijski štetne materije koje se javljaju u atmosferi površinskih kopova nastaju kao posledica tehnoloških procesa u cilju dobijanja rude i to pri masovnom miniranju, utovaru, transportu, drobljenju i pri dejstvu prirodnih faktora-vetrova [1]. U atmosferu životne okoline iz površinskih kopova dospevaju materije u vidu gasova i prašine. Glavni zagađivači

---

[*] *Institut za rudarstvo i metalurgiju Bor*

[**] *Ovaj rad je proistekao kao rezultat projekta TR33023 "Razvoj tehnologija flotacijske prerade ruda bakra i plemenitih metala radi postizanja boljih tehnoloških rezultata" finansiranog od strane Ministarstva prosvete, nauke i tehnološkog razvoja Republike Srbije*

vazduha koje proističu iz površinskih rudarskih radova obuhvataju ukupne suspendovane čestice (USČ) i materije sa ekvivalentnim aerodinamičkim prečnikom manjim od 10 µm (PM10) [2].

Zagađenje vazduha u oblasti površinskih kopova zavisi od stepena godišnje proizvodnje i intenziteta emisije zagađujućih materija, konfiguracije terena oko površinskim kopova i klimatskih parametara [3]. U tom slučaju, cela oblast površinskog kopa je izvor zagađenja životne sredine. Izvan površinskih kopova, prašina se širi vetrom, obično u pravcu dominantnih vetrova i formira se oblak disperzije zagađenja vazduha [3].

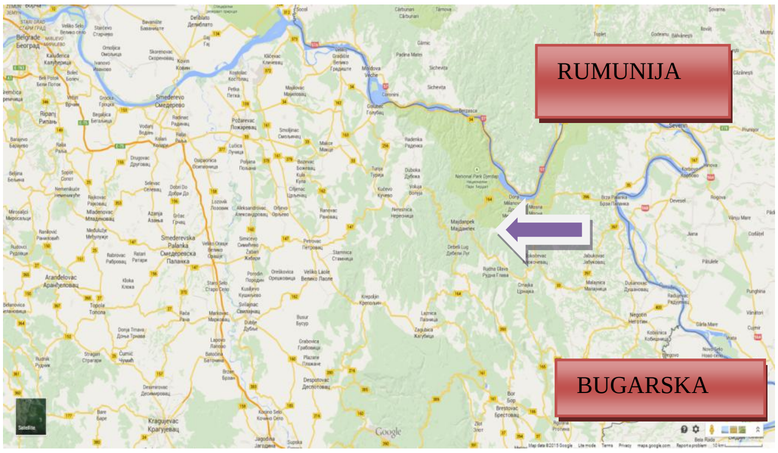
Najveće aerozagađenje koje se iznosi iz kopova je na njihovoj ivici dok se sa udaljavanjem od ivice kopova u smeru duvanja vetrova aerozagađenje smanjuje, odnosno razređuje (dekoncentriše) [1]. Ovo pravilo važi za prašinu jer gasovi, uglavnom, difuzuju. Imisija prašine u životnoj okolini kopova zavisi od veličine čestica prašine koje se vetrenim strujama iznose iz kopova. Najkrupnije čestice (veće od 10 mm) počinju da se talože u neposrednoj blizini ivice kopova, dok se sitnije čestice manje od 10 mm (PM10, PM2,5) energijom vetra u pravcu njegovog duvanja transportuju i talože dalje od ivice. Najsitnije čestice prašine iznete vetrenim strujama iz kopova se ne talože, već ostaju da lebde u vazduhu. Površinski kopovi za bližu okolinu predstavljaju linijski izvor prašine. Iznošenje prašine iz kopova zavisi od prirodnih šema provetravanja koje mogu biti: protočne, recilkulacione, konvektivne i inverzne. Nivoi USČ i PM10 u regionima površinskih rudarskih radova smanjuju kvalitet vazduha i mogu izazvati silikozu, crna pluća (CWP), kao i povećanu smrtnost. Oni takođe smanjuju vidljivost i utiću na okolnu floru i faunu [4]. Čestica u vazduhu su takođe poznato imaju ključnu ulogu delovanja na klimu [5], ljudsko zdravlje [6] i multi-fazne atmosferske procese [8,9].

Zbog složenosti izvođenja rudarskih radova na etažama površinskog kopa Južni revir i velike količine vode na dnu površinskog kopa i specifičnosti objekata flotacijskih jalovišta i nepredvidivosti tačnog vremena i mesta mogućeg nastajanja udesa i veličine havarija, neophodno je predvideti mere zaštite radne i životne sredine pri proširenju površinskog kopa Južni revir [10].

1. LOKALITET POVRŠINSKOG KOPA JUŽNI REVIR MAJDANPEK

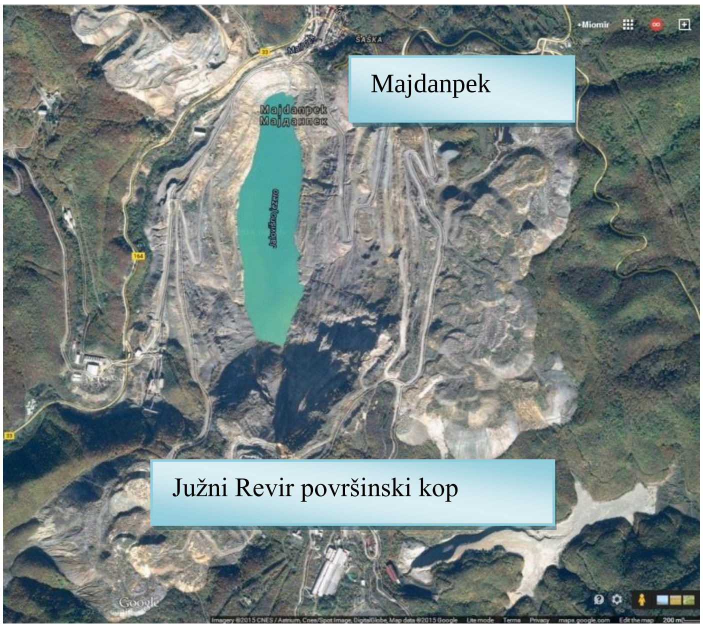
Majdanpek se nalazi u Istočnoj Srbiji, u blizini grada Bor. Severno od Majdanpeka se nalazi reka Dunav koja ujedno predstavlja i granicu Srbije i Rumunije (slika 1).

Površinski kop Južni revir nalazi se na južnoj strani Majdanpeka u Srbiji i okružen je sa svih strana brdima i visokim odlagalištima jalovine (raskrivke), slika 2.



Sl. 1. *Majdanpek sa okolinom*

Jedini otvor površinskog kopa je prema severu, odnosno gradu., slika 1. Svi postupci u površinskom kopu Južni revir usmereni na dobijanju rude bakra uz pomoć bušačko minerskih radova i snažnih utovarno transportnih mašina doprinose ukupnom stanju kvaliteta atmosfere u kopu i van njega.



Sl. 2. *Površinski kop Južni Revir - Majdanpek*

Duža osa površinskog kopa iznosi približno 2.450 m, dok kraća osa iznosi 1 600 m. Najviša tačka kopa je približno na nivou +588 m. Najniža tačka na kopu je na 120,4 m. Visina etaža je bila 15 m. To predstavlja potencijalnu opasnost po životnu sredinu, jer može doći do pojave klizišta većih razmera u kopu i ugrožavanja regionalnog asfaltnog puta, korita reke Mali Pek i pojave pukotine na zgradama u donjem delu grada i ugrožavanja stanara.

2. PODACI O IZVORIMA EMISIJE ŠTETNIH MATERIJA

Proširivanjem površinskog kopa i radom rudarskih mašina stvara se prašina koja se, usled konfiguracije terena oko kopa, vetrenim strujama iznosi u gradsku sredinu.

Radom rudarske opreme u kopu emituje se prašina i gasovi i zagađuje se atmosfera kopa. Pored tehnoloških procesa na kvalitet atmosfere u prostoru kopa utiču i prirodni faktori - vetrovi. Sva zagađenja koja nastaju u površinskom kopu se prirodnim šemama provetravanja iznose i koncentrišu u grad. Strujanje vazduha na kopu javlja se kao posledica delovanja sunčeve energije (insolacije) i vetrova. Najčešće šeme prirodnog kretanja vazduha na kopu su: inverzna i konvektivna. Glavni izvori emisije gasova i prašine su mašine koje rade na tehnološkim fazama dobijanja rude bakra u površinskom kopu Južni revir.

Prema ranijim merenjima na površinskim kopovima bakra u RTB-u Bor, prognozirane su moguće emisije prašine pri dobijanju rude bakra po mašini i prikazane su u tabeli 1.

Tabela 1. *Prognozirana emisija prašine na površinskom kopu Južni revir*

Red broj	Vrsta opreme	Koncentracija (mg/m^3)	
	Period	**Leti**	**Zimi**
1	Kamion	3,77	1,05
2	Bager	3,92	3,14
3	Bušilica	5,51	4,61
4	Utovarivač	3,40	2,27
5	Buldozer	8,66	3,10
6	Grejder	7,20	2,10

Na osnovu broja mašina u radu i poznatih snaga motora mobilnih mašina koje će raditi na kopu kao i na osnovu sastava izlaznih gasova iz motora, prognoza emisije izduvnih gasova koji nastaju u kopu radom mobilne opreme data je u tabeli 2.

Tabela 2. *Prognoza emisije gasova po jednoj mašini*

Vrsta opreme	Snaga motora	Količina izduvnih gasova	Ukupne emisije gasova (m^3/s) pri njihovom sadržaju u izduvnom gasu				
	kW	m^3/s	CO_2 =10%	CO =0,12	NO_4 =0,04	SO_2 =0,04	Aldehidi 0,002
Kamion KOMATSU HD785-7	875	0,6125	0,0611	0,00003	0,000245	0,000245	0,000001
Utovarivač L-950	783	0,548	0,055	0,000657	0,0002192	0,0002192	0,000010
Buldozer D8T	231	0,1615	0,016	0,00019	0,0000646	0,0000646	0,00000032
Gejder	208	0,145	0,015	0,000174	0,000058	0,000058	0,0000029
Autocisterna	450	0,315	0,032	0,000378	0,000126	0,000126	0,0000063

Za sagorevanje 1 kg nafte, količina gasova koja se oslobađa pri radu motora sa unutrašnjim sagorevanjem se kreće između 13 i 15 m^3/kg. Koncentracija gasova u kopu zavisi od odnosa sagorljivih komponenti u gorivu, a to su: ugljenik, vodonik i sumpor kao i od hemijskog ispravnog odnosa gorivo-vazduh. Na površinskim kopovima u Majdanpeku koristi se gorivo D_2 kod koga se sumpor kreće do jednog težinskog procenta, a to je 500 ppm SO_2. Potrebna količina vazduha za razređenje škodljivih komponenti u izduvnim gasovima motora sa unutrašnjim sagorevanjem zavisi od koncentracije tih komponenti.

Kod tečnog goriva D_2, dominantni faktor kojim se definiše potrebna količina vazduha za dekoncentraciju gasova iz atmosfere kopa uzima se SO_2 jer je njegova MDK vrednoost jednaka 4 ppm. Za razređenje 1,0 m^3 SO_2 u atmosferi kopa potrebno je 125 m^3 vazduha da bi se štetna koncentracija u vazduhu kopa svela na MDK vrednost.

3. SREDSTVIMA I METODE ZA SMANJENJE UTICAJA NA ŽIVOTNU SREDINU

Da bi se zaštitila atmosfera u kopu i gradu potrebno je na kopu preduzeti predložene kompleksne mere zaštite.

Zaštitne mere za bušenja bušotina

Mere zaštite koje treba preduzeti na površinskom kopu za zaštitu vazduha od prašine i gasova pri bušenju i miniranju:

- Mere zaštite na **bušenju** minskih bušotina:
- Suvo i mokro otprašivanje bušotina,
- Eksploziv mora imati pozitivan kiseonički bilans koji osigurava potpunu detonaciju,
- Uslove stabilnosti eksploziva najmanje 3 meseca,
- Dobra homogenizacija komponenti pri izradi eksploziva
- Organizovano i sistematsko ispitivanje stvaranja otrovnih gasova u laboratorijskim uslovima
- Eliminisanje papirno – parafinskog omotača patrona eksploziva i njegova zamena omotačima koji su pogodniji u pogledu bilansa kiseonika.
- Pravilno skladištenje eksploziva prema upustvu proizvođača i upotreba u predviđenom roku trajanja
- Eksplozivi kojima je prošao rok upotrebe vratiti proizvođaču
- Postavljanje udarne patrone na dnu bušotine (povečana efikasnost miniranja, a manja količina gasova)
- Primena vodenih čepova od plastične mase za začepljenje bušotina pri miniranju ili vodenih balona iznad minskih bušotina (zapremine 50 l sa kapislom eksploziva 50 gr/buretu)
- Dovoz eksploziva na radilište vrši proizvođač,

Mere zaštite na utovaru

- Orošavanje izminiranog materijala vodom pre utovara pomoću autocisterne sa instalacijom i uređajem za orošavanje (voda istiskuje CO iz šupljina i vezuje okside azote).

Mere zaštite na transportu

- Obavezno polivanje (orošavanje) transportnih puteva u toku sušnog perioda autocisternom sa instalacijom i uređajem za orošavanje, za 1,0 km puta potrebno je 0,5 do 2,0 l/s
- Korišćenjem dizel goriva konstantnog elementarnog sastava,
- Zamena kamionskog transporta tračnim transportnim sistemom.

Mere zaštite na odlaganju

- Orošavanje etažnih platoa na odlagalištu jalovine,
- Rekultivacija odlagališta jalovine po Projektu rekultivacije

3.1. Mere zaštite grada od prašine sa kopa

Adekvatna mera zaštite se dobija postavljanjem cevovoda od PVC po ivici kopa prema gradu sa uređajem za stvaranje vodene zavese radi obaranja prašine. Cevovod može da bude povezan sa sistemom za odvodnjavanje površinskog kopa Južni revir.

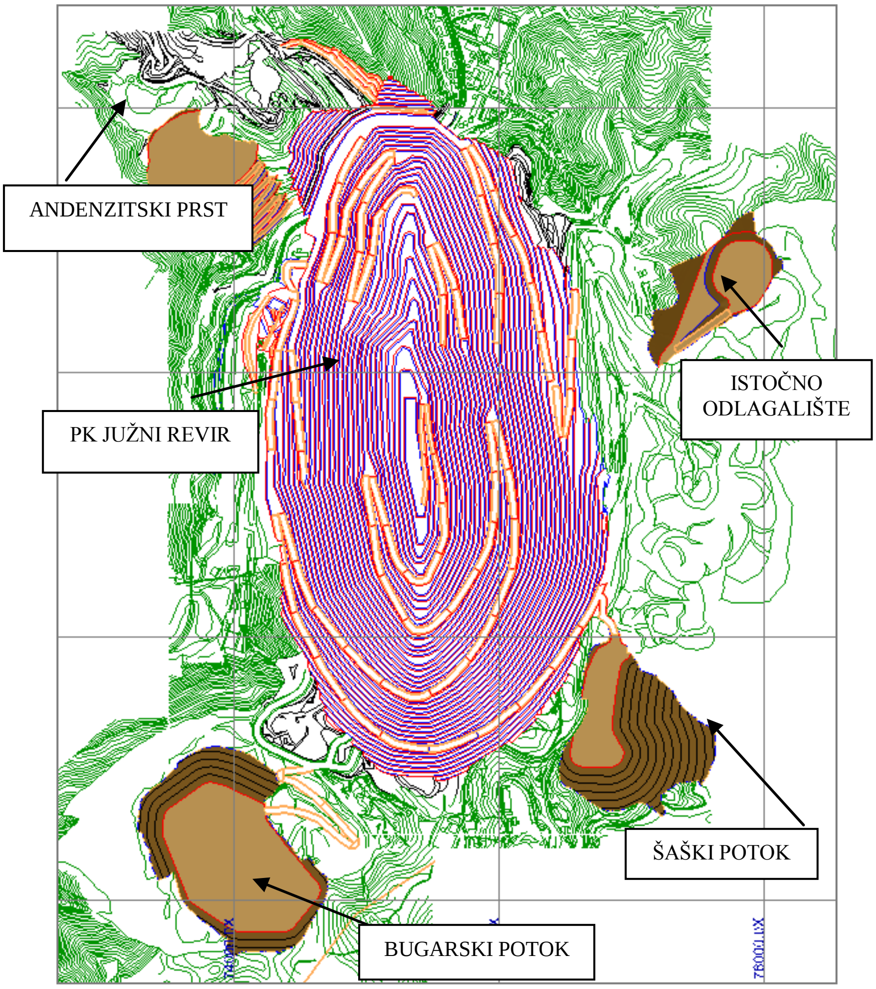
Druge mere su: uvođenje dodatnih organizaciono-tehničkih mera i striktna primena uputstva proizvođača mašina radi efikasnog suzbijanja gasova i prašine pri radu proizvodnih mašina u kopu.

4. REKULTIVACIJA DEGRADIRANIH POVRŠINA ODLAGALIŠTA JALOVINE PK JUŽNI REVIR

Pri proširivanju površinskog kopa Južni revir po fazama od 1 do 6, otkopava se jalovina i formiraju se četiri odlagališta od čega tri sa konačnim granicama i jedno na kome ima prostora za odlaganje po novim budućim projektima. (Sl. 3.)

Na istočnoj strani površinskog kopa formirano je odlagalište Kovej. Na zapadnoj strani površinskog kopa formirana su odlagališta Andezitski prst i Bugarski potok. Odlagalište Ujevac je formirano dalje od površinskoh kopova Južni i Severni revir i transport jalovine je tračnim transpotom i može da primi jalovinu sa oba površinskog kopa u Majdanpeku i za sada nema konačne granice i ne razmatra se za rekultivaciju.

Odlagališta jalovine se formiraju na već degradiranim površinama i u industrijskoj zoni. Zbog uštede na transportnim troškovima, jalovina se odlaže sa završne ravni pri čemu nastaju visoke kosine nagiba 31°.



Sl. 3. *2D prikaz završnog stanja površinskog kopa i odlagališta*

Rekultivacija degradiranih površina na odlagalištima jalovine Andezitski prst, Kovej, Bugarski potok i Deponija podrazumeva radove usmerenih na ponovnom kultivisanju površina. S obzirom da tlo degradiranih površina ne sadrže dovoljno hranljivih materija za normalan razvoj biljaka u cilju rekultivacije treba koristi optimalni vid sa fazama agrotehničke, tehničke i biološke rekultivacije.

4.1. Podaci o strukturi i nameni korišćenja zemljišta

Prema fizičko hemijskim osobinama tla, geomorfologiji odlagališta jalovine, eksponiranost površina jugu, klimatskim uslovima i prirodnoj vegetaciji u okruženju u obzir dolazi biološka faza optimalne rekultivacije i to na:

- Završnim ravnima odlagališta jalovine - pošumljavanje,
- Završnim kosinama odlagališta – pošumljavanje.

Ukupne degradirane površine na odlagalištima jalovine površinskog kopa Južni revir za rekultivaciju po lokacijama prikazane su u tabeli 3.

Tabela 3. *Ukupne degradirane površine za rekultivaciju*

Odlagališta	Kota, mnv	Ravne površine, m^2	Kota, mnv	Kose površine, m^2	Ukupne površine , m^2
Andezitski prst (AP)	500	106 049	500/425	11 340	117 389
Kovej	596	48 659	596/575	15 033	63 692
Bugarski potok	595	220 710	595/550	147 563	368 273
Deponija	580	64 564	580/415	173 332	237 896

4.2. Podaci o izboru kultura za rekultivaciju

Raspored vrsta po površinama odlagališta prilikom pošumljavanja dat je u tabeli 4 i vršen je na osnovu mikrostaničnih uslova i istraživanja koja su vršena u periodu od 1988-1989 godine u Majdanpeku na odlagalištu AP od strane Instituta za Šumarstvo Beograd, Tehničkog fakulteta Bor i Instituta za bakar u Boru i na osnovu rezultata postignutih na rekultivaciji u V. Krivelju i Cerovu.

Tabela 4. *Struktura vrsta po površinama*

Odlagališta jalovine	Struktura površina	Struktura vrsta	Površine, m^2
Andezitski prst (AP)	Završna ravan	Crni bor	106 049,00
	Završna kosina	Breza+trepetljika	11 340,00
Kovej	Završna ravan	Crveni hrast	48 659,00
	Završna kosina	Bagrem	15 033,00
Bugarski potok	Završna ravan	Brest	318 730,00
	Završna kosina	Bagrem	203 240,00
Deponija	Završna ravan	Breza+trepetljika	64 564,00
	Završna kosina	Bagrem	173 332,00

5. OPIS NAČINA REKULTIVACIJE DEGRADIRANIH POVRŠINA

Cilj revitalizacije degradiranih površina na odlagalištima jalovine u Majdanpeku jeste zaštita životne sredine. Degradirane površine pripadaju klasi tehnogenih zemljišta sa nedovoljnim udelom hranljivih materija zbog čega je potrebno primeniti optimalnu rekultivaciju sa fazama agrotehničke, tehničke i biološke rekultivacije [10].

1. **Faza agrotehnička optimalne rekultivacije** predstavlja etapu u kojoj se sprovodi niz mera usmerene na uspostavljanju produktivnosti na veštačkim tvorevinama – antroposolima. U slučaju degradiranih površina u Majdanpeku podrazumeva se osposobljavanje postojećih pristup-

nih puteva i naknadno planiranje površina na završnih ravni (pri završnom procesu odlaganja zbog sprečavanja stvaranja jezera na ravnim površinama se ostavljaju neisplanirane gomile jalovine).

2. **Tehnička faza optimalne rekultivacije** uključuje: otkopavanje, utovar, transport, i istovar humusa.
3. **Biološka faza optimalne rekultivacije** podrazumeva kompleks biotehničkih i fitomeliorativnih mera za uzgajanje šumskih kultura na odlagalištima jalovine u cilju obnavljanja ekosistema.

5.1. Ukupni troškovi rekultivacije

Ukupni troškovi rekultivacije obuhvataju sledeće troškove: agrotehničke faze (135.900 €), tehničke faze (11.291 €), biološke faze (409.505 €), nege i zaštite (87.447 €), neplanirane troškove (16.000 €). Ukupni troškovi rekultivacije iznose 660.143 €.

ZAKLJUČAK

Rudnik bakra Majdanpek predstavlja važan deo sistema Rudarsko topioničarskog basena Bor. Proširenje površinskog kopa Južni revir i Severni revir u Majdanpeku uz primenu kompleksnih mera zaštite omogućava kontinuitet u proizvodnji rude bakra što daje **pozitivan uticaj** na socijalnu strukturu (nacionalnu i etničku) stanovništva u smislu otvaranja novih radnih mesta i ostajanju mladih da rade i žive u Majdanpeku kao i oživljavanje sela u okolnim opštinama.

Optimalni vid rekultivacija degradiranih površina kombinovana sa autorekultivacijom i polurekultivacijom predstavlja trajno rešenje za očuvanje životne sredine grada Majdanpeka, omogućava bolje uslove mikroklime kao i bolji izgled okoline.

LITERATURA

[1] M. Mikić, D. Kržanović, M. Jovanović, Suzbijanje stvaranja i podizanja prašine na površinskim kopovima pri kamionskom transportu, Inovacije i razvoj, 1/2009, 3-14.

[2] Sinha S, Banerjee S, Characterization of haul road dust in an Indian opencast iron mine. Atmos Environ 1997; 31:2809–14.

[3] T. Apostolovski Trujić, M. Mikić, V. Tasić, Air quality control in the area of environmental influence, The 46th International October Conference on Mining and Metallurgy-Proceedings, Serbia, 2014, 545-549.

[4] Wheeler AJ, Williams I, Beaumont RA, Manilton RS. Characterization of particulate mattersampled during a study of children's personal exposure to airborne particulatematter in a UK urban environment. Environ Monit Assess 2000;65:69–77.

[5] Zhang R, Li G, Fan J, Wu D, Molina M. Intensification of pacific storm track linked to Asian pollution. Proc Natl Acad Sci USA 2007;104:5295–9.

[6] Davidson C, Phalen R, Solomon P. Airborne particle matter and human health: A review.Aerosol Sci Technol 2005;39:737–49.

[7] Molina M, Molina L, Zhang R, Meads R, Spencer D. The reaction of $ClONO_2$ with HCl on aluminum oxide. Geophys Res Lett 1997;24(13):1619–22.

[8] Tie X, Madronich S, Walters S, Zhang R, Rasch P, Collins W. Effect of clouds on photolysis and oxidants in the troposphere. J Geophys Res 2003;108:4642–64.

[9] M. Mikić, D. Kržanović, R. Rajković. Effect of exploitation at social community, and other public facilities in zone of Open pit Južni Revir in Majdanpek, Mining 2012, Privredna Komora Srbije, 397-402.

[10] M. Mikić, R. Rajković, D. Kržanović. Recultivation of degraded area at Open pit južni revir in Majdanpek, Mining 2012, Privredna Komora Srbije, 491-499.

MINING AND METALLURGY INSTITUTE BOR
UDK: 622

ISSN: 2334-8836 (Štampano izdanje)
ISSN: 2406-1395 (Online)

UDK: 622.271:627.51(045)=111

doi:10.5937/MMEB1503017R

Radmilo Rajković[*], *Saša Stepanović*[*], *Daniel Kržanović*[*], *Miomir Mikić*[*]

DEFENCE SYSTEM FROM WATER OF THE OPEN PIT GRAČANICA – GACKO[**]

Abstract

The open pit Gračanica - Gacko has very complex conditions of watering with occurrences of significant inflow of water as the result of short-term precipitation of high-intensity. This paper presents a review of the influential parameters on size of watering and review a defense system of the open pit from water.

Keywords: *open pit Gračanica - Gacko, influential factors of watering, defense system from water*

INTRODUCTION

Selection of technical - technological solution for defense the open pit Gračanica with a part of the Field C and roof zone from surface and groundwater depends on the natural and technical - technological factors. The natural factors important in terms of drainage include the morphological features of the terrain, hydrographic features of the terrain, climatic characteristics of the area, hydrological characteristics of the area and hydrological characteristics of the terrain. The technical - technological factors include the available complex of equipment and general conditions of exploitation [1].

The concept of defence from water must provide a reliable protection of mining facilities in compliance with the legislation for this area, with maximum use of the existing equipment at the open pit [4, 5, 6, 7].

INFLUENTIAL FACTORS

The Gatačko field represents the intermountain depression filled with the Neogene sediments formed in the phase of terrain relaxation upon cessation of directed tectonic pressures (Oligocene - Miocene). Now, it represents, for the most part, the alluvial surface of very slight decline from entering the river Mušnica in the field east of Avtovac to the mouth of the Gojkovića stream in Mušnica in the west.

Right tributaries of Mušnica, Gračanica i Gojkovića stream, with tributaries the Rajića stream Trnovac, flow as well as Mušnica from north to south to entering the field, cutting off diagonally prominently expressed decametric calcarenite packages in the Upper Cretaceous, mainly calcareous flysch. Tributaries of these three flows usually have orientation the northwest - southeast, parallel with calcarenite packages carved in softer marls or major and minor water flows form a rectangular hydrographic network conditioned by lithology of flyzsch formation in the northeast of the formacije severoistočno of Gatačko field.

---

[*] *Mining and Metallurgy Institute Bor, radmilo.rajkovic@irmbor.co.rs*

[**] *This work is the result of the Project TR37001 "The Impact of Mining Waste from RTB Bor on the Pollution of Surrounding Water Systems with the Proposal of Measures and Procedures for Reduction Harmful Effects on the Environment", funded by the Ministry of Education, Science and Technological Development of the Republic of Serbia*

Mušnica, Gračanica and Gojkovića stream with their lower parts flow directly through the productive part of the coalbearing Gatački basin and their flows and amount of water in them have a significant impact on the surface coal mining and protection of the open pit from surface and partly ground water. Maximum and minimum flow rates in all three surface flows are a direct consequence of climatic conditions in the region or varying amounts of precipitation in certain seasons.

At the time of flood, periodically, from late autumn to early spring, the lowest southern and southwestern parts of the field are flooded with the water pillar, depth of up to 0.6 m, which decreases with a steep gradient immediately after cessation of heavy rainfall. Flooding occur due to the formation of natural prechasm retention, because there is no a usual chasm zone at the lowest southwestern part of the field due to the existing geological situation and the gorge near in Srdjevića cannot miss in a short period the big storm water collected by Mušnica.

Climate of wider area of Gacko is a continental - mountainous which means a long and cold winters (in the period November - Aprill with temperatures as low as -30°C) and relatively short summers (June -August) with temperature of up to 30°C. With a temperature range at annual level are also typical and heavy snowfall causing disruption of traffic on the roads to the northern and rarely western areas. It should be also counted on the occasional storm surges of strong winds, which can reach speeds of up to 150 km/h, and jeopardize the transmission electricity systems, as well as heavy rains in a short period when the open pit is threatened by abundant inflows of surface and partly groundwater. Precipitation amounts for return period of 60 years are given in Table 1 [2].

Table 1 *Precipitation amounts for a period of 60 years*

	l / m^2
Maximum hourly rainfall amounts	56.0
Maximum daily rainfall amounts	198.4
Maximum monthly rainfall amounts	636.0
Maximum annual rainfall amounts	3 012.5

Deposition of Neogene sediments with coal was performed in inter-mountain depression formed in the karst area. Coal deposit is entirely located below the alluvial surface with several streams drained by the largest flow in the field by the small river Mušnica. Mušnica through the Srdjevic gorge drains the Gatačko field on its southwestern edge, and a few kilometers away ends up in the chasm zone below Videz. In the period of heavy rainfall, the lowest part of the Gatačko field is blue, because a back pressure is created in the Srdjevic gorge. And in the southeastern and southwestern edge, there are several sources, whose water flows out by small streams across the alluvial surface into Mušnica. The conditions from previous described statements, lithology of the Neogene coal-bearing formation, as well as the overall geological characteristics of its older substrate, influenced the formation of several aquifers - water-bearing horizons, both in the coal-bearing formation and in its immediate environment. The coal deposit Gacko deposit in terms of hydrogeological characteristics belongs to very complex deposits.

In the coalbearing formation of Gacko, the extremely most common lithological member are marls (coaly, sandy, limed, tufaceous) then clay, coal, subordinate tuffs and very rarely weakly bonded sandstones and conglomerates. The basic collector in the geological pillar of above the sediment, more than 450 m thick, is a coal seam, especially coal in the main and the first foot wall of coal seam. Coals are medium to low water permeable rocks, depending on the depth of distribution. The category of low water permeable rocks also includes sandy marls as well as marls above the main coal seam but only if they have poorly developed frac ture system. There is a datum that tuffs can be partly water permeable in some places. All other listed lithological members are watertight.

According to the extensive detailed hydrogeological explorations in the West Field of the open pit Gracanica, it was concluded that the rivers Mušnica i Gračanica participate in the recharge of aquifers in in the Neogene coalbearing formation with 80%, since 10% of water comes from the flysch formation and 10% from the field rim and of rainfall [2]. In some areas, the recharge is also done from the Jurassic formations, where they are in a direct contact with the coal seams as it is the case in the northeastern part of the Central and East Fields. Emptying of aquifers in the Jurassic and Cretaceous units takes place in the northeastern and southwestern rim of the basin through a number of sources (much higher yields are those on the northeastern contact with the Neogene sediments). The aquifers in the area of syncline axis have sometimes the artesian and sometimes sub-artesian character.

In the area of the Central Field, the groundwater flows from northeast to the southwest with gradient of underground flow I = 0.007 – 0.01 [2]. In the East field, the flow direction is toward the northwest, nearly parallel to a flow of Musnica gradient the flow gradient I = 0.006 – 0.005 [2]. Recharge of aquifers in the roof coal seams is mainly from rainfall (infiltration through the thin Quaternary cover) and from surface flows, mainly Musnica. The direction of flow is as in the previous case and with a small flow gradient. Bearing in mind the previously given as well as displays on the geological map and geological - accounting profiles, the interconnections of individual aquifers can be observed, their interconnections with the terrain surface as well as conections to the divisions that were transgressed by the Neogene sediments.

The system of coal and overburden exploitation at the open pit Gračanica in a part of the Field C and elevated zone is defined as a function of geological - structural conditions, engineering - geological and hydrogeological characteristics of the working environment, disposable complex of equipment and general operating conditions. A continuous, mixed and discontinuous technology of exploitation is applied on overburden production. Combined technology of exploitation involves a discontinuous overburden excavation with hydraulic shovels, loaders, as well as continuous excavation the solid parts using combine and internal transport by trucks to the crushing plants for waste. A part of discontinuous equipment is engaged to the requirements of technological process and coal production. Disposal of overburden is carried out on the West outer landfill and internal landfill of the Field B at the open pit Gracanica. A combined technology of selective excavation is applied for coal production. Coal excavation is carried out by hydraulic shovels. Transportation of coal excavated by hydraulic excavators to the primary crusher is carried out by trucks. From the primary crushers, coal is transported by conveyor belts to the secondary crusher of the power plant.

DEFENCE SYSTEM FROM WATER

In accordance with the work progress on the excavation of overburden and coal, the defense from water will be carried out in two locations: a part of the Field C, and a part of the Roof zone.

The concept of defense a part of the Field C is that, where possible, water from atmospheric precipitation gravitating towards the open pit to be accepted by lateral canals with dams and gravity taking out of the open pit area, and groundwater and water from atmospheric precipitation falling directly on the area of the open pit to be accepted into the water collectors and to be taken by pumps and pipelines into the river Gracanica [1]. Protection of the Field C of the water due to the atmospheric precipitation gravitating towards the open pit will be done with two circumferential canals: the channel OK1 on the north side of the open pit, and the the channel OK2 which extends parallel to the front line of mining works in progress and on the south side of the open pit flows into the old riverbed of Musnica.

Protection of the Field C on groundwater and water from atmospheric precipitation falling directly on the area of the open pit will be done with the current system, which includes two water-collectors: the VS-C1 and VS-C2 from which the water is lead by pumps and pipes into the river Gracanica. For groundwater occuring in the northern part of the Field C, the two holes will be made below the transport route for coal transport. For regulation the water flow on the working front, the storey channels EK0 - EK4 will be made which are connected by transverse channels PK1 and PK2.

Protection of the Roof zone on water due to atmospheric precipitation gravitating towards the open pit will be done by a peripheral canal and a dam OK3 around the entire open pit. Water from this canal will partly go into the old river bed Musnica and partly in the canal OK4. Protection of the Roof zone on groundwater and water from atmospheric precipitation falling directly on the area of open pit will be done by creating a water collector where the pumps and pipeline will be set which will be led through the peripheral embankment to the canal OK4 on the southwest side of the open pit. The water flows into this canal from the canal OK3. Water from canal OK4 are drained by the old river bed Musnica outside the area of the open pit. The storey canals EK5 - EK9 and transverse canal PK3 - PK5 are predicted at the open pit.

Due to the stability, a part of the old riverbed Musnica from the bridge on the south side of the Field C, distance of 200 m, will be covered with a protective foil. Position of the water protection facilities is shown in Figure 1.

The positions and volume of water collectors VS-C1 and VS-C2 in the final stage in a part of the Field C are determined by the available space in these locations. The available volumes of water collectors are VS-C1: 166 665 m^3 and VS-C2: 65 985 m^3[3]. Calculation of the required volumes of water collectors is done according to maximum eight-hour rainfalls for a return period of 50 years. According to the hydrogeological characteristics of the area, the obtained value will be increased by 5% due to the influx of groundwater into the open pit. Required volumes of water collectors are VS-C1: 236 680 m^3 and VS-C2: 146 740 m^3[3]. Volumes of water collectors are lower than calculated. Due to large sizes of water collectors that would accept maximum water from rainfalls for the fifty-year-period, the sinking of the lowest level is allowed except that there is no equipment on it, and there is no interruption in production. During precipitation of high intensity (which are of short duration), the space is predicted for temporary accumulation in the water-collector VS-C1 at the bottom of the open pit. The space on the lowest elevation E870 to the level K875 is 380 000 m^3 [3] what is larger volume than needed. During precipitation of high intensity, it is necessary to remove the machinery and manpower from the space allocated for temporary accumulation.

The water-collector VS-PZ in the final stage of works on the Roof zone is made on the level E905 and the depth of water collector is 5 m. The position and sizes of water collectors are conditioned by development of works at the open pit. Volume of this water collector is 10 975 m^3 [3]. The area authoritative for sizing the water collector is a complete surface inside the dike. Required volume of water collector VS-PZ is 78 890 m^3 [3]. Volume of water collector is lower than calculated. Due to large sizes of water collectors that would accept maximum water from rainfalls for the fifty-year-period, the sinking of the lowest level is allowed except that there is no equipment on it, and there is no interruption in production. During precipitation of high intensity (which are of short duration), the space is predicted for temporary accumulation in the water-collector VS-C1 at the bottom of the open pit. The space on the lowest elevation E905 K915 is 270 000 m^3 [3] what is larger volume than needed. During precipitation of high intensity, it is necessary to remove the machinery and manpower from the space allocated for temporary accumulation.

Sizing of pumping systems in a part of the Field C was carried out according to the condition that maximum eight-hour water inflows have to be reduced for the amount of water that can be accepted by water-collectors and pumped for 36 hours. The amount of water that needs to be pumped out is: PS-C1: 236 680 m^3, PS-C2: 146 740 m^3 [3]. The required pumping capacity is: PS-C1: 0.54 m^3/s, PS-C2: 0.62 m^3/s[3]. Height pumping for both pumping stations is Hg = 70 m. Pump head is increased by 10% for local resistance and is H = 77 m [3].

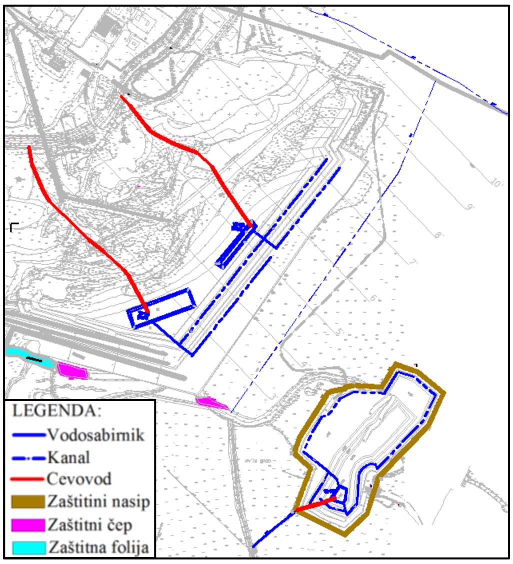


Figure 1 *Position of water protection facilities*

At the pump station PS-C1 the existing pumps Flygt 2250 HT and pump Flygt 3240 CS are retained with moving to a new location and extension of the pipeline. The additional pipeline length needed for pumps in development phase of works is 100 m for every existing pipeline. The new pump which is set is Flygt CS 3240 connected to the pipeline φ300 mm. The first 30 meters of the pipeline is flexible and the rest is steel pipeline. Pipeline length is 800 m. At the pump station PS-C2 the existing pumps Flygt 2250 HT and pump Flygt 3240 CS are retained with moving to a new location and extension of the pipeline. The additional pipelines needed for pumps in development phase of works is 350 m for every existing pipeline. The new pump Flygt CS 3240 is set connected to the pipeline φ300 mm. The first 30 m of this pipeline is flexible and the rest is steel pipeline. Pipeline length is 750 m.

Sizing the pumping plants in a part of the Roof was carried out according to the condition that maximum eight-hour inflow of water to be pumped for 24 hours. As the volume of water to be pumped is 78 890 m^3, required hour pumping capacity is 0.91 m^3/s. Height of pumping is Hg = 40 m. Pump head is increased by 10% for local resistance and is H = 44 m. For these conditions pumping will be done by Flygt 2250 MT pumps. One section consists of two pumps of this type, which are arranged in series. Five such sections are needed, each with individual pipeline φ300 mm. The investor has the required number of pumps. The acquisition of a plastic piping length of 200 m for each of the three new sections is required.

Circumferential dike is made of marl. The height of dike is 1.5 m, width of crown 1 m, and a slope of lateral sides 1: 2. Length of dike is 1 830 m. Plugs in the old riverbed Musnica are made of marl, length of 100 m for plug 1 and 50 m for plug 2.

Protective foil in the old riverbed Musnica is set fromthe bridge on the south side of the Field C upstream in length of 200 m. Required minimum thickness of foil is 2 mm. The foil surface is 520 m^2. Profile with the set foil is shown in Figure 2.

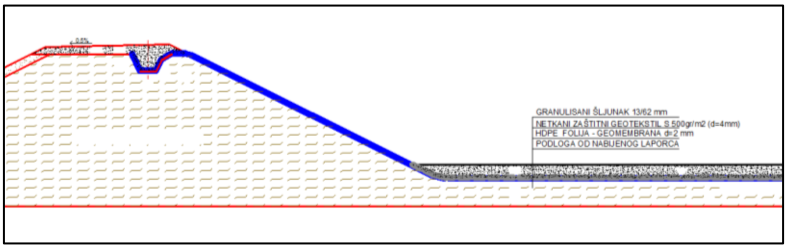


Figure 2 *Profile with set foil*

CONCLUSION

Sizing a defense system from water ata the open pit Gračanica - Gacko is particularly a complex issue. Particularly important is determination the inflow of precipitation and groundwater. Properly defined inflow and hydraulic connections determine the type and number of facilities for defense from water [4, 5, 6, 7].

The present defense system from water at the open pit Gračanica - Gacko has primarily a function to provide a reliable protection of mining facilities in the case of large inflows as a consequence of maximum precipitation of a short intensity.

A significant feature of this defense system from water is also maximum utilization the existing pumping plants and pipelines with minimizing procurement of a new equipment, which is extremely important in terms of investments.

In designing the defense system of the open pit from water, the experience of the open pit Gračanica - Gacko, with additional measures of bringing the water quality within the prescribed limits, should be also used at the open pits of RTB Bor. By combination and proper selection of facilities for defense from water and maximum utilization of the existing resources, the presented system is an optimal solution in terms of safety, investment, maintenance, energy consumption and required workforce.

REFERENCES

[1] R. Simić, V. Kecojević: Facilitties for Water Drainage at the Open Pits, Faculty of Mining and Geology, University of Belgrade, 1996;

[2] Additional Mining Project on Exploitation a Part of the Fields C of the Open Pit Gračanica - Gacko, Technical Project on Defense the Open Pit of Water; Center for Surface Mining Belgrade Ltd., Belgrade, 2010;

[3] Simplified Mining Project on Exploitation with Expansion the Existing Front of Works in the Southern Part and a Part of the Roof Coal (Roof Zone) of the Open Pit Gračanica - Gacko; Mining and Metallurgy Institute Bor; Bor, 2015.

[4] R. Rajković, M. Ignjatović, B. Rajković, D Kržanović: Water Accumulated Drainage at the Open Pit Bor with Gould Pumps; II International Symposium “Mining 2011“ Mining Presents State and Future Prospects and Sustainable Development; Vrnjačka banja 10 – 13 May 2011; pp.378-384

[5] R. Rajković, D. Kržanović, D. Mitić: Quantity of Water and Pump System for Drainage at the Open Pit of the Coal Mine “Potrlica“ – Pljevlja; Mining Engineering 1/2010; pp.89-102;

[6] R. Rajković, B. Rajković, R. Lekovski; Operating Regime of Wilo Pumps for Drainage Conditions of Veliki Krivelj Copper Open Pit; 39th International October Conference on Mining and Metallurgy IOCMM 2007; Sokobanja, Serbia, 07-10 October 2007; pp. 75-79;

[7] R. Lekovski, M. Miljković, R. Rajković; Mathematical Modeling of Flood Wave; 39th International October Conference on Mining and Metallurgy IOCMM 2007; Sokobanja, Serbia, 07 - 10 October 2007; pp. 173-178;

INSTITUT ZA RUDARSTVO I METALURGIJU BOR ISSN: 2334-8836 (Štampano izdanje)
UDK: 622 ISSN: 2406-1395 (Online)

UDK: 622.271:627.51(045)=163.41 doi:10.5937/MMEB1503017R

Radmilo Rajković[*]*, Saša Stepanović*[*]*, Daniel Kržanović*[*]*, Miomir Mikić*[*]

SISTEM ODBRANE OD VODA POVRŠINSKOG KOPA GRAČANICA – GACKO[**]

Izvod

Površinski kop Gračanica Gacko ima izuzetno složene uslove ovodnjenosti uz pojave značajnih priliva voda kao posledice kratkotrajnih padavina velikog intenziteta. Ovim radom je dat prikaz uticajnih parametara na veličinu ovodnjenosti i prikaz sistema za odbranu kopa od voda.

Ključne reči: *Površinski kop Graćanica – Gacko, uticajni faktori ovodnjenosti, sistem odbrane od voda*

UVOD

Izbor tehničko - tehnološkog rešenja odbrane površinskog kopa Gračanica sa delom Polja C i Povlatne zone od površinskih i podzemnih voda zavisi od prirodnih i tehničko - tehnoloških faktora. U prirodne faktore bitne sa aspekta odvodnjavanja spadaju morfološke odlike terena, hidrografske odlike terena, klimatske odlike područja, hidrološke karakteristike područja i hidro-geološke karakteristike terena. U tehničko - tehnološke faktore spadaju raspoloživi kompleks opreme i opšti uslovi eksploatacije[1].

Koncepcija odbrane od voda mora da pruži pouzdanu zaštitu rudarskih objekata, uz pridržavanje zakonske regulative za ovu oblast, uz maksimalno korišćenje postojeće opreme na kopu [4, 5, 6, 7].

UTICAJNI FAKTORI

Gatačko polje predstavlja među planinsku depresiju ispunjenu neogenim sedimentima, formiranu u fazi relaksacije terena po prestanku usmerenih tektonskih pritisaka (oligocen-miocen). Sada predstavlja, najvećim delom, aluvijalnu površ veoma blagog pada od ulaska reke Mušnice u polje istočno od Avtovca do ušća Gojkovića potoka u Mušnicu na zapadu.

Desne pritoke Mušnice, Gračanica i Gojkovića potok, sa pritokama Rajića potok i Trnovac, teku, kao i Mušnica, od severa ka jugu do ulaska u polje, presecajući dijagonalno markantno izražene dekametarske pakete kalkarenita u gornjokrednom, pretežno karbonatnom flišu. Pritoke ova tri toka uglavnom imaju orjentaciju severozapad – jugoistok, paralelno sa pružanjem kalkarenitskih paketa usečene su u mekše laporce, odnosno glavni i manji vodeni tokovi čine pravougaonu hidrografsku mrežu uslovljenu litologijom flišne formacije severo-istočno od Gatačkog Polja.

---

[*] *Institut za rudarstvo i metalurgiju Bor, radmilo.rajkovic@irmbor.co.rs*

[**] *Ovaj rad je jednim delom proistekao iz projekta TR37001 „Uticaj rudarskog otpada iz RTB Bor na zagadjenje vodotokova, sa predlogom mera i postupaka za smanjenje štetnog dejstva na životnu sredinu", koji je finansiran sredstvima Ministarstva prosvete, nauke i tehnološkog razvoja Republike Srbije*

Mušnica, Gračanica i Gojkovića potok svojim donjim delovima tokova teku direktno preko produktivnog dela ugljonosnog Gatačkog basena pa njihovi tokovi i količina voda u njima imaju značajan uticaj na površinsku eksploataciju uglja i zaštitu kopa od površinskih i delom podzemnih voda. Maksimalni i minimalni proticaji u sva tri navedena površinska tokadirektna su posledica klimatskih prilika u regionu, odnosno različite količine padavina u pojedinim godišnjim dobima.

U vreme povodanja, periodično, od kasne jeseni do ranog proleća, najniži južni i jugozapadni delovi polja su poplavljeni stubom vode dubine do 0,6 m, koji se strmim gradijentom smanjuje odmah posle prestanka obilnih padavina. Plavljenja nastaju usled formiranja prirodne pretponorske retenzije, jer na najnižem jugozapadnom delu polja nema, zbog postojeće geološke situacije, uobičajene ponorske zone, pa tesnac kod Srđevića ne može u kratkom periodu da propusti velike oborinske vode koje je prikupila Mušnica.

Klima šireg područja Gacka je kontinentalno – planinska što podrazumeva duge i hladne zime (u periodu novembar – april sa temperaturom i do -30°C) i relativno kratkim letima (juni - avgust) uz temperaturu i do 30°C. Uz velik raspon temperatura na godišnjem nivou karakteristične su i velike snežne padavine što uzrokuje prekide saobraćaja na komunikacijama prema severnim i ređe zapadnim područjima. Treba računati i na povremene snažne olujne udare vetrova, koji mogu dostizati brzinu i do 150 km/h i ugroziti i prenosne elektrosisteme, kao i obilne kiše u kratkom vremenskom periodu kada je ugrožen površinski kop obilnim doticajima površinske i delom podzemne vode. Količine padavina za povratni period od 60 godina date su tabelom 1 [2].

Tabela 1. *Količine padavina za period od 60 godina*

	l / m^2
Maksimalna časovna količina padavina	56,0
Maksimalna dnevna količina padavina	198,4
Maksimalna mesečna količina padavina	636,0
Maksimalna godišnja količina padavina	3 012,5

Depozicija neogenih sedimenata sa ugljem izvršena je u međuplaninskoj depresiji formiranoj u karsnom okruženju. Ležište uglja se u celini nalazi ispod aluvijalne površi sa nekoliko potoka, koje drenira najveći tok u polju – rečica Mušnica. Mušnica kroz Srđevića klanac odvodnjava Gatačko Polje na njegovom jugozapadnom obodu i nekoliko kilometara dalje završava u ponorskoj zoni ispod Videža. U period obilnih padavina najniži deo Gatačkog Polja se plavi, jer se stvara uspor u Srđevića klancu. I na jugoistočnom i na jugozapadnom obodu nalazi se po nekoliko izvora, čije vode malim potocima preko aluvijalne površi odlaze u Mušnicu. Uslovi iz napred iznetih konstatacija, litologija neogene ugljonosne formacije, kao i ukupne geološke karakteristike njene starije podloge, uticali su na formiranje nekoliko izdani - vodonosnih horizonata, kako u samoj ugljonosnoj formaciji tako i u njenom neposrednom okruženju. Ležište uglja Gacko u pogledu hidrogeoloških osobina spada u veoma složena ležišta.

U ugljonosnoj formaciji Gacka izrazito najzastupljeniji litološki član su laporci (ugljeviti, peskoviti, vapnoviti, tufitični), zatim gline, ugalj, podređeno tufovi i sasvim retko slabo vezani peščari i konglomerati. Osnovni kolektor u geološkom stubu navedenih sedimenata, debelom preko 450 m, predstavljaju ugljeni slojevi, posebno ugalj u glavnom i prvom podinskom ugljenom sloju. Ugljevi su srednje do slabovodopropusne stene, u zavisnosti od dubine rasprostranjenja. U kategoriji slabo-vodopropusnih stena mogu doći i peskoviti laporci, kao i laporci iznad glavnog ugljenog sloja ali samo ukoliko imaju slabo razvijen pukotinski sistem. Postoji podatak da mestimično i tufovi mogu biti delom vodopropusni. Svi ostali navedeni litološki članovi su vodonepropusni.

Prema obimnim detaljnim hidrogeološkim istraživanjima na Zapadnom polju površinskog kopa Gračanica, zaključeno je da reke Mušnica i Gračanica učestvuju u prihranjivanju izdani u neogenoj ugljonosnoj formaciji sa 80%, dok 10% vode potiče iz flišne formacije a 10% sa oboda polja i od padavina [2]. U nekim područjima prihranjivanje se vrši i iz jurskih formacija, tamo gde su u direktnom kontaktu sa ugljenim slojevima kao što je slučaj na severoistočnom delu centralnog i istočnog polja. Pražnjenje izdani u jurskim i krednim jedinicama vrši se na severoistočnom i jugozapadnom obodu basena preko nekoliko izvora (znatno veće izdašnosti su oni na severoistočnom kontaktu sa neogenim sedimentima). Izdani u području ose sinklinale imaju ponegde arteški a ponegde subarteški karakter. U području Centralnog Polja podzemne vode teku od severoistoka ka jugozapadu sa gradijentom podzemnog toka I=0.007 – 0.01 [2]. U Istočnom polju smer toka je ka severozapadu, skoro paralelno toku Mušnice, sa gradijentom toka I=0.006 – 0.005 [2]. Prihranjivanje izdani u krovinskim ugljenim slojevima je uglavnom od pada-vina (infiltracija kroz tanak kvartarni pokrivač) i od površinskih tokova, uglavnom Mušnice. Smer toka je kao i u prethodnom slučaju i sa malim gradijentom toka. Imajući u vidu do sada izneto, kao i prikaze na geološkoj karti i geološkim – obračunskim profilima, mogu se uočiti međusobne veze pojedinih izdani, njihove veze sa površinom terena, kao i veze sa jedinicama na koje su neogeni sedimenti transgredirali.

Sistem eksploatacije uglja i otkrivke na površinskom kopu Gračanica u delu Polja C i povlatnoj zoni definisan je u funkciji geološko - strukturnih uslova, inženjersko – geoloških i hidrogeološkoh karakteristika radne sredine, raspoloživog kompleksa opreme i opštih uslova eksploatacije. Na proizvodnji otkrivke se primenjuje kontinualna, kombinovana i diskontinualna tehnologija eksploatacije. Kombinovana tehnologija eksploatacije podrazumeva diskontinualno otkopavanje otkrivke sa hidrauličnim bagerima kašikarima, utovaračem, kao i kontinualno otkopavanje čvrstih delova kombajnom i unutrašnji transport kamionima do drobiličnih postrojenja za jalovinu. Deo diskontinualne opreme se angažuje prema zahtevima tehnološkog procesa i na proizvodnji uglja. Odlaganje otkrivke se vrši na Zapadno spoljašnje odlagalište i na unutrašnja odlagalište Polja B površinskog kopa Gračanica. Na proizvodnji uglja se primenjuje kombinovana tehnologija selektivnog otkopavanja. Otkopavanje uglja se vrši hidrauličnim bagerima kašikarima. Transport uglja otkopanog hidrauličnim bagerima do primarnih drobilica je kamionima. Od primarnih drobilica, ugalj se transporterima sa trakom transportuje do sekundarne drobilice termoelektrane.

SISTEM ODBRANE OD VODA

Saglasno dinamici izvođenja radova na otkopavanju otkrivke i uglja, odbrana od voda vršiće se na dva lokaliteta: deo Polje C, i deo Povlatna zona.

Koncepcija odbrane dela Polje C je da se, gde je to moguće, vode od atmosferskih padavina koje gravitiraju ka kopu prihvate obodnim kanalima sa nasipima i gravitacijski odvedu van područja kopa, a podzemne vode i vode od atmosferskih padavina koje padnu direktno na područje kopa prihvate u vodosabirnike i pumpama i cevovodima odvedu u reku Gračanicu[1]. Zaštita dela Polje C od voda usled atmosferskih padavina koje gravitiraju ka kopu, vršiće se sa dva obodna kanala: kanal OK1 sa severne strane kopa, i kanal OK2 koji se pruža paraleleno sa frontom napredovanja radova i sa južne strane kopa se uliva u staro korito reke Mušnice. Zaštita dela Polje C od voda podzemnih voda i voda od atmosferskih padavina koje padnu direktno na područje kopa vršiće se postojećim sistemom koji obuhvata dva vodosabirnika: VS-C1 i VS-C2 iz kojih se voda pumpama i cevovodima dovodi u reku Gračanicu. Za podzemne vode koje se javljaju u severnom delu Polja C, napraviće se dva propusta ispod transportnog puta za transport uglja. Za regilaciju kretanja vode na radnom frontu, biće urađeni etažni kanali EK0 – EK4 koji su spojeni poprečnim kanalima PK1 i PK2.

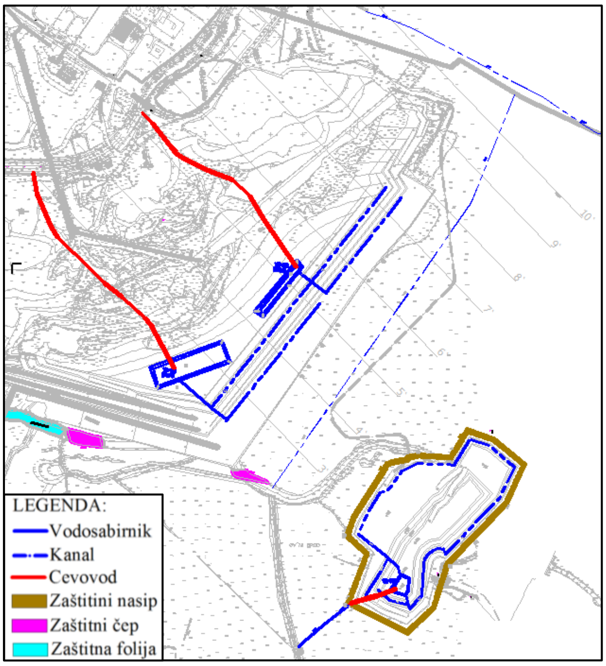
Zaštita dela Povlatna zona od voda usled atmosferskih padavina koje gravitiraju ka kopu, vršiće se obodnim kanalom i nasipom OK3 oko celog kopa. Vode iz ovog kanala delom će ići u staro korito reke Mušnice a delom u kanal OK4. Zaštita dela Povlatna zona od podzemnih voda i voda od atmosferskih padavina koje padnu direktno na područje kopa vršiće se izradom vodosabirnika u koji će biti postavljene pumpe i cevovodom će se preko obodnog nasipa dovoditi do kanala OK4 na jugozapadnoj strani kopa. U ovaj kanal dospevaju i vode iz kanala OK3. Vode iz kanala OK4 odvode se starim koritom reke Mušnice van područja kopa. Na kopu su predviđeni etažni kanali EK5 – EK9 i poprečni kanali PK3 – PK5.

Zbog stabilnosti, deo starog korita reke Mušnice od mosta sa južne strane Polja C u dužini od 200 m biće obložen zaštitnom folijom. Položaj objekata zaštite od voda prikazan je na slici 1.

Položaji i zapremina vodosabirnika VS-C1 i VS-C2 u završnoj fazi u delu Polja C uslovljeni su raspoloživim prostorom na ovim lokacijama. Raspoložive zapremine vodosabirnika su VS-C1: 166.665 m^3 i VS-C2: 65.985 m^3 [3]. Proračun potrebnih zapremina vodosabirnika vrši se prema maksimalnim osmočasovnim padavinama za povratni period od 50 godina. Prema hidrogeološkim karakteristikama područja, dobijena vrednost će se uvećati za 5% usled priliva podzemnih voda u kop. Potrebne zapremine vodosabirnika su VS-C1: 236 680 m^3 i VS-C2: 146 740 m^3 [3]. Zapremine vodosabirnika su manje od proračunatih. Zbog velikih dimenzija vodosabirnika koji bi prihvatili maksimalne vode od padavina za pedesetogodišnji period, dozvoljava se potapanje najniže etaže s tim da se na njoj ne nalazi oprema, i ne dolazi do prekida u proizvodnji. U vreme padavina velikog intenziteta (koje su kratkog trajanja) predviđen je prostor za privremenu akumulaciju kod vodosabirnika VS-C1 na dnu kopa. Prostor na najnižoj otvorenoj etaži E870 do kote K875 iznosi 380.000 m^3 [3] što je veća zapremina od potrebne. U vreme padavina velikog intenziteta potrebno je mehanizaciju i ljudstvo skloniti iz prostora predviđenog za privremenu akumulaciju.

Vodosabirnik VS-PZ u završnoj fazi radova na Povlatnoj zoni se izrađuje na etaži E905 a dubina vodosabirnika je 5 m. Položaj i dimenzije vodosabirnika uslovljene su razvojem radova na kopu. Zapremnina ovog vodosabirnika iznosi 10.975 m^3 [3]. Površina merodavna za dimenzionisanje vodosabirnika je kompletna površina unutar odbrambenog nasipa. Potrebna zapremina vodosabirnika VS-PZ iznosi 78.890 m^3 [3]. Zapremina vodosabirnika je manja od proračunate. Zbog velikih dimenzija vodosabirnika koji bi prihvatili maksimalne vode od padavina za pedesetogodišnji period, dozvoljava se potapanje najniže etaže s tim da se na njoj ne nalazi oprema, i ne dolazi do prekida u proizvodnji. U vreme padavina velikog intenziteta (koje su kratkog trajanja) predviđen je prostor za privremenu akumulaciju na dnu kopa. Prostor na najnižoj otvorenoj etaži E905 do kote K915 iznosi 270.000 m^3 [3] što je veća zapremina od potrebne. U vreme padavina velikog intenziteta potrebno je mehanizaciju i ljudstvo skloniti iz prostora predviđenog za privremenu akumulaciju.

Dimenzionisanje pumpnih postrojenja u delu Polje C izvršeno je prema uslovu da se maksimalni osmočasovni prilivi vode umanjeni za količinu vode koju mogu da prihvate vodosabirnici ispumpaju za 36 h. Količina vode koja treba da se ispumpa je: PS-C1: 236 680 m^3, PS-C2: 146 740 m^3 [3]. Potrebni kapacitet ispumpavanja iznosi: PS-C1: 0,54 m^3/s, PS-C2: 0,62 m^3/s [3]. Visina ispumpavanja za obe pumpne stanice iznosi $H_g = 70$ m. Napor pumpi je uvećan za 10% za lokalne otpore i iznosi H = 77 m [3].



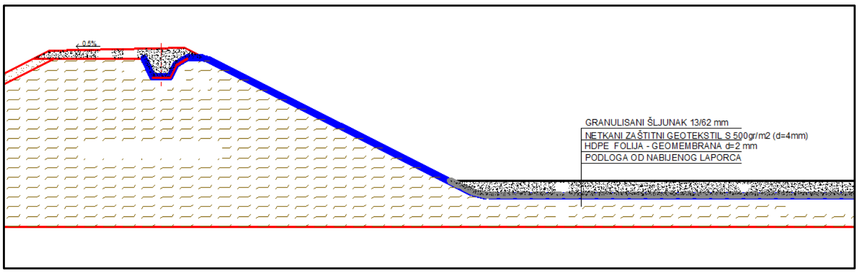
Sl. 1. *Položaj objekata zaštite od voda*

Na pumpnoj stanici PS-C1 zadržavaju se postojeće pumpe Flygt 2250 HT i pumpa Flygt 3240 CS uz seljenje na novu lokaciju i produženje cevovoda. Dodatna dužina cevovoda potrebna za pumpe iz faze razvoja radova iznosi 100 m za svaki postojeći cevovod. Nova pumpa koja se postavlja je Flygt 3240 CS vezana na cevovod ∅300 mm. Prvih 30 m ovog cevovoda je fleksibilno a ostali deo čelični cevovod. Dužina cevovoda iznosi 800 m. Na pumpnoj stanici PS-C2 zadržavaju se postojeće pumpe Flygt 2250 HT i pumpa Flygt 3240 CS uz seljenje na novu lokaciju i produženje cevovoda. Dodatna dužina cevovoda potrebna za pumpe iz faze razvoja radova iznosi 350 m za svaki postojeći cevovod. Postavlja se nova pumpa Flygt 3240 CS vezana na cevovod ∅300 mm. Prvih 30 m ovog cevovoda je fleksibilno a ostali deo čelični cevovod. Dužina cevovoda iznosi 750 m.

Dimenzionisanje pumpnih postrojenja u delu povlatne zone izvršeno je prema uslovu da se maksimalni osmočasovni prilivi vode ispumpaju za 24 h. Kako je količina vode koja treba da se ispumpa 78.890 m^3, potreban časovni kapacitet ispumpavanja iznosi 0,91 m^3/s. Visina ispumpavanja iznosi H_g = 40 m. Napor pumpi je uvećan za 10% za lokalne otpore i iznosi H = 44 m. Za ove uslove ispumpavanje će se vršiti pumpama Flygt 2250 MT. Jedna sekcija se sastoji od dve pumpe ovog tipa koje su redno vezane. Potrebno je 5 ovakvih sekcija, svaka sa pojedinačnim cevovod ∅300 mm. Investitor poseduje potreban broj pumpi. Potrebna je nabavka plastičnog cevovoda dužine 200 m za svaku od tri nove sekcije.

Obodni nasip se izrađuje od laporca. Visina nasipa je 1,5 m, širina krune 1 m a nagib bočnih strana 1:2. Dužina nasipa iznosi 1.830 m. Čepovi u starom koritu reke Mušnice izrađuju se od laporca dužina čepova iznosi 100 m za čep 1 i 50 m za čep 2.

Zaštitna folija u starom koritu reke Mušnice postavlja se od mosta sa južne strane dela Polja C uzvodno u dužini od 200 m. Potrebna je folija minimalne debljine 2 mm. Površina folije iznosi 520 m^2. Profil sa postavljenom folijom prikazan je na slici 2.



Sl. 2. *Profil sa postavljenom folijom*

ZAKLJUČAK

Dimenzionisanje sistema odbrane od voda kod površinskog kopa Gračanica – Gacko je posebno složeno pitanje. Izuzetno je značajno određivanje priliva od padavina i podzemnih voda. Pravilno određen priliv i hidrauličke veze opredeljuju vrstu i broj objekata za odbranu od voda [4, 5, 6, 7].

Prikazani sitem zaštite od voda površinskog kopa Gračanica – Gacko prvenstveno ima funkciju da obezbedi pouzdanu zaštitu rudarskih objekata u slučaju velikih priliva koji su posledica maksimalnih padavina kratkog intenziteta.

Značajna karakteristika ovog sistema zaštite od voda je i maksimalno iskorišćenje postojećih pumpnih postrojenja i cevovoda uz minimiziranje nabavke nove opreme, što je izuzetno važno sa aspekta investicionih ulaganja.

Pri projektovanju sistema odbrane kopa od voda, iskustva sa površinskog kopa Gračanica – Gacko, uz dodatne mere dovođenja kvaliteta vode u propisane granice, trebaju da se iskoriste i na površinskim kopovima RTB-a Bor. Kombinacijom i pravilnim izborom objekata zaštite od voda i maksimalnim iskorišćenjem postojećih resursa prikazani sistem je optimalno rešenje sa aspekta sigurnosti, ulaganja, održavanja, potrošnje energije i potrebne radne snage.

LITERATURA

[1] R. Simić, V. Kecojević: Objekti za odvođenje voda na površinskim kopovima; Rudarsko geološki fakultet u Beogradu, 1996.

[2] Dopunski rudarski projekat eksploatacije dela Polja C površinskog kopa Gračanica – Gacko, Tehnički projekat odbrane površinskog kopa od voda; Centar za površinsku eksploataciju Beograd d.o.o., Beograd, 2010.

[3] Uprošćeni rudarski projekat eksploatacije sa proširenjem postojećeg fronta radova u južnom delu i delu krovinskih ugljeva (povlatna zona) površinskog kopa Gračanica – Gacko; Institut za rudarstvo i metalurgiju Bor; Bor, 2015.

[4] R. Rajković, M. Ignjatović, B. Rajković, D Kržanović: Water accumulated drainage at open pit Bor with Gould pumps; II international symposium „Mining 2011" Mining presents state and future prospects and sustainable development; Vrnjačka banja 10 – 13 maj 2011; str. 378 – 384

[5] R. Rajković, D. Kržanović, D. Mitić: Quantity of water and pump system for drainage at the open pit of the coal mine "Potrlica" – Pljevlja; Mining engineering 1/2010; str. 89 – 102;

[6] R. Rajković, B. Rajković, R. Lekovski; Operating Regime of Wilo Pumps for Drainage Conditions of Veliki Krivelj Copper Open Pit; 39th International October Conference on Mining and Metallurgy IOCMM 2007; Sokobanja, Serbia, 07 – 10 October 2007; str. 75-79

[7] R. Lekovski, M. Miljković, R. Rajković; Mathematical Modeling of Flood Wave; 39th International October Conference on Mining and Metallurgy IOCMM 2007; Sokobanja, Serbia, 07 – 10 October 2007; str. 173-178

MINING AND METALLURGY INSTITUTE BOR
UDK: 622

ISSN: 2334-8836 (Štampano izdanje)
ISSN: 2406-1395 (Online)

UDK: 622.272:622.79(045)=111

doi:10.5937/MMEB1503029D

Lidija Đurđevac Ignjatović[*]*, Dragan Ignjatović*[*]*, Milenko Ljubojev*[*]*, Dragan Zlatanović*[**]

BASIC REQUIREMENTS OF BACKFILLING WITH FLOTATION TAILINGS IN THE BOR RIVER UNDERGROUND MINE[***]

Abstract

The use of backfill in underground mining is increased due to a need for systematic backfilling the mine openings and workings. Backfilling is applied in order to prevent fires and explosions, improve the mine ventilation, improve the rock stability, reduce the subsidence effects on surface, as well as for economical and environmental factors. Sources of materials are usually from mining industry (e.g. fly ash, gypsum, slag, infertile overburden, tailings, filter dust, residues from mineral processing) or other industries. The ore body Bor River of the Bor Copper Mines is planned to be exploited by the sublevel stopping method. In order to ensure greater efficiency in the exploitation of the ore body, it is proposed, after the excavation of chambers, to move on to the excavation of the main pillars. To ensure the stability of the excavation area, it is necessary to fill the excavated chambers with material of good physical and mechanical properties.

For this purpose, a possibility of filling the chambers with backfilling consisted of flotation tailings, small amount of cement and water, will be tested. This paper reviews the basic requirements of backfilling that will be applied in the excavated chambers.

Keywords: *backfilling, flotation tailings, sublevel stopping, basic requirements*

1 INTRODUCTION

The underground **cemented paste backfill** (CPB) is an important component of underground stope extraction. As the mining operations progress, paste backfill is placed into previously mined stopes to provide a stable platform for miners to work on and ground support for the walls of the adjacent adits by reduction the amount of open space that could potentially be filled by a collapse of the surrounding pillars [1]. The underground paste backfill provides not only ground support to pillars and walls, but also helps in preventing caving and roof falls and enhances pillar recovery, thereby improving productivity [2], [3]. Thus, the placement of paste backfill provides an extremely flexible system for coping with changes in the ore body geometry that result in changes in stope width, dip, and length [4]. Paste backfill is usually transported underground through the reticulated pipelines. Paste backfill is composed of mill tailings generated during mineral processing, mixed with additives such as the Portland cement, lime, pulverized fly ash, and smelter blast furnace slag, which react as the binding

---

[*] *Mining and Metallurgy Institute Bor*

[**] *Innovation Centre of Faculty of Mechanical Engineering, Belgrade*

[***] *This paper is the result of the Project No. TR33021 „Research and Monitoring the Changes of the Stress Strain State in the Rock Mass „In-Situ“ around the Underground Rooms with Development of Models with Special Reference to the Tunnel of the Krivelj River and Pit Bor“, funded by the Ministry of Education, Science and Technological Development of the Republic of Serbia.*

agents. Binding agents develop a cohesive strength within CPB so that exposed fill faces become a self-supporting when adjacent stopes are extracted.

Backfilling costs in underground mining operations must be critically examined to identify the potential cost savings [5]. Although paste backfilling is somewhat expensive, it is indispensable for the most underground mines as it provides a crucial ground support for mine safety and mining operations. Therefore, the fill should be cost-effective and capable of achieving the desired ground support and stability. An analysis of fill stability must consider the geometric boundaries of the fill in terms of optimal economic use of CPB. Mine openings and exposed fill faces in large underground mines vary in shape from high and narrow to low and wide. Additionally, a wall rock next to the backfill may be either steeply dipping or relatively flat-lying. The extraction sequence can be modified to reduce the number of CPB-filled stopes, or the stope geometries could be modified to reduce the required strength for CPB exposure [7].

This paper reviews the basic requirements in terms of physical and mechanical characteristics of the backfill that will be applied in the excavated chambers.

2 CALCULATION THE HORIZONTAL PRESSURE ON FILLED STOPE

In general, since self-weight stresses govern backfill design, the traditional design has been a freestanding wall requiring a **uniaxial compressive strength** (UCS) equal to the overburden stress at the bottom of the filled stope. In many cases, however, the adjacent rock walls actually help support the fill through boundary shear and arching effects. Therefore, backfill and rock walls may be mutually supporting [2]. In backfilled stopes, when arching occurs (which is the case in many mines, depending on stope dimensions), the vertical pressure on the bottom of the filled stope is less than the weight of overlying fill (overburden weight) due to a horizontal pressure transfer, somewhat like a trap door [7]. This pressure transfer is due to the frictional and/or cohesive interaction between fill and wall rock. When the pillars or stope walls begin to deform into the filled opening, the fill mass provides lateral passive resistance. Passive resistance is defined as the state of maximum resistance mobilized when force pushes against a fill mass and the mass exerts resistance to the force [8]. The pressure transferred horizontally to the sidewalls should be included in the required fill strength design. Horizontal pressures affected by fill arching are determined by five analytical or semi-analytical solutions that account for cohesion at the fill-sidewall interface and/or frictional sliding along the sidewalls. These solutions are the Martson's model and its modified version, Terzaghi's model, Van Horn's model and Belem-Benzaazoua model [9].

3 REQUIRED CHARACTERS OF PASTE BACKFILL

The required strength for paste backfill depends on the intended function. To provide an adequate ground support, the required uniaxial/unconfined compressive strength (UCS) of the fill should be at least 1.5 MPa (in case of the Bor River mine), whereas for free-standing fill applications, UCS is commonly lower than 1 MPa [10]. A typical vertical exposure measures 4–6 m wide by 30–45 m high. A UCS of 100 kPa is commonly adopted as the liquefaction potential limit. The required static strength for paste without exposures may be arbitrarily selected at 200 kPa. Previous work indicates that fill mass UCS varies from 0.2 MPa to 4 MPa, while the surrounding rock mass UCS varies from 5 MPa to 240 MPa [9].

The mechanical effects of fill differ from those of the primary ore pillars. Research and in situ testing have shown that fill is incapable of supporting the total weight of overburden ($\sigma_v = \gamma H$), and acts as a secondary support system only.

The fill modulus of elasticity varies from 0.1 GPa to 1.2 GPa, while the surrounding rock mass elasticity varies from 20 GPa to 100 GPa. It can be assume that any vertical loading is a result of roof deformation (Fig. 1), and that design UCS can be estimated by the following relationship:

$$UCS_{\text{design}} = (E_p \varepsilon_p) FS | = E_p \left(\frac{\Delta H_p}{H_p} \right) FS$$

where E_p = rock mass or pillar elastic modulus; e_p = pillar axial strain; ΔH_p = strata deformation (m); H_p = strata initial height (m); and F_S = factor of safety.

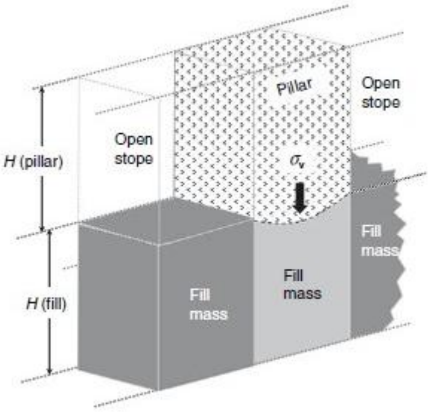


Figure 1 *Schematic view of vertical loading on the backfill block next to a pillar*

Once the required strength has been determined, mix variables are optimized to provide the desired mix that achieves target strength and minimum cementation usage. Mix variables considered include binder content Bw% (by dry mass of tailings) and binder type, tailings particle size distribution (PSD) and mineralogy, mix solids concentration by mass (Cw%) or volume (CV%), and mixing water geochemistry. To design a certain uniaxial compressive strength (UCS design), the variables are adjusted to produce an optimal mix design. The other essential requirement is that the backfill must be economical. These costs wield a significant impact on the mine operating costs. Paste backfill costs alone are typically between 10% and 20% of total mine operating costs, with binder agents accounting for up to 75% of backfill costs.

One of the most important characters of the paste backfill is pumpability. It can be determined using the standard or modified ASTM slump test, Fig. 2.

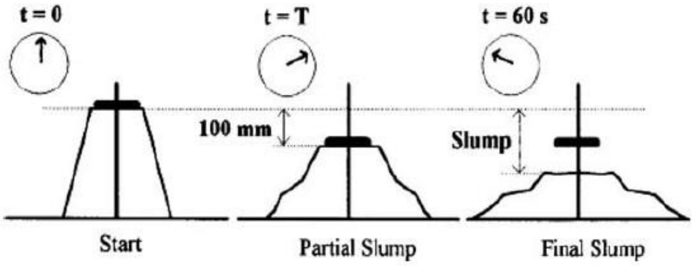


Figure 2 *Schematic diagrams of the modified slump cone test based on measuring slumping time T*

4 CONCLUSION

This paper provides an overview of the design and application the paste backfill in the Bor River underground mine. In applying the paste backfill, the limiting strength and pressures developed in the fill mass must be determined according to the geometry of the opened stopes and initial stress conditions. To define this criteria, optimization of paste backfill mix design is essential to determine the optimal mixture to achieve the desired limiting strength, rheological behavior, cost effects, pumpability and many other crucial properties.

REFERENCES

[1] Barret JR, Coulthard MA, Dight PM, Determination of Fill Stability, Mining with Backfill, Proceedings of 12th Canadian Rock Mechanics Symposium, Canadian Institute of Mining and Metallurgy, Quebec, Special Vol. 19, pp. 85–91, (1978);

[2] Mitchell RJ, Stability of Cemented Tailings Backfill, Computer and Physical Modelling in Geotechnical Engineering. Balkema, Rotterdam, pp. 501–507, 1989;

[3] Mitchell RJ, Model STUDIES on the Stability of Confined Fills, Can Geotech J 26:210–216, 1989;

[4] Wayment WR, Backfilling With Tailings - A New Approach, Proceedings of 12th Canadian Rock Mechanics Symposium, Mining with Backfill. Canadian Institute of Mining and Metallurgy, Quebec, Special Vol. 19, pp. 111–116, 1978;

[5] Stone DMR, The Optimization of Mix Designs for Cemented Rockfill, Proceedings of Fifth International Symposium on Mining with Backfill, MINEFILL'93, Johannesbourg, SAIMM, pp. 249–253, 1993;

[6] Stone DMR, The Optimization of Mix Designs for Cemented Rockfill, Proceedings of Fifth International Symposium on Mining with Backfill, MINEFILL'93, Johannesbourg, SAIMM, pp. 249–253, 1993;

[7] Terzaghi K, Theoretical Soil Mechanics, John Wiley & Sons, New York, 1943;

[8] Hunt RE, Geotechnical Engineering Analysis and Evaluation, McGraw Hill, New York, 729 pp. 1986;

[9] T. Belem, M. Benzaazoua, Design and Application of Underground Mine Paste Backfill Technology, Geotech Geol Eng, pp. 147-174, 2008;

[10] Li L, Aubertin M, Simon R, Bussie`re B, Belem T (2003), Modeling Arching Effects in Narrow Backfilled Stopes with Geotech Geol Eng (2008) 26: 147–174 173 FLAC. In: Proceedings of 3rd International FLAC Symposium, May 31, 2003, Sudbury, A.A. Balkema, Rotterdam, pp. 211–218.

MINING AND METALLURGY INSTITUTE BOR ISSN: 2334-8836 (Štampano izdanje)
UDK: 622 ISSN: 2406-1395 (Online)

UDK: 621.967.2:620.9(045)=111 doi:10.5937/MMEB1503033S

Saša Štatkić[*], Djukan Vukić*[**], Žarko Milkić*[*], Leposava Ristić*[***]*

ENERGY EFFICIENCY OF BELT CONVEYOR AT CONSTANT SPEED OPERATION[****]

Abstract

Belt conveyor drives at the open pit mines consist of motors with large installed power. Each analysis of their energy efficiency presents an important factor for proper control to achieve better financial effects. The paper considers efficiency of each belt conveyor in the V ECS (excavator-belt conveyor-spreader) system at the open pit mine "Drmno" as a function of time, determined based on measured values for the observed period of time. This paper analyses variations of efficiency depending on the load at constant speed. Conversion of electrical energy into mechanical by means of electrical motors and mechanical transmission is performed on belt conveyors. Therefore, the efficiency of drive station driven by electrical motors of multi motor drive is defined as a relation between the output mechanical power of multi motor drive and its input electrical power. Information about the motor torques is obtained from frequency converters, within integrated models which estimate the value of motor torque. Information about the belt speed is achieved by measuring the number of drive drum revolutions in certain period of time. Electrical power for supplying all consumers at the belt conveyor drive station is gained by measuring the power in the supply medium voltage cubicle.

Keywords*: belt conveyor, frequency converter, induction motor drive, efficiency*

1 INTRODUCTION

Belt conveyor station consists of two motors per each of two drive drums, which convey the rubber belt. Exterior of one belt conveyor station is shown in Figure 1, while Figure 2 presents the transfer chute and two gears connected with drive drum [2].

Figure 1 *Photo of belt conveyor station J-V-3 of V ECS system at open pit mine "Drmno"*

---

[*] *Faculty of Technical Sciences, University in Pristina, Kosovska Mitrovica, Serbia, e-mail: statkic@etf.rs*
[**] *Faculty of Agriculture, University in Belgrade, Serbia*
[***] *Faculty of Electrical Engineering, University in Belgrade, Serbia*
[****] *Results presented in the paper are a part of the Project TR33016 "Research, Development and Application of Energy Efficiency Programs and Measurements for Electrical Drives", funded by the Ministry of Education, Science and Development of the Republic of Serbia*

Figure 2 *Transfer chute and two gears connected with drive drum*

One of the most important technological requirements in the designing phase of the V ECS system was to enable regulation of belt speed. Due to that, the configuration of electrical drive consisting of squirrel cage induction motor supplied from frequency converter is adopted in the design phase, [1]. Figure 3 presents a disposition of containers for frequency converters (FC Container) and electrical equipment (E Container), as well as position of transformer on the platform of belt conveyor station [2].

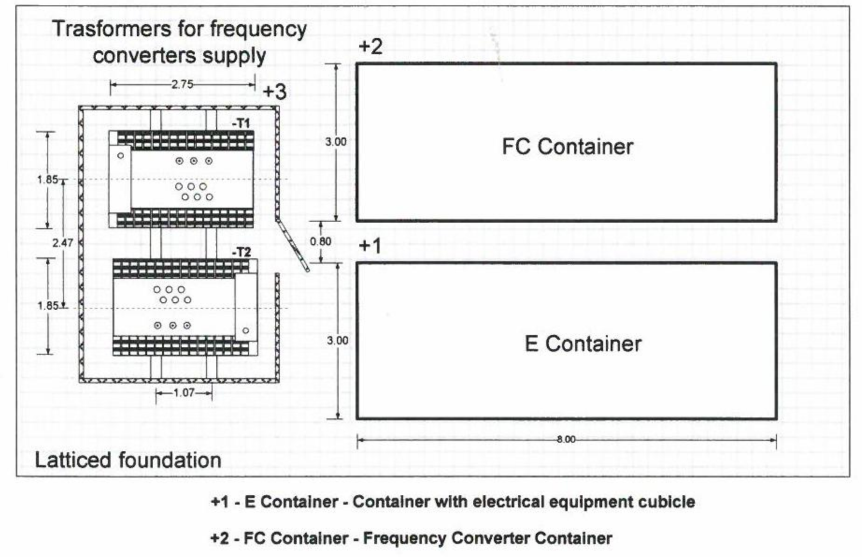


Figure 3 *Disposition of containers and transformers on platform of belt conveyor station*

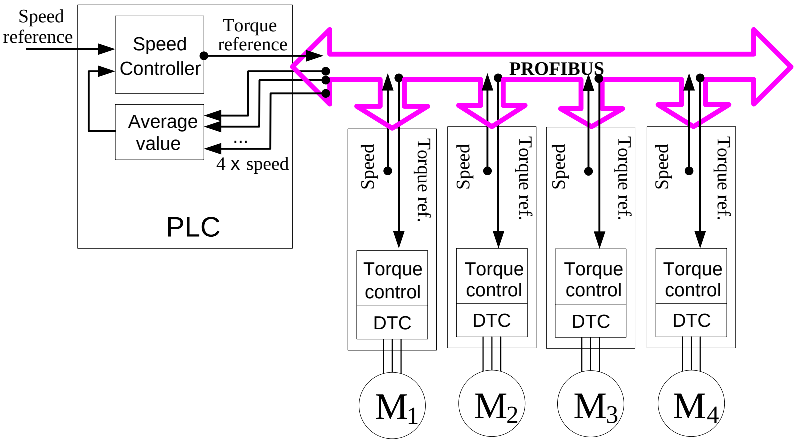


Figure 4 *Controller of the average value of speed of belt conveyor multi motor drive*

2 DESCRIPTION OF ELECTRICAL DRIVES

Induction motor fed by frequency converter, has reinforced insulation of the stator windings for operation under non sinusoidal voltages and galvanic isolated bearings. According to the given data and performed mining calculations, the required value of motor rated power is determined (Pn=1000 kW), as well as the synchronous rated motor speed (1000 rpm). Owing to required power of the drive (1000 kW), voltage level of 690 V was selected for rated voltage of motor, frequency converter and secondary transformer windings. Technical characteristics of squirrel cage induction motor are:

- Motor type:
  2. RZKIT 710 L-6 B3
- Motor manufacturer:
  Sever Subotica
- Rated power for supply from frequency converter:
  1.000 [kW]
- Rated power for power grid supply:
  1.300 [kW]
- Rated voltage: 690 [V]
- Rated speed: 994 [rpm]
- Rated motor torque:
  9.607 [Nm]
- Power factor: $\cos\varphi = 0,85$
- Motor efficiency at rated load:
  $\eta_n = 0,96$

For squirrel cage induction motor which has rated power of 1000 kW and rated voltage of 690 V, the frequency converter, manufactured by ABB, which meets all basic requirements for controlled belt conveyor drive was selected for supply. Within the frequency converter with catalog designation ACS800-07-1740-7, sensors for DC link voltage and motor phase currents measurements were integrated. Based on these measured values, as well as on the defined rated values for motor parameters, within the dynamical model of motor integrated in the processor of frequency converter, quantities of torque, flux and motor speed are calculated. Frequency converter enables acquisition of estimated torque and speed signals, [3].

Direct torque control presents modern control algorithm, which is today commonly applied within frequency converters. It provides extremely fast drive response to com mand values, enabling realization of very complex control structures. Within the V ECS system at open pit mine „Drmno“ [1,3], control of electrical drives is performed in the superior control system with speed controller, which controls the average speed of all belt conveyor drives, (Figure 4). The output from this controller is reference torque, which is forwarded equally to all frequency converters operating in the direct torque control mode. This control structure enables equality and the same performance of each frequency converter in the control structure. Consequently, the controlled multi motor belt conveyor drive is flexible to change of the number of constituting drives during the exploitation due to variable configuration of open pit mine. This control strategy provides equal load sharing among individual drives also in cases when number of drives is less than four, as it is explained in details in literature [4,5].

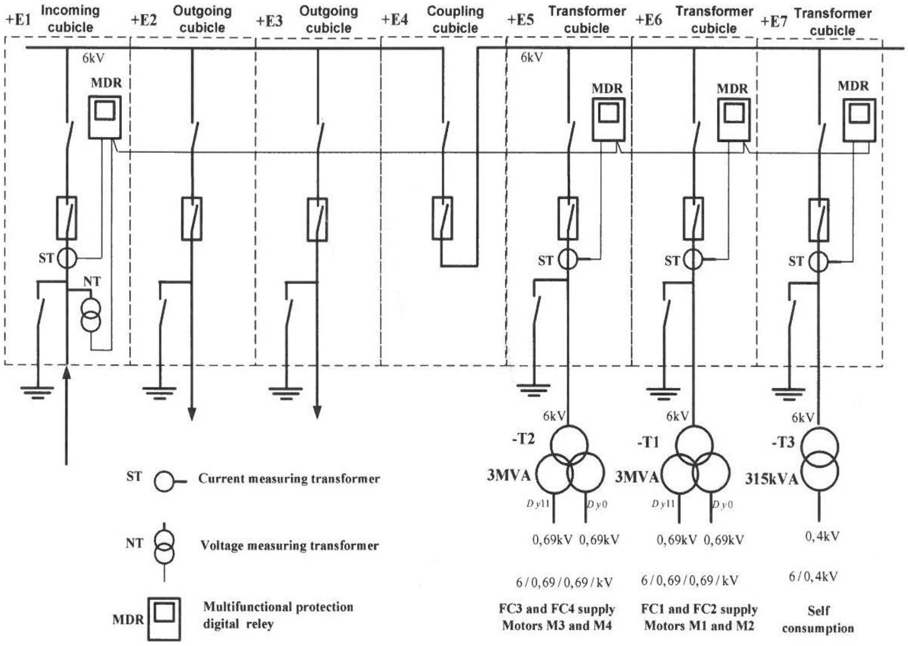


Figure 5 *Single phase schematic diagram of 6 kV cubicles in E container on drive station*

Multifunctional digital protection relay, SIPROTEC 4 Type 7SJ63, is used in all medium voltage cubicles for the purpose of proper relay protection, as it is presented in Figure 5. Beside protecting functions, this device possesses the monitoring functions, which include measuring of active P, reactive Q and apparent power S, based on measurement of currents and voltages of all three phases. It also supports the Profibus industrial communication protocol for connecting to the control network on drive station. All measured values, as well as all protecting functions for the given medium voltage cubicle are forwarded to the supervision and control system in the Control centre [2,3], trough local control network on the belt conveyor drive section and optical cable network.

3 CONTROL CENTER DESCRIPTION

Block diagram of the remote control structure of V ECS system [3,4,5], realized at the open pit mine “Drmno” is presented in Figure 6. Each belt conveyor drive station has a control structure as shown in Figure 4. It is connected through the optical cable network to the control system in the Control center.

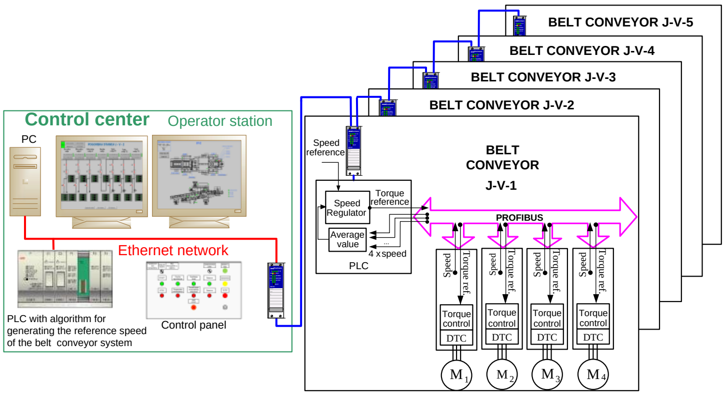


Figure 6 *Block diagram of control structure realized on open pit mine „Drmno”*

Application software for remote control of V ECS system is implemented within the PLC which is located in the Control center, Figure 7. This software enables the process of remote control and supervision of all belt conveyors within the V ECS system.

In accordance with modern trends, which are used to control similar systems in order to increase time utilization, the control of belt conveyor system is realized from the unique control center which provides information about the state, values and parameters of the system, important for technological process. Details of control and communication equipment and command panel in the Control center are presented in Figures 7 and 8. Visualization of all relevant parameters of the control system trough graphical screens is obtained using the system for supervision and control (SCADA), applied in the Control center.

Figure 7 *PLC, I/O modules and equipment for optical communication in Control center*

Figure 8 *Command panel for remote control of V ECS system in the Control center*

Besides graphical screens which present chosen values in real time, the supervision system additionally performs their archiving in the determined period of time. The archived data for the period of two hours are used in the paper. A new variable is defined, which presents the time function of the drive station efficiency. It was not implemented in the existing system for supervision and control. As a result, the new options arise: to present time diagram of the drive station efficiency, or to present it as a function of material quantity on the belt, motor torque or speed of the belt. This is very important when the system of belt conveyors operates in the variable speed mode of operation, aiming to achieve the optimum value of the process efficiency under the existing technical constraints of the system.

4 DRIVE STATION TORQUES

All drives at one belt conveyor drive station consist of motors, gears and drive drums of the same characteristics. In the observed period of time when data analyses is performed, due to configuration of V ECS system, three main drives existed per each drive station. Starting from the fact that the equal load sharing between drives is provided, the average torque value of all drives on one belt conveyor drive station is given with (1).

$$m_{ps\_sr}(t) = \sum_{1}^{3} \frac{m_{ei}(t)}{3} \,. \qquad (1)$$

Figure 9 presents the time diagrams of average torques of all belt conveyor drive stations within V ECS system, recorded in the two hours period.

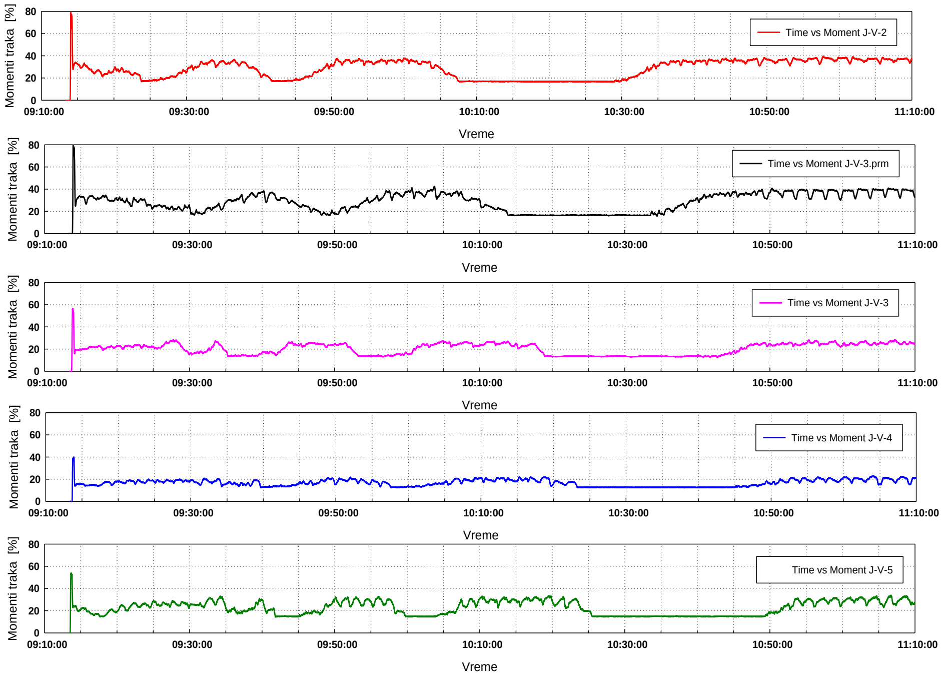


Figure 9 *Average torques of all belt conveyor drive stations within V ECS system*

The average value of drive station torque is proportional to the total load value. As presented in Figure 9, in no load periods of belt conveyor operation (straight line on time diagrams), load value does not exceed 20% of the rated load. During the transport of material with the system of belt conveyors, the load is variable and its value does not exceed 40 % of the rated value. Lengths of belt conveyors are significantly less than designed value (3.200 m) and therefore, the load is significantly less than rated value.

5 EFFICIENCY

The belt conveyor drive station is an electromechanical system that converts electrical energy into mechanical work required for material transport. At the output shaft of the gear, the torque is *i* times greater that the motor torque and η_r times smaller due to the efficiency of mechanical coupling:

$$m_{bu}\ t = \eta_r \cdot m_{ps\_sr}\ t \cdot i\,. \qquad (2)$$

Tension force on the drum rim, produced by one drive is:

$$F_{bu} = \frac{m_{bu}}{D_{bu}/2} = \frac{\eta_r \cdot m_{ps\_sr} \cdot i}{D_{bu}/2}\,. \qquad (3)$$

Mechanical power transferred from the drive to the belt, is:

$$P_{meh} = F_{bu} \cdot v_{tr} = \frac{\eta_r \cdot m_{ps\_sr} \cdot i}{D_{bu}/2} \cdot v_{tr}\,. \qquad (4)$$

Total mechanical power of all active drives, which is transferred to the belt conveyor using two drive drums, is not directly measured. It is indirectly calculated based on the measured belt speed [m/min], estimated percentage value of electrical motor torque [%] and parameters of mechanical transmission. According to literature [6], the efficiency of mechanical transmission is 0.92 in the case of belt conveyor with two drive drums equipped with gears. The drum diameter is 0.75 m, while the gear ratio is 17.26.

$$P_{meh\_ps}\ t = \sum_{1}^{3} F_{bui}\ t \cdot v_{tr} = 3 \cdot \frac{\eta_r \cdot m_{ps\_sr}\ t \cdot i}{D_{bu}/2} \cdot v_{tr} = 3 \cdot \frac{0{,}92 \cdot m_{ps\_sr}\ t \cdot 17{,}26}{1{,}5/2} \cdot v_{tr} \cdot (5)$$

Electrical power measured in the incoming cubicle (+E1) presents the sum of active powers of frequency converters FC1, FC3 and FC4 that supplies motors M1, M3 and M4, as well as transformer T3 for self consumption. The self consumption is negligible comparing to the power of main drives and has no significant influence to the efficiency of the drive station.

$$P_{el\_ps}\ t = P_{el\_M1}\ t + P_{el\_M3}\ t + P_{el\_M4}\ t + P_{el\_T3}\ t\,. \qquad (6)$$

Calculated value of the time dependent drive station efficiency is defined as the ratio between the output mechanical power transferred to the belt and active electrical power consumed from supply grid:

$$\eta_{ps}\ t = \frac{P_{meh\_ps}\ t}{P_{el\_ps}\ t}\,. \qquad (7)$$

It can be concluded, while observing power balance of one drive station, that the drive station efficiency is equal to the product of efficiencies of each belt conveyor drive component and that it depends on load:

$$\eta = \eta_r \cdot \eta_m \cdot \eta_{fp} \cdot \eta_{tr} \qquad (8)$$

η_r - efficiency of mechanical transmission of belt conveyor drive station consisting of two drive drums with gears,

η_m - motor efficiency,

η_{fp} - frequency converter efficiency,

η_{tr} - transformer efficiency.

Efficiency of belt conveyor drive station at rated load (100%) is 83%. This calculated value is greater than all recorded values of efficiency in the observed period of time, as expected, because the value of load was less than the rated value (Table 1). While frequency converters operate at rated frequency, what corresponds to the constant speed mode of belt conveyor drive operation, they have smaller change of efficiency comparing to induction motors at reduced loads. Power transformers also have smaller change of efficiency due to load change. Efficiency of mechanical transmission is constant and equal to the rated value, because the speed was not changed.

Table 1 *Calculated values of belt conveyor drive efficiency for characteristic load values*

Load [%]	Transformer	FC	Motor	Mechanical transmission	Transformer T3	Summ
15	0.96	0.96	0.86	0.92	0.96	0.70
35	0.97	0.97	0.93	0.92	0.97	0.78
100	0.98	0.98	0.96	0.92	0.98	0.83

6 RESULTS OF MEASUREMENTS

Two vertical axes with different units and different scales are used on diagrams presented in Figures 10 to 13. Values of the active power, obtained by measurements in the incoming cubicle +E1, are assigned to the vertical axes on the left. To the same axes and into the same scale are assigned to indirectly calculated values of mechanical power of drive drums. The belt conveyor drive efficiency is given in percentage and presented on vertical axes, on the right. For each belt conveyor is given the same type of diagram and all diagrams have synchronized time axes.

In all diagrams it can be seen periods when the belt conveyors are empty in operation, without material. Within this period of time, the load of each belt conveyor multimotor drive is constant and has the lowest value. Mechanical power in those periods of time is equal to the mechanical losses due to the motional resistances of empty belt operation. During those periods of empty belt operation, the total efficiency of the belt conveyor station is reduced in relation to the periods when material is transported. The greatest influence to this reduction has the characteristic of induction motor efficiency, according to which the motor efficiency is reduced when operating at loads lower then rated. In periods of loaded belts of belt conveyor, the loading of multimotor drive is variable and depends on the flow of material coming from excavator. Mechanical power of belt conveyor has the required value to overcome all motional resistances of loaded belt. Increased loading of a belt causes an increase of drive station efficiency.

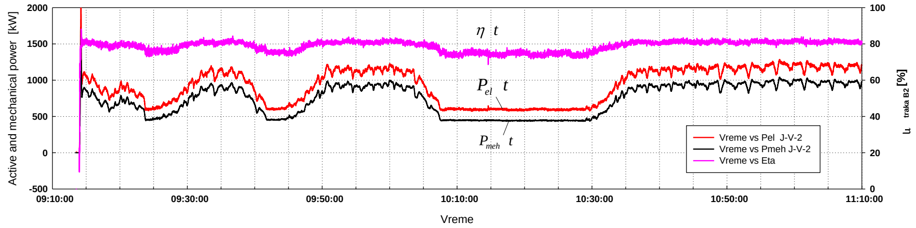


Figure 10 *Active power, mechanical power and efficiency for belt conveyor drive station B2*

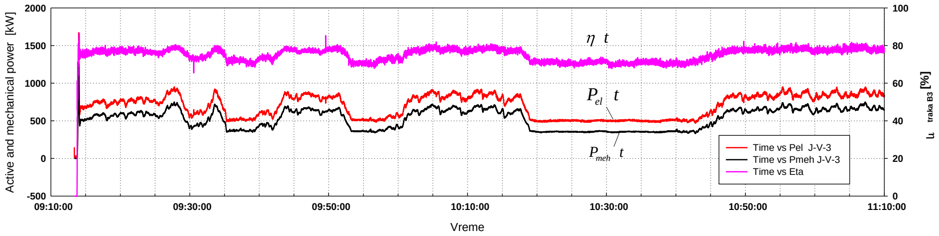


Figure 11 *Active power, mechanical power and efficiency for belt conveyor drive station B3*

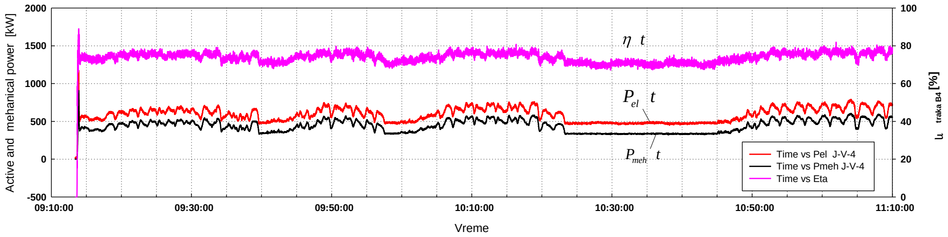


Figure 12 *Active power, mechanical power and efficiency for belt conveyor drive station B4*

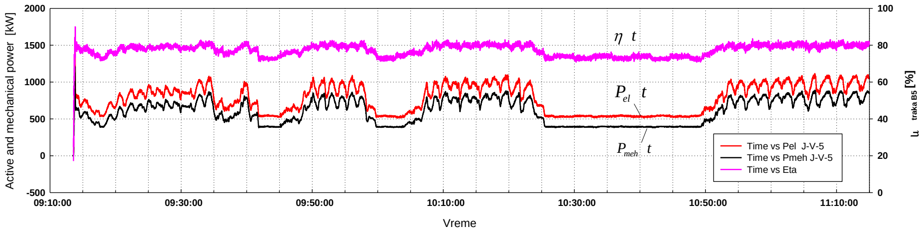


Figure 13 *Active power, mechanical power and efficiency for belt conveyor drive station B5*

7 CONCLUSION

Efficiency of belt conveyor drive station at constant speed operation depends on the loading percentage of drive. Theoretical estimation the drive station efficiency provides the values that are in accordance with the values of efficiency obtained based on the experimental measurements. Optimization of electrical energy consumption, i.e. improvement of efficiency within the constant speed operation of a belt conveyor is practically unachievable, because all optimization algorithms imply the speed control of a belt multi-motor drive, or the material cross section [5]. For the optimization of energy consumption at constant speed belt conveyor operation, the following actions can be applied:

- To choose drive components with greater efficiency,
- Adopt the number of drives on belt conveyor station in accordance to the belt conveyor length,
- Reduce the time of empty belt operation, caused by stoppages on an excavator,
- Longer operation with higher loading percentage, caused by excavator capacitance.

In order to achieve the optimization of consumption, it is required to apply a speed regulation as a function of load, i.e. material flow [4, 5]. Speed reduction leads to increase of material cross section which further cause greater mechanical loading and better transport efficiency. Therefore, not only in the no load operation of belt conveyors, but also when the belt is loaded, it is possible to optimize the electrical energy consumption, if belt conveyor operates for longer periods with higher percentage of loads.

REFERENCES

[1] M. Bebić, B. Jeftenić, D. Jevtić, N. Rašić, L. Ristić, S. Štatkić "Application of Controlled Induction Motors Supplied from Frequency Converters on Belt Conveyors", XIV International Symposium on Power Electronics – Ee 2007 Novi Sad, November 2007 (in Serbian);

[2] B. Jeftenić, M. Bebić, L.Ristić, D. Jevtić, I. Mihailović, N.Rašić, S. Štatkić, "Remote Control and Supervision of the System of Controlled Belt Conveyor Drives", 15th International Symposium on Power Electronics - Ee 2009 Novi Sad, October 2009 (in Serbian);

[3] B. Jeftenić, L. Ristić, I. Mihailović, D. Jevtić, M. Bebić, S. Štatkić, N. Rašić, "Capabilities and Experience in the Application of Energy Efficient Technologies in Bulk Material Transport", 2nd Regional Conference Industrial Energy and Environmental Protection in South Eastern European Countries - IEEP 2010, ISBN 978-86-7877-012-8, pp 1-8, Zlatibor, June 22nd -26th, 2010 (in Serbian);

[4] L. Ristić, M. Bebić, S. Štatkić, I. Mihailović, D. Jevtić, B. Jeftenić, "Bulk Material Transportation System in Open Pit Mines with Improved Energy Efficiency", Proc. of the 15th WSEAS International Conference on Systems (Part of the 15th WSEAS CSCC Multiconfrence), ISBN: 978-1-61804-023-7, ISSN: 1792-4235, Corfu Island, Greece, July 14-16, 2011, pp. 327 – 332;

[5] D. Jevtić, I. Mihailović, L. Ristić, M. Bebić, S. Štatkić, N. Rašić, B. Jeftenić, "Improving Energy Efficiency of Belt Conveyor System" Proc. of the 16th International Symposium on Power Electronics - Ee2011, Novi Sad, Republic of Serbia, 26th – 28th, October, 2011, ISBN 978-86-7892-356-2, COBISS.SR-ID 266961671

[6] R. Borović, „Transport with Belt Conveyors at the Open Pit Mines", Faculty of Mining and Geology, Belgrade, 1997, ISBN 86-7352-004-5, (Table 9.7).

INSTITUT ZA RUDARSTVO I METALURGIJU BOR ISSN: 2334-8836 (Štampano izdanje)
UDK: 622 ISSN: 2406-1395 (Online)

UDK: 621.967.2:620.9(045)=163.41 doi:10.5937/MMEB1503033S

Saša Štatkić[*], *Đukan Vukić*[**], *Žarko Milkić*[*], *Leposava Ristić*[***]

ENERGETSKA EFIKASNOST TRANSPORTERA SA GUMENOM TRAKOM PRI KONSTANTNOJ BRZINI[****]

Izvod

Transporteri na površinskim kopovima imaju velike instalirane snage motora i analiza njihove energetske efikasnosti predstavlja važan faktor u pravilnom upravljanju radi postizanja boljih finansijskih efekata. U ovom radu je na primeru transportera V BTO sistema na površinskom kopu „Drmno“ računskim putem na osnovu izmerenih vrednosti određena vremenska promena stepena iskorišćenja pojedinih transportera za posmatrani period rada. Izvršena je analiza promene stepena iskorišćenja transportera u zavisnosti od opterećenja pri konstantnoj brzini. Kako se na transporterima vrši pretvaranje električne energije u mehaničku posredstvom elektromotora i mehaničkog prenosa, to je stepen iskorišćenja pogonske stanice koju pokreću motori definisan odnosom korisne (mehaničke) snage svih pogona i uložene električne snage za napajanje svih pogona na jednom transporteru. Informacija o momentima motora dobijena je sa frekventnih pretvarača koji u svom modelu motora estimiraju elektromagnetni moment motora. Informacija o brzini trake je dobijena merenjem broja obrtaja pogonskog bubnja. Električna snaga svih potrošača na transporteru dobijena je merenjem aktivne snage u dovodnoj srednjenaponskoj ćeliji.

Ključne reči: *transporter, frekventni pretvarač, asinhroni motor, stepen iskorišćenja*

1. UVOD

Na posmatranim transporterima gumenu traku pokreću dva pogonska bubnja sa po dva motora koji se nalaze na pogonskoj stanici. Izgled konstrukcije jedne pogonske stanice za pokretanje transportera sa gumenom trakom prikazan je na sl. 1, dok je na sl. 2 prikazan presipni levak i dva reduktora koji su spregnuti sa pogonskim bubnjem, [2].

Sl. 1. *Fotografija pogonske stanice tračnog transportera J-V-3, V BTO sistem na površinskom kopu „Drmno“*

---

[*] *Fakultet tehničkih nauka, Univerzitet u Prištini, Kosovska Mitrovica , Srbija; e-mail: statkic@etf.rs*

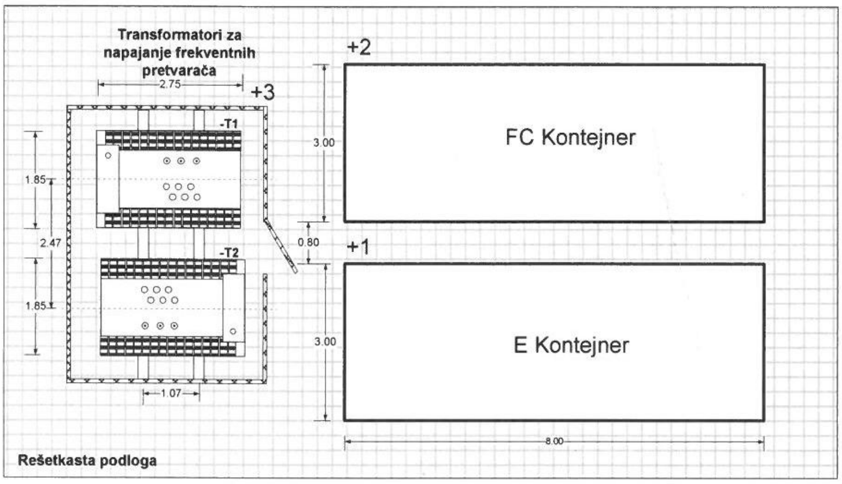
[**] *Poljoprivredni fakultet, Univerzitet u Beogradu, Srbija*

[***] *Elektrotehnički fakultet, Univerzitet u Beogradu, Srbija*

[****] *Ovi rezultatu su deo projekta TR33016 "Istraživanje, razvoj i primena programa i mera energetske efikasnosti elektromotornih pogona" finansiranog od Ministarstva prosvete, nauke i tehnološkog razvoja Republike Srbije*

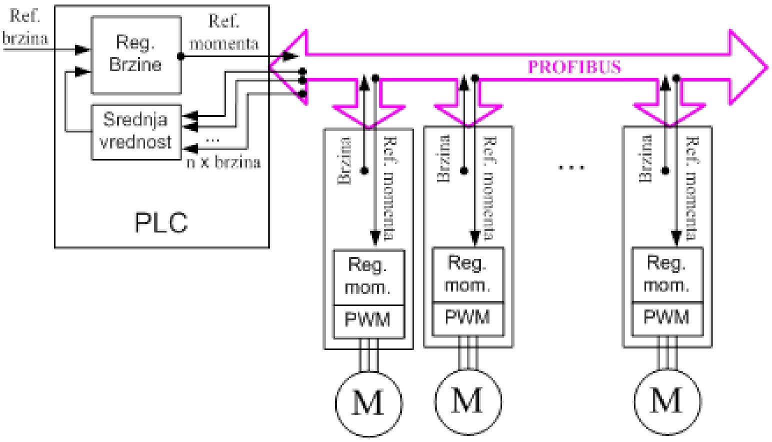
Sl. 2. *Presipni levak i dva reduktora sregnuta sa pogonskim bubnjem*

Jedan od važnih tehnoloških zahteva pri planiranju V BTO sistem bio je da se brzina traka može regulisati. Iz tog razloga je pri projektovanju usvojena konfiguracija elektromotornog pogona sa asinhronim kaveznim motorom koji se napaja iz frekventnog pretvarača, [1]. Na slici 3 prikazan je raspored kontejnera za frekventne pretvarače (FC kontejner) i elektro opremu (E kontejner), kao i položaj transformatora na platformi pogonske stanice, [2].



+1 - E Kontejner – Kontejner sa razvodnim ormanima elektro opreme
+2 - FC Kontejner – Kontejner frekventnih pretvarača

Sl. 3. *Raspored kontejnera i transformatora na platformi pogonske stanice*



Sl. 4. *Regulator srednje brzine višemotornog pogona transportera sa gumenom trakom*

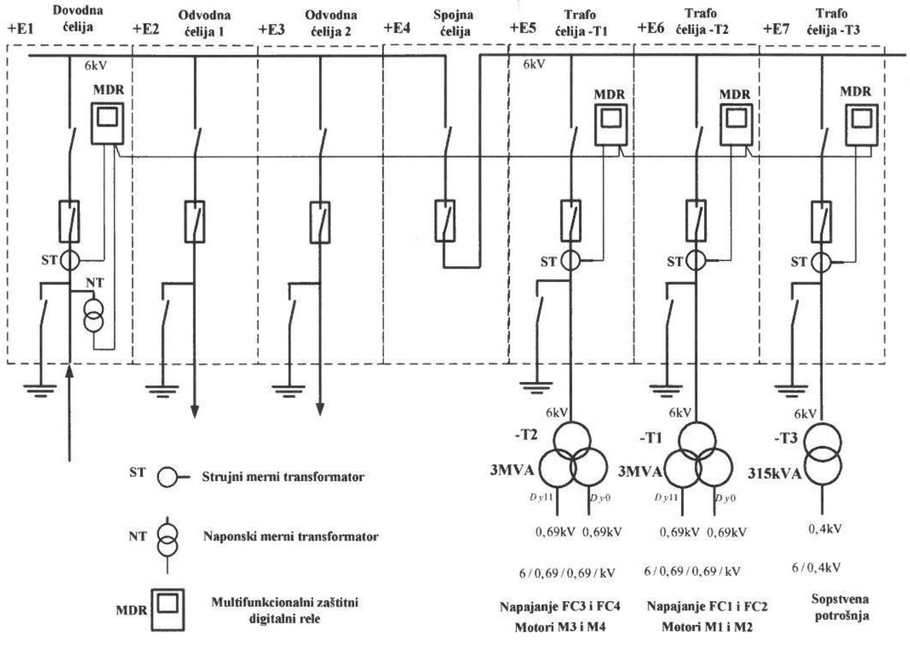
2. OPIS ELEKTROMOTORNIH POGONA

Asinhroni motor koji je predviđen za napajanje iz frekventnog pretvarača, ima ojačanu izolaciju namotaja statora za rad sa nesinusnim naponima i galvanski izolovane ležajeve. Prema datim parametrima i izvršenim rudarskim proračunima određena je potrebna nazivna snaga motora (Pn=1000 kW) i nazivna sinhrona brzina motora (1000 o/min). Zbog potrebne snage pogona (1000 kW) izabran je naponski nivo 690 V za nazivni napon motora, frekventnog pretvarača i sekundarnih namotaja transformatora. Tehničke karakteristike asinhronog kaveznog motora su:

- Tip motora:
  2. RZKIT 710 L-6 B3
- Proizvođač motora:
  Sever Subotica
- Nazivna snaga za napajanje iz frekventnog pretvarača:
  1.000 [kW]
- Nazivna snaga za napajanje iz mreže:
  1.300 [kW]
- Nazivni napon: 690 [V]
- Nazivna brzina: 994 [o/min]
- Nazivni moment motora:
  9.607 [Nm]
- Faktor snage: $\cos\varphi = 0,85$
- Stepen iskorišćenja pri nazivom opterećenju: $\eta_n = 0,96$

Za napajanje kaveznog asinhronog motora nazivne snage 1000 kW i nazivnog napona 690 V, izabran je frekventni pretvarač nazivnog napona 690 V, proizvođača ABB, koji zadovoljava osnovne zahteve za regulisani elektromotorni pogon transportera sa gumenom trakom. U frekventnom pretvaraču kataloške oznake ACS800-07-1740-7 integrisani su senzori za merenje napona jednosmernog kola i faznih struja motora. Na osnovu ovih izmerenih veličina, kao i definisanih nazivnih parametara motora, u dinamičkom modelu motora koji je integrisan u procesoru frekventnog pretvarača sračunavaju se vrednosti momenta, fluksa i brzina motora. Frekventni pretvarač omogućuje merenje i akviziciju estimiranih signala momenta i brzine [3].

Direktna kontrola momenta je savremeni algoritam upravljanja koji se danas standardno primenjuje kod frekventnih pretvarača obezbeđuje izuzetno brzi odziv pogona na upravljačke komande, tako da je moguće realizovati vrlo složene upravljačke strukture. U okviru V BTO sistema na površinskom kopu „Drmno“ [1,3] upravljanje pogonima realizovano je u okviru nadređenog upravljačkog sistema sa regulatorom brzine koji reguliše srednju brzinu pogona svih pogona transportera, (slika 4). Izlaz iz ovog regulatora je referentni momenat, i prosleđuje se ravnopravno svim pretvaračima, koji rade u režimu kontrole momenta. Kod ovakvog sistema upravljanja svi frekventni pretvarači su ravnopravni u strukturi upravljanja, i imaju istu ulogu. Ovim je regulisani pogon transportera fleksibilan na promenu broja pogona koji se menja u toku eksploatacije u zavisnosti od konfiguracije površinskog kopa. Ovakav način upravljanja obezbeđuje ravnopravnu raspodelu opterećenja između pogona i u slučajevima kada je broj pogona manji od četiri, što je u radovima [4,5] detaljno objašnjeno.

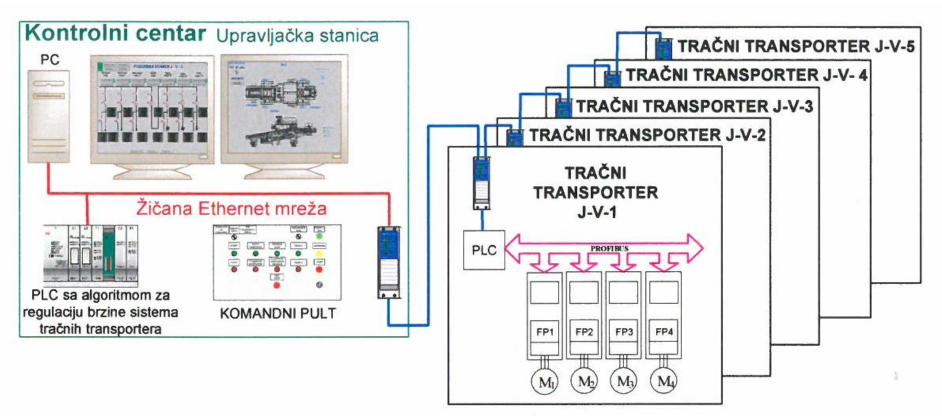


Sl. 5. *Jednopolna šema 6 kV razvodnih ormana u E kontejneru na pogonskoj stanci*

Za odgovarajuću relejnu zaštitu u svim srednjenaponskim ćelijama koristi se multifunkcionalni digitalni zaštitni rele SIPROTEC 4 Tip 7SJ63, (slika 5). Ovaj uređaj pored zaštitnih funkcija ima i monitornig funkcije u koje spadaju merenja aktivne P, reaktivne Q i prividne snage S na osnovu izmerenih struja i napona sve tri faze. Multifunkcionalni digitalni zaštitni rele SIPROTEC 4 Tip 7SJ63 podržava i Profibus industrijski komunikacijski protokol i preko njega je povezan sa upravljačkom mrežom na pogonskoj stanici (PS). Sve izmerene veličine, kao i sve zaštitne funkcije za datu SN ćeliju, preko lokalne upravljačke mreže na PS i preko optičke kablovske mreže se prosleđuju do sistema za nadzor i upravljanje u kontrolnom centru [2,3].

3. OPIS KONTROLNOG CENTRA

Blok dijagram upravljačke strukture za daljinsko upravljanje V BTO sistema [3,4,5], realizovane na površinskom kopu „Drmno”, prikazan je na slici 6. Svaka pogonska stanica ima upravljačku strukturu kao na slici 4 i povezana je preko optičke kablovske mreže sa upravljačkim sistemom u kontrolnom centru.



Sl. 6. *Blok dijagram upravljačke strukture, realizovane na površinskom kopu „Drmno”*

Aplikativni program za upravljanje V BTO sistema implementiran je u PLC-u koji se nalazi u kontrolnom centru, slika 7. Pomoću ovog programa ostvaruje se proces daljinskog upravljanja i nadzora svih transportera u okviru V BTO sistema.

U skladu sa savremenim trendovima koji se koriste kod upravljanja sličnim sistemima, a u cilju povećanja vremenskog iskorišćenja, upravljanje sistemom transportera je realizovano iz jedinstvenog kontrolnog centra u kojem su dostupne informacije o stanju, veličinama i parametrima sistema bitnim za tehnološki proces. Detalj upravljačke i komunikacione opreme i komandnog pulta u kontrolnom centru prikazan je na slikama 7 i 8.

Sl. 7. *PLC, I/O moduli i oprema za optičku komunikaciju u kontrolnom centru*

Sl. 8. *Komandni pult za daljinsko upravljanje V BTO sistemom u kontrolnom centru*

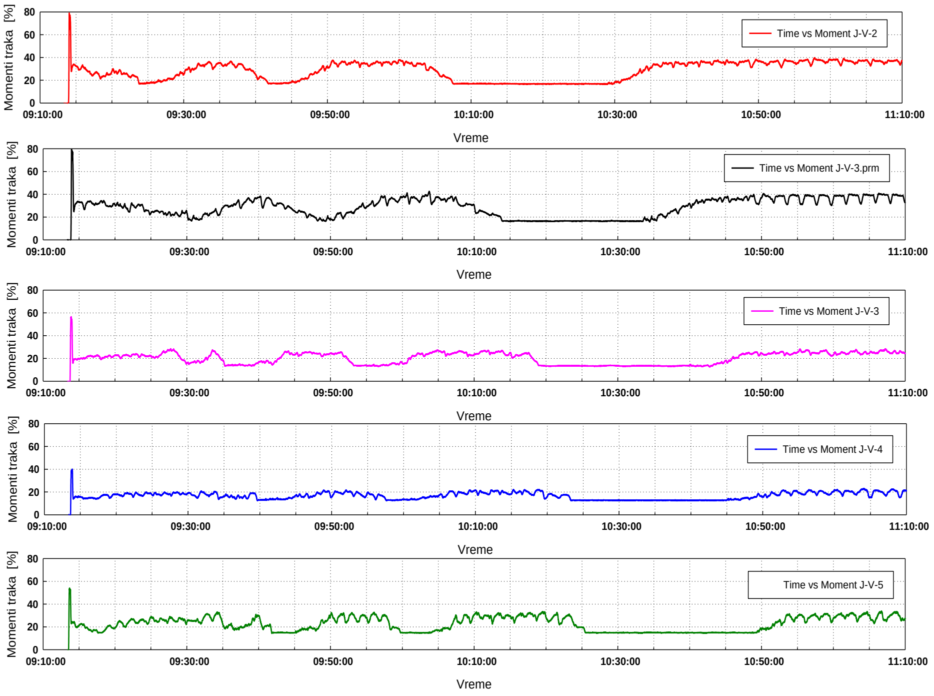
Realizovanim nadzorno - upravljačkim (SCADA) sistemom u kontrolnom centru omogućena je vizuelizacija svih relevantnih parametara upravljačkog sistema, korišćenjem grafičkih prikaza. Pored grafičkih prikaza izabranih veličina u realnom vremenu, pomenuti sistem za nadzor vrši istovremeno i njihovo arhiviranje za određeni period. U ovom radu su upotrebljeni arhivirani podaci za jedan period koji je trajao dva časa. Definisana je nova veličina, vremenska promena stepena iskorišćenja pogonske stanice, koja nije bila implementirana u postojeći nadzorno - upravljački sistem.

4. MOMENTI POGONSKIH STANICA

Svi pogoni na jednoj pogonskoj stanici transportera sa gumenom trakom imaju motore, reduktore i pogonske bubnjeve istih karakteristika. U toku posmatranog perioda rada za koji su analizirani podaci, sve pogonske stranice su imale po tri glavna pogona zbog konfiguracije V BTO sistema. Polazeći od činjenice da je raspodela opterećenja između pogona ravnomerna srednja vrednost momenta svih pogona na jednoj pogonskoj stanici je data kao:

$$m_{ps\_sr}\ t = \sum_{1}^{3} \frac{m_{ei}\ t}{3} \tag{1}$$

Na slici 9 prikazane su snimljene srednje vrednosti momenta svih pogonskih stanica V BTO sistema u toku jednog perioda u trajanju od dva časa.



Sl. 9. *Srednje vrednosti momenta svih pogonskih stanica u V BTO sistemu*

Srednja vrednost momenta pogonske stanice je srazmerna ukupnom opterećenju. Sa dijagrama na slici 9 uočava se da u periodima kada je traka prazna (prava linija) vrednost opterećenja ne prelazi 20% od nazivnog opterećenja. U toku transporta materijala na trakama opterećenje je promenljivo i njegova vrednost ne prelazi 40% nazivnog opterećenja. Dužine traka u posmatranom periodu su značajno manje od projektovane dužine (3.200 m) i iz tog razloga opterećenje je značajno manje od nazivnog.

5. STEPEN ISKORIŠĆENJA

Pogonska stanica je elektromehanički sistem koji vrši pretvaranje električne energije u mehanički rad za transport materijala. Na izlaznom vratilu reduktora moment je *i* puta veći od momenta motora i η_r puta manji za stepen iskorišćenja mehaničkog prenosa:

$$m_{bu}\ t\ = \eta_r \cdot m_{ps\_sr}\ t\ \cdot i \qquad (2)$$

Sila na obimu bubnja je koja potiče od jednog pogona je:

$$F_{bu} = \frac{m_{bu}}{D_{bu}/2} = \frac{\eta_r \cdot m_{ps\_sr} \cdot i}{D_{bu}/2} \qquad (3)$$

Mehanička snaga koju predaje jedan pogon prema traci iznosi:

$$P_{meh} = F_{bu} \cdot v_{tr} = \frac{\eta_r \cdot m_{ps\_sr} \cdot i}{D_{bu}/2} \cdot v_{tr} \qquad (4)$$

Ukupna mehanička snaga koju predaju svi aktivni pogoni na transporteru preko dva pogonska bubnja se direktno ne meri već se izračunava na posredan način, na osnovu izmerene brzine kretanja trake [m/min] i estimirane procentualne vrednosti elektromagnetnog momenta motora [%] i karakteristika prenosnog mehanizma. Prema [6] stepen iskorišćenja mehaničkog prenosa kod dvobubanjskog transportera sa reduktorima iznosi 0,92. Poluprečnik bubnja je dužine 0,75 m, dok je prenosni odnos reduktora 17,26.

$$P_{meh\_ps}\ t\ = \sum_{1}^{3} F_{bui}\ t\ \cdot v_{tr} = 3 \cdot \frac{\eta_r \cdot m_{ps\_sr}\ t\ \cdot i}{D_{bu}/2} \cdot v_{tr} = 3 \cdot \frac{0,92 \cdot m_{ps\_sr}\ t\ \cdot 17,26}{1,5/2} \cdot v_{tr} \qquad (5)$$

Električna snaga koja se meri u dovodnoj ćeliji (+E1) predstavlja sumu aktivnih snaga frekventnih pretvarača FC1, FC3 i FC4 koji napajaju motore M1, M3 i M4, kao i transformatora T3 sopstvene potrošnje. Snaga sopstvene potrošnje je zanemarljiva u odnosu na snagu glavnih pogona i ne utiče bitno na stepen iskorišćenja pogonske stanice.

$$P_{el\_ps}\ t\ = P_{el\_M1}\ t\ + P_{el\_M3}\ t\ + P_{el\_M4}\ t\ + P_{el\_T3}\ t \qquad (6)$$

Izračunata vremenska promena stepena iskorišćenja pogonske stanice definisana je kao odnos korisne mehaničke snage koja se predaje traci i utrošene aktivne električne snage koja se uzima iz napojne mreže:

$$\eta_{ps}\ t\ = \frac{P_{meh\_ps}\ t}{P_{el\_ps}\ t} \qquad (7)$$

Posmatrajući bilans snaga na pogonskoj stanici stepen iskorišćenja pogonske stanice jednak je proizvodu stepena iskorišćenja svake komponente pogona transportera i zavisi od opterećenja:

$$\eta = \eta_r \cdot \eta_m \cdot \eta_{fp} \cdot \eta_{tr} \qquad (8)$$

η_r - stepen iskorišćenja mehaničkog prenosa dvobubanjskog transportera sa reduktorima
η_m - stepen iskorišćenja motora
η_{fp} - stepen iskorišćenja frekventnog pretvarača
η_{tr} - stepen iskorišćenja transformatora

Stepen iskorišćenja pogonske stanice pri nazivnom opterećenju (100%) iznosi 83%. Ova izračunata vrednost je veća od svih snimljenih vrednosti stepena iskorišćenja u posmatranom periodu, što je i očekivano jer su opterećenja bila manja od nazivne vrednosti, (tabela 1). Frekventni pretvarači pri nazivnoj učestanosti, što odgovara režimu rada sa konstantnom brzinom trake, pri smanjenju opterećenja imaju manju promenu stepena iskorišćenja u odnosu na asinhrone motore. Energetski transformatori takođe imaju manju promenu stepena iskorišćenja pri promeni opterećenja. Stepen iskorišćenja mehaničkog dela prenosa je konstantan i jednak nazivnoj vrednosti jer se brzina nije menjala.

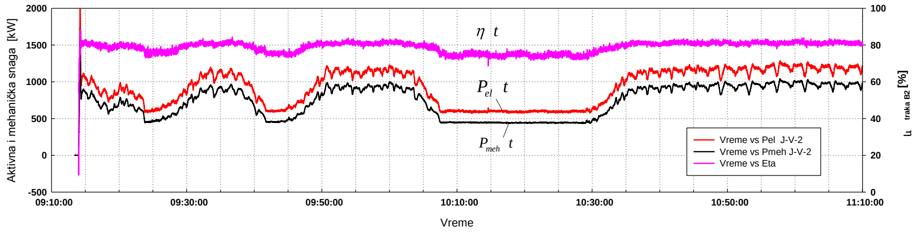
Tab. 1. *Izračunate vrednosti stepena iskorišćenja transportera za karakteristične vrednosti opterećenja*

Opterećenje [%]	Transformator	FC	Motor	Mehanika	Trafo T3	Sumarni
15	0.96	0.96	0.86	0.92	0.96	0.70
35	0.97	0.97	0.93	0.92	0.97	0.78
100	0.98	0.98	0.96	0.92	0.98	0.83

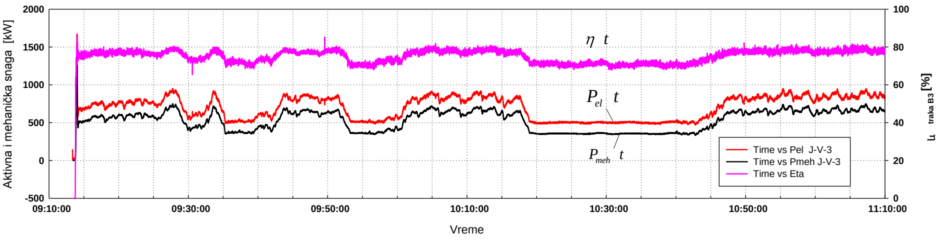
6. REZULTATI MERENJA

Na dijagramima (Slika 10 – Slika 13) upotrebljene su dve vertikalne ose sa različitim jedinicama i različitom razmerom. Vertikalnoj osi levo, dodeljene su vrednosti električne aktivne snage koje su dobijene je merenjem u dovodnoj ćeliji +E1. Na istoj osi dodeljene su u istoj razmeri i posredno izračunate vrednosti mehaničke snage na pogonskim bubnjevima. Stepen iskorišćenja transportera je dat u procentima i prikazan je na desnoj vertikalnoj osi. Za svaki transporter je dat istovetan dijagram i svi dijagrami imaju sinhronizovanu vremensku osu.

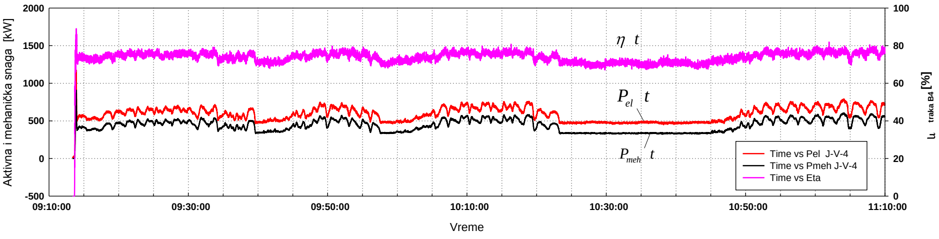
Na svim dijagramima mogu se uočiti periodi kada su trake radile prazne, bez materijala. U toku ovih perioda opterećenje pogona je konstantno i ima najmanju vrednost. Mehanička snaga transportera u ovim periodima pokriva samo mehaničke gubitke koji potiču od otpornih sila kretanja prazne trake. U toku ovih perioda kada na traci nema materijala, stepen iskorišćenja cele pogonske stanice pada na manju vrednost u odnosu na periode rada kada na traci ima materijala. Na ovo smanjenje najveći uticaj ima karakteristika stepena iskorišćenja asinhronog motora, prema kojoj se stepen iskorišćenja motora smanjuje pri opterećenjima manjim od nazivnog. U periodima kada na traci ima materijala opterećenje pogona je promenljivo i zavisi od protoka materijala koji stiže sa bagera. Mehanička snaga transportera pokriva sve otpore kretanja trake sa materijalom. Usled porasta opterećenja raste i stepen iskorišćenja pogonske stanice.



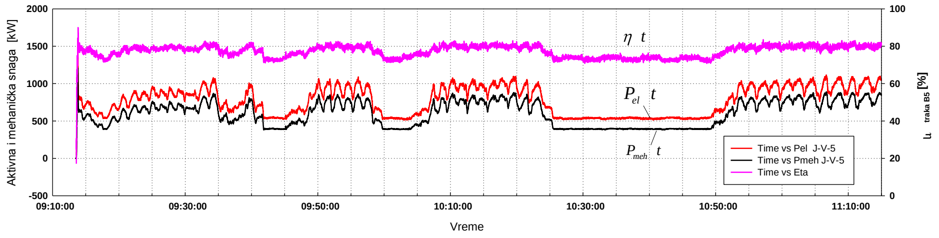
Sl. 10. *Aktivna električna snaga, mehanička snaga i stepen iskorišćenja, transporter B2*



Sl. 11. *Aktivna električna snaga, mehanička snaga i stepen iskorišćenja, transporter B3*



Sl. 12. *Aktivna električna snaga, mehanička snaga i stepen iskorišćenja, transporter B4*



Sl. 13. *Aktivna električna snaga, mehanička snaga i stepen iskorišćenja, transporter B5*

7. ZAKLJUČAK

Stepen iskorišćenja pogonske stanice pri konstantnoj brzini trake zavisi od procentualnog opterećenja pogona. Teorijska procena stepena iskorišćenja pogonske stanice daje vrednosti koje se slažu sa vrednostima stepena iskorišćenja dobijenih na osnovu eksperimentalnih snimaka. Optimizacija potrošnje električne energije, odnosno poboljšanje stepena iskorišćenja, u režimima rada kada je brzina trake konstantna praktično je neizvodljiva, jer svi algoritmi za optimizaciju podrazumevaju kontrolu brzine trake ili preseka materijala [5]. Za optimizaciju potrošnje energije pri konstantnoj brzini trake mogu se preduzeti sledeće mere:

- Izabrati komponente pogona sa većim stepenom iskorišćenja,
- Prilagoditi broj pogona na transporteru prema dužini trake,
- Smanjiti vreme rada sa praznom trakom, što zavisi od zastoja na bageru,
- Duži rad sa većim procentualnim opterećenjem, što zavisi od kapaciteta bagera.

Za ostvarivanje optimizacije potrošnje potrebno je primeniti regulaciju brzine u zavisnosti od opterećenja, odnosno protoka materijala [4,5]. Smanjivanje brzine dovodi do povećanja preseka materijala, što dalje dovodi do većeg mehaničkog opterećenja i boljeg stepena iskorišćenja transportera. Dakle, ne samo u režimima praznog hoda transportera već i kada traka ima materijala moguće je optimizacija potrošnje električne energije ako transporter radi u dužim periodima sa većim procentualnim opterećenjem.

LITERATURA

[1] M. Bebić, B. Jeftenić, D. Jevtić, N. Rašić, L. Ristić, S. Štatkić „Primena regulisanih asinhronih pogona napajanih iz frekventnih pretvarača na tračnim transporterima”, XIV Međunarodni simpozijum Energetska elektronika – Ee 2007 Novi Sad, Novembar 2007

[2] B. Jeftenić, M. Bebić, L. Ristić, D. Jevtić, I. Mihailović, N. Rašić, S. Štatkić, „Daljinski nadzor i upravljanje regulisanim pogonima sistema tračnih transportera”, 15th International Symposium on Power Electronics, October 2009, Novi Sad.

[3] B. Jeftenić, L. Ristić, I. Mihailović, D. Jevtić, M. Bebić, S. Štatkić, N. Rašić „Mogućnosti i iskustva u primeni energetski efikasnih tehnologija u transportu rastresitog materijala”, Zbornik radova (CD) sa II regionalne konferencije: industrijska energetika i zaštita životne sredine u zemljama jugoistočne Evrope - IEEP 2010, ISBN 978-86-7877-012-8, pp 1-8, Zlatibor, 22.-26. jun 2010.

[4] L. Ristić, M. Bebić, S. Štatkić, I. Mihailović, D. Jevtić, B. Jeftenić „Bulk Material Transportation System in Open Pit Mines with Improved Energy Efficiency”, Proc. of the 15th WSEAS International Conference on Systems (Part of the 15th WSEAS CSCC Multiconfrence), ISBN: 978-1-61804-023-7, ISSN: 1792-4235, Corfu Island, Greece, July 14-16, 2011, pp 327-332.

[5] D. Jevtić, I. Mihailović, L. Ristić, M. Bebić, S. Štatkić, N. Rašić, B. Jeftenić, „Improving Energy Efficiency of Belt Conveyor System” Proc. of the 16th International Symposium on Power Electronics - Ee2011, Novi Sad, Republic of Serbia, 26th – 28th, October, 2011, ISBN 978-86-7892-356-2, COBISS.SR-ID 266961671

[6] R. Borović, „Transport trakastim transporterima na površinskim kopovima”, Rudarsko-geološki fakultet, Beograd, 1997, ISBN 86-7352-004-5, (tabela 9.7).

MINING AND METALLURGY INSTITUTE BOR
UDK: 622

ISSN: 2334-8836 (Štampano izdanje)
ISSN: 2406-1395 (Online)

UDK: 550.8.013>622.235(045)=111

doi:10.5937/MMEB1503053L

Suzana Lutovac[*]*, Nebojša Vidanović*[*]*, Čedomir Beljić*[*]*, Zoran Gligorić*[*]

SOIL OSCILLATION LAW PARAMETER DETERMINATION WITH THE APPLICATION OF LAGRANGE'S THEOREM AT THE "KOVILOVAČA" OPEN PIT[**]

Abstract

Large scale mining as a method of extraction of mineral raw materials have a growing application with the aim to increase the quantity of blasted mass, and to reduce costs of production as well. Increasing the quantity of blasted mass requires the use of large amounts of explosives, leading to an increase in the negative effects of mining. Under negative effects of mining the seismic effect of blasting, effect of air waves, sound effect, scattering the blasted rock mass, and similar are assumed.

In order both to evaluate and control the seismic effect of blasting, as well as to plan it, the determination of soil oscillation law is required, with the strike: mine field - facilities to be protected. One of the most commonly used equations is that of M.A. Sadovski defining the law of alteration in the oscillation velocity of the soil depending on distance, explosive amount, and conditions of blasting and geologic characteristics of the soil, being determined on the basis of test blasting for the specific work environment. The Sadovsky equation is determined based on trial minings for a specific work environment.

In this paper, a special attention was paid to the seismic effect of blasting. In accordance with this, an analysis of the method for determining the soil oscillation law parameters, proposed by the Russian professor M.A. Sadovsky, was performed. For determination of parameters in the Sadovsky equation, in addition to the usual model - the least squares method, one more model is shown with the use of Lagrange's theorem. Thereby, it has been stated that both models can be used to calculate the oscillation velocity of the rock mass.

Keywords: *working environment, blasting, seismic effect, oscillation velocity, soil oscillation law*

1 INTRODUCTION

As the relation between the soil oscillation velocity and basic parameters affecting its magnitude, being: the amount of explosive, a distance from the blast site, characteristics of the rock material and a type of blasting, the equation of M.A. Sadovski, where the oscillation velocity v is given in the form of of the function, is most frequently used:

$$v = K \cdot R^{-n},$$

where R is a reduced distance, and K and n parameters conditioned by soil charac teristics and blasting conditions, thereby v is the decreasing convex function of the variable R.

By the application of the law of rock mass oscillation while blasting, the determination of the soil oscillation velocity is enabled for each blast operation in advance, thus blasting is, as regards seismic effect, under control, which gives an opportunity to plan the magnitude of shock waves for each future blast operation [2].

---

[*] *University of Belgrade, Faculty of Mining and Geology, Đušina 7, 11000 Belgrade, Serbia, e-mail: suzana.lutovac@rgf.bg.ac.rs; nebojsa.vidanovic@rgf.bg.ac.rs; cedomir.beljic@rgf.bg.ac.rs; zoran.gligoric@rgf.bg.ac.rs*;

[**] *This paper has resulted from the Project No. 33025 and 33029 financed by the Ministry of Education of the Republic of Serbia realized by the Faculty of Mining and Geology in Belgrade*

In this way the adverse blasting effects are reduced. The adverse effects of blasting imply, in addition to the seismic ones, those of air blast waves, fly rock, etc. Thus production efficiency is increased and, at the same time, construction and mining facilities, as well as the environment in the vicinity of the blast site are protected.

2 THE SOIL OSCILLATION LAW

To establish the correlation between the oscillation velocity and three basic parameters affecting its size: the explosive quantity, properties of rock material and the distance, there have been developed several mathematical models in the world. One of most frequently used models, i.e. equations, is the equation of Sadovski defining the law on velocity alteration of soil oscillation depending on the distance, the explosive quantity, and the way of blasting [10]. The law defined in this way offers the possibility to determine the seismic effect of blasting towards a facility or a settlement, whereby the connection, between the velocity of soil oscillation and consequences that can affect facilities, is used.

The equation of M.A Sadovski is given in the form:

$$\mathrm{v} = \mathrm{K} \cdot \left(\frac{\mathrm{r}}{\sqrt[3]{\mathrm{Q}}} \right)^{-\mathrm{n}} \qquad (1)$$

where:

- v - velocity of soil oscillation [cm/s]
- K - coefficient conditioned by soil characteristics and blasting conditions determined by terrain surveying,
- n - exponent, conditioned by soil properties and mining conditions and determined by field measurements as well,
- r - distance from the blast site to the monitoring point [m],
- Q - amount of explosive [kg].

2.1 Derivation of equation of rock mass oscillation law

The equation of Sadovski has been derived from the condition: if the radius of charge and the distance from the blast site to the monitoring point increase in the same or approximately the same ratio, the soil oscillation velocity remains the same [1], i. e. that is :

$$\mathrm{v} = \mathrm{K_v} \cdot \left(\frac{\mathrm{r_o}}{\mathrm{r}} \right)^{\mathrm{n}}, \qquad (2)$$

The radius of the explosive charge r_0 and the amount of explosive Q are related by the equation:

$$Q = \frac{4}{3} \cdot \pi \cdot r_o^3 ,$$

from where there is:

$$r_o = \sqrt[3]{\frac{3 \cdot Q}{4 \cdot \pi}} . \qquad (3)$$

By replacing the value r_o from the equation (3), in the equation, the following is obtained (2):

$$v = K_v \cdot \left(\frac{\sqrt[3]{\frac{3 \cdot Q}{4 \cdot \pi}}}{r} \right)^n = K_v \cdot \left(\sqrt[3]{\frac{3}{4 \cdot \pi}} \right)^n \cdot \left(\frac{\sqrt[3]{Q}}{r} \right)^n = K_v \cdot K_1 \cdot \left(\frac{r}{\sqrt[3]{Q}} \right)^{-n} = K \cdot \left(\frac{r}{\sqrt[3]{Q}} \right)^{-n} = K \cdot R^{-n}$$

Whereas:

$$\left(\sqrt[3]{\frac{3}{4 \cdot \pi}} \right)^n = K_1 ; \; K_v \cdot K_1 = K ; \; \frac{r}{\sqrt[3]{Q}} = R$$

whereby:

R - reduced distance is the distance from blasting point to observation point reduced to a quantity of explosive and given in the following form $R = \frac{r}{r_0}$

Thus, it was obtained the oscillation law of rock mass, i.e. the equation of Sadovski in the form:

$$v = K \cdot R^{-n} \tag{4}$$

2.2 Models of determination the soil oscillation law parameters

There are two parameters K and n in the equation (4) which should be determined for the specific work environment and by particular blasting conditions. With regard to the characteristics of the rock mass oscillation law, it is possible to determine the parameters K and n in a number of ways, i.e. models, thereby using the values obtained by experimental measurements.

♦ Determination of parameters by model 1

The smallest square method is mainly used to obtain the parameters K and n which represents a common model [3].

♦ Determination of parameters according to model 2

In the rock mass oscillation velocity law given by equation (4) in the form:

$$v = K \cdot R^{-n} \tag{4}$$

parameter n can be determined by successive approximations applying the Lagrange's theorem [8].

If rock mass oscillation velocity law given in equation (4) we differentiate by R, the following is obtained obtain:

$$v' = -n \cdot K \cdot R^{-n-1},$$

i.e.

$$v' = -\frac{n}{R} \cdot K \cdot R^{-n}. \tag{5}$$

Bearing in mind (4), equation (5) is reduced to:

$$v' = -\frac{n \cdot v}{R} \tag{6}$$

From (6) the following is found:

$$n = -v' \cdot \frac{R}{v} \tag{7}$$

If the derivative v' at some point R_c could not be found then from the equation (7), n can be determined. Value of derivative v′ can be determined using one of the formulas for numerical differentiation. For this purpose the Stirling's formula is frequently used in case of equidistant values for variable R. Here it is necessary that h is a small number, which is not the case with blasting operations in mining engineering.

Previous studies have shown that the value of the parameter n moves principally in the interval from 1 to 3, most often at an interval from 1 and 2.

To determine the parameter n, the Lagrange's theorem will be used, which states:

Let f(x) be a function continuous to [a,b] and differentiable on an interval (a, b). Then there is at least one c,

$a < c < b$,

for which it is:

$$\frac{f(b) - f(a)}{b-a} = f'(c).$$

In this case, given that the velocity is continuous, decreasing and convex function on [R_1, R_s], and differentiable on an interval (R_1,R_s), so the Lagrange's theorem is valid for it:

$$\frac{v(R_s) - v(R_1)}{R_s - R_1} = v'(R_c),$$

$$R_1 < R_c < R_s. \tag{8}$$

Bearing in mind the formulas (4) and (5), formula (8) is reduced to:

$$\frac{k \cdot R_s^{-n} - k \cdot R_1^{-n}}{R_s - R_1} = -k \cdot n \cdot R_c^{-n-1}, \tag{9}$$

namely to:

$$\frac{R_s^{-n} - R_1^{-n}}{R_s - R_1} = -n \cdot R_c^{-n-1},$$

$$R_1 < R_c < R_s. \tag{10}$$

From the equation (10) the following is obtained:

$$R_c = \left(\frac{n\cdot(R_s - R_1)}{R_1^{-n} - R_s^{-n}}\right)^{\frac{1}{n+1}},$$

$R_1 < R_c < R_s$. (11)

In practice it may be taken that R_1 is the smallest reduced distance, while R_s is the greatest reduced distance observed during blasting operations, i.e measurements.

In the formula (8), the values $v(R_s)$, $v(R_1)$, R_s and R_1 we take from the table of experimental data, so that we have:

$$\frac{v_s - v_1}{R_s - R_1} = v'(R_c). \qquad (12)$$

In this manner we find a derivative $v'(R_c)$ at point R_c, whereas R_c is given using formula (11).

In practice the formula (8) is used so that the values $v(R_s)$ and $v(R_1)$ are taken from tables of the experimental data obtained for corresponding reduced distances R_s i R_1, whereas for R_s the greatest reduced distance is taken, while for R_1 the smallest reduced distance is taken for each observed table.

To find the value $v'(R_c)$, in accordance with the formula (8), the formula will be used:

$$v'(R_c) = \frac{v_s - v_1}{R_s - R_1}, \qquad (13)$$

whereas:

v_s – registered rock mass oscillation velocity for the greatest reduced distance R_s,

v_1 – registered rock mass oscillation velocity for the smallest reduced distance R_1.

In this way $v'(R_c)$ is obtained, and then R_c is determined according to formula (11). In the formula (11) in determining the value R_c the parameter n appears. For an initial approximate value of the parameter n, it will be assumed that:

$n = n_o = 1{,}5$.

Now, according to the formula (11), for n = 1.5, the following is :

$$R_c = \left(\frac{1{,}5\cdot(R_s - R_1)}{R_1^{-1{,}5} - R_s^{-1{,}5}}\right)^{\frac{1}{2{,}5}}, \qquad (14)$$

where the obtained value R_c lies between values R_j i R_{j+1} given in the table of experimental data, which means:

$R_j < R_c < R_{j+1}$.

The value $v_c = v(R_c)$ should be obtained with the value for R_c determined in such a manner, whereas:

$v_j < v_c < v_{j+1}$.

To find the value $v_c = v(R_c)$, the interpolation formula will be applied:

$$v_c = v_j + \frac{v_{j+1} - v_j}{R_{j+1} - R_j}\cdot(R_c - R_j).$$

(15)

With the value v_c found in such a way, in accordance with the formula (7), the parameter n is obtained as:

$$n = -v'\cdot\frac{R_c}{v_c}, \qquad (16)$$

which will be marked wit n_1, so according to the formula (8):

$$n_1 = -v'\cdot\frac{R_c}{v_c}. \qquad (17)$$

Now, with value n_1 found like this, the formula (11) is used to determine the new values of R_c, where n_1 is put instead of n, where the previous procedure is continued for finding a new approximate value n_2 of parameter n.

In practice, after several iterations, a satisfactory value of the parameter n is obtained.

The value of parameter K we obtain from the formula (4), whereas:

$$K = v\cdot R^n \qquad (18)$$

In the equation (18) for n, the value obtained in the previous way is taken.

In so doing, data for pairs (R_m, v_m), m = 1, 2, ..., N, are used from the table of experimental data, so that:

$$K_1 = v_1 \cdot R_1^n$$
$$K_2 = v_2 \cdot R_2^n$$
$$...$$
$$K_N = v_N \cdot R_N^n,$$

whereby, for parameter K, the arithmetic mean is used, namely:

$$K = \frac{K_1 + K_2 + ... + K_N}{N}. \quad (19)$$

In this way, the model for solving the rock mass oscillation law is determined, taking:

$$v = K \cdot R^{-n}$$

which is valid for given environment, where blasting operations were performed.

3 DEFINING THE STATISTICAL CRITERIA

To evaluate the degree of correlation between recorded (measured) and calculated data in this paper, the *coefficient of linear correlation r* [5] was used between the logarithm of reduced distance R and the logarithm of the oscillation velocity v. Additionally, it was also taken into account the *curveline dependency index ρ* [4] between the reduced distance R and the oscillation velocity v.

The evaluation of the relationship degree of two variables [8] to values of the curveline dependency index *ρ* is given in the following survey:

$0.0 < \rho < 0.2$ - none or highly poor correlation,
$0.2 < \rho < 0.4$ - poor correlation,
$0.4 < \rho < 0.7$ - significant coorelation,
$0.7 < \rho < 1.0$ - strong or highly strong correlation.

The same is valid for the absolute value of linear correlation coefficient r.

As a convenience measure of the obtained functional relationship for the given experimental data, the criterion „3S“ was also used [6]. This criterion uses the squares of differences between the obtained experimental data and the calculated ones for oscillation velocities of v. If those differences are one after another ε_1, ε_2 ... ε_N, then it is :

$$S = \sqrt{\frac{\varepsilon_1^2 + \varepsilon_2^2 + ... + \varepsilon_N^2}{N}} \quad (20)$$

According to this criterion, for the evaluation of convenience of the obtained functional correlation, the following relations are valid:

- if it is $|\varepsilon_{max}| \geq 3S$, the obtained functional correlation is rejected as unfavorable,
- if it is $|\varepsilon_{max}| < 3S$, the functional correlation is accepted as a good one.

4 REVIEW OF MASSIVE BLASTING AT THE “KOVILOVAČA“ OPEN PIT - DESPOTOVAC

4.1 General characteristics of the “Kovilovača" open pit

The “Kovilovača“ limestone deposits have an exceptionally simple geological structure. Limestones of this area are massive or layered with layers of thickness from 0.20 to 0.80 m, the direction of propagation is NE-SW and a slope of about 42° towards the southwest. These rocks, in engineering and geological terms, belong to a group of associated rocks, which are cracked and carstified [7]. During previous exploitation and exploitation works, no significant burst deformations, which would significantly influence the process of exploration and exploitation, were noted in the deposit. Only after blasting, blocks of rocks 0.50 m^3 occur, which could be attributed to the effect of small faults and carstified cracks in the deposit.

By examination the physical and mechanical properties of the working environment, the following values are obtained:

- angle of internal friction	$\varphi = 31^{o}\ 35'$
- cohesion	$C = 138.33$ [kN/m^2]
- volume weight	$\gamma = 26.26$ [kN/m^3]
- compressive strength	$\sigma_p = 808.08$ [daN/cm^2]
- tensile strength	$\sigma_z = 75.90$ [daN/cm^2]
- velocity of longitudinal elastic waves	$c_p = 6{,}661.00$ [m/s]
- velocity of transverse elastic waves	$c_s = 2{,}852.67$ [m/s]
- dynamic elasticity modulus	$E_{din} = 62.46$ [GN/m^2]
- dynamic Poisson's ratio	$\mu_{din} = 0.39$ [GN/m^2]

4.2 Blasting Method

Measurements of seismic shocks at the ”Kovilovača” open pit were performed during blasting, conducted for the purpose of deposit exploitation [9]. Two blasting operations were performed.

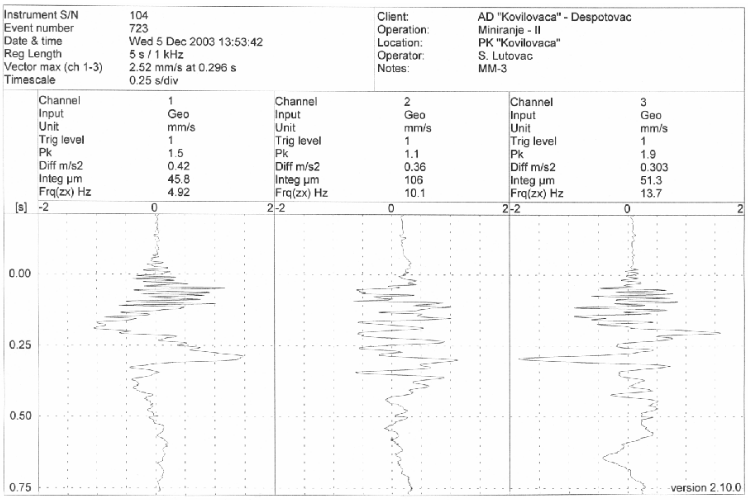
Balkanit 60/1500, detonex 65/1500 and ANFO 70/1500 were used as explosives. Activation of explosives in the borehole was performed using the nonel detonators with retardations of 500 ms in the borehole, while the retardation between boreholes on the surface was 25 ms and 42 ms. Activating of nonel tube was performed using electric detonator.

Basic data related to the number of boreholes (N_b), the overall explosive amount (Q_{uk}), the maximal exsplosive amount by deceleration interval (Q_i), overall borehole depth (L_{uk}), and average stemming length (L_{pc}), are presented in Table 1.

Table 1 *Survey of blasting parameters*

Blasting	N_b	Q_{uk}[kg]	Q_i[kg]	L_{uk}[m]	$L_{p\check{c}}$[m]
I	34	3623.0	108.0	842.0	2.2
II	7	3264.0	92.0	918.0	2.2

The record of soil oscillation velocity for blasting number II - measuring point 3 is shown in Fig.1



Instrument S/N	104	Client:	AD "Kovilovaca" - Despotovac
Event number	723	Operation:	Miniranje - II
Date & time	Wed 5 Dec 2003 13:53:42	Location:	PK "Kovilovaca"
Reg Length	5 s / 1 kHz	Operator:	S. Lutovac
Vector max (ch 1-3)	2.52 mm/s at 0.296 s	Notes:	MM-3
Timescale	0.25 s/div		

Channel	1	Channel	2	Channel	3
Input	Geo	Input	Geo	Input	Geo
Unit	mm/s	Unit	mm/s	Unit	mm/s
Trig level	1	Trig level	1	Trig level	1
Pk	1.5	Pk	1.1	Pk	1.9
Diff m/s2	0.42	Diff m/s2	0.36	Diff m/s2	0.303
Integ µm	45.8	Integ µm	106	Integ µm	51.3
Frq(zx) Hz	4.92	Frq(zx) Hz	10.1	Frq(zx) Hz	13.7

Figure 1 *Image of soil oscillation velocity for blasting II-MM3*

4.3 Calculation of soil oscillation law parameters

Values of distances from blast sites to monitoring points r, the amount of explosive Q, calculated values of reduced distances R, recorded values of soil oscillation velocities by components v_t,v_v,v_l and resulting oscillation velocities v_{rez} for blasting from I to II of totally ten measuring points MM are given in Table 2.

Table 2 *Survey of blasting parameters and measurement results*

No	Blasting	MM	r [m]	Q [kg]	R	v_t [cm/s]	v_v [cm/s]	v_l [cm/s]	v_{rez}[cm/s]
1	I	MM–1	335.0	3.623.0	21.8117	0.1460	0.0517	1.2000	1.2100
2	I	MM–3	850.0	3.623.0	55.3430	0.0138	0.0270	0.0617	0.0687
3	I	MM–7	950.0	3.623.0	61.8540	0.0222	0.0422	0.0623	0.0785
4	I	MM–8	1.155,0	3,623.0	75.2014	0.0327	0.0317	0.0246	0.0518
5	II	MM–3	860.0	3,264.0	57.9760	0.1400	0.1010	0.1830	0.2516
6	II	MM–5	830.0	3,264.0	55.9536	0.0206	0.0133	0.0407	0.0475
7	II	MM–6	965.0	3,264.0	65.0545	0.0045	0.0337	0.0555	0.0651
8	II	MM–6a	970.0	3,264.0	65.3916	0.0202	0.0568	0.0711	0.0932
9	II	MM–7	960.0	3,264.0	64.7174	0.0174	0.0477	0.0708	0.0871
10	II	MM–9	855.0	3,264.0	57.6390	0.0200	0.1070	0.0245	0.1116
11	II	MM–10	880.0	3,264.0	59.3234	0.0729	0.0936	0.0156	0.1197
12	II	MM–10a	885.0	3,264.0	59.6614	0.0134	0.1530	0.0426	0.1594

On the basis of data given in Table 2, the soil oscillation law is calculated by the formula (4) - by the models 1 and 2. The calculation of the curve was carried out for values of reduced distances from R = 21.8117 to R = 75.2014. Thus curve parameters were calculated enabling us determination the equation of soil oscillation in the form of :

♦ Model 1

$$v_1 = 2.131{,}52 \cdot R^{-2{,}4410} \qquad (21)$$

whereby the linear dependence between log v and log R was obtained, expressed by the equation (21), with *the linear correlation coefficient r* amounting: r = -0,8613

Graphic survey of soil oscillation law is shown in Figure 2.

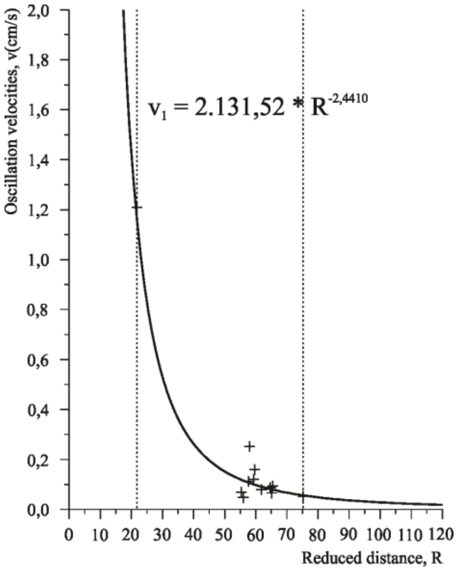


Figure 2 *Graphic survey of soil oscillation law curve at the OP „Kovilovača"*

♦ **Model 2**

$$v_2 = 38{,}9387 \cdot R^{-1{,}4227} \qquad (22)$$

On the basis of the obtained equations of soil oscillation (21) and (22), it is possible to calculate values of soil oscillation velocities for corresponding reduced distances for models 1 and 2.

Table 3 presents the survey of reduced distances R, recorded oscillation velocities v_r, calculated oscillation velocities v_{i1}, v_{i2} as well as the difference between recorded and calculated soil oscillation velocities for models 1 and 2.

Table 3 *Survey of recorded and calculated soil oscillation velocities for models 1 and 2*

No	R	v_r [cm/s]	v_{i1} [cm/s]	v_{i2} [cm/s]	$v_r - v_{i1}$	$v_r - v_{i2}$
1*	21.8117	1.2100	1.1507	0.4851	0.0593	0.7249
2	55.3430	0.0687	0.1185	0.1290	-0.0498	-0.0603
3	61.8540	0.0785	0.0904	0.1101	-0.0119	-0.0316
4	75.2014	0.0518	0.0561	0.0834	-0.0043	-0.0316
5	57.9760	0.2516	0.1058	0.1207	0.1458	0.1309
6	55.9536	0.0475	0.1154	0.1270	-0.0679	-0.0795
7	65.0545	0.0651	0.0799	0.1025	-0.0148	-0.0374
8	65.3916	0.0932	0.0789	0.1017	0.0143	-0.0085
9	64.7174	0.0871	0.0809	0.1032	0.0062	-0.0161
10	57.6390	0.1116	0.1073	0.1217	0.0040	-0.0101
11	59.3234	0.1197	0.1001	0.1168	0.0196	0.0029
12	59.6614	0.1594	0.0987	0.1159	0.0607	0.0435

Based on the data in Table 3, a statistical analysis was carried out and the following values were obtained:

Model 1:

The curveline dependency index ρ_1 between the reduced distance R and soil oscillation velocity is:

$\rho_1 = 0,9843$ (there is a *strong correlation* between R an v, given in the formula (22)).

The maximum differnce between the recorded and calculated oscillation velocities of the soil $\left(\varepsilon_{max}\right) = \max\left|\varepsilon_i\right|$, amounts:

$\varepsilon_{max1} = 0.1458$; $S_1 = 0.0552$;

$3S_1 = 0.1656$.

As there is $\varepsilon_{max1} < 3S_1$, supposed *functional relationship is accepted as a good one.*

Model 2:

$\rho_2 = 0.8513$ – for 11 values (there is a *strong correlation* between R an v, given in the formula (23)).

$\varepsilon_{max2} = 0.1309$; $S_2 = 0.0577$;

$3S_2 = 0.1713$

$\varepsilon_{max2} < 3S_2$ (supposed *functional relationship is accepted as a good one*).

5 CONCLUSION

To establish the relationship between the oscillation velocity of the rock mass and basic parameters affecting its magnitude, being: the amount of explosive, the distance from the blast site, characteristics of the rock mass and the type of blasting, it is the equation of M. A. Sadovski that is used most commonly.

In this study, parameters n and K in the law of Sadovsky were determined in two ways – models in the given work environment. The first model is the usual method of least squares, and the second model is derived by applying the Lagrange's theorem. Thereby corresponding functions were obtained presenting the oscillation velocities of the rock mass depending on a reduced distance. The calculated corresponding indexes of the curveline correlation point out that there is a highly strong curveline relationship between the reduced distance and oscillation velocity of the rock mass expressed in the obtained functions.

Comparing values of the recorded oscillation velocities of the rock mass with the corresponding calculated ones, it can be seen that they are approximately the same. On the basis of obtained values of curveline dependency coefficients and the values of linear correlation coefficients between the reduced distance logarithm and the oscillation velocity logarithm, it can be concluded that both models can be used for calculating the oscillation velocity of the rock mass.

REFERENCES

[1] Medvedev S. V. (1964): Seismika gornwh vzrwvov, Nedra, Moskva, str. 42-43.

[2] Trajković S., Slimak Š., Lutovac S,. (2005): Technique of Blasting and Eartquakes, Faculty of Mining and Geology, Belgrade, pp. 199.

[3] Simeunović D,.(1985): Mathematics, Faculty of Mining and Geology – Mining Department, Belgrade pp. 102-103.

[4] Ivanović B., (1973): Theoretical Statistics, Naučna knjiga, Belgrade, pp. 90 (in Serbian).

[5] Simonović V., (1995): Introduction to the Theory of Probability and Mathematical Statistics, TEKON - Tehnokonsalting, Belgrade, (in Serbian).

[6] Vukadinović S., (1970): Elements of Probability and Mathematical Statistics, Technique for Copying of the Bureau of Construction, Belgrade, pp. 329-331.

[7] Trajković S., Tokalić R., Lutovac S., (2004): Study of Seismic Impactson the Surrounding Building Structures as the Result of Blasting at the Open Pit "Kovilovača" - Despotovac, Faculty of Mining and Geology, Belgrade, pp. 1-47.

[8] Lutovac S., (2010). Model for Determining Parameters of the law Oscillation of the Rock Mass in blasting, Ph. D. Thesis, Faculty of Mining and Geology, Belgrade, pp. 1-240.

[9] Trajković S., Lutovac S., Tokalić R.; (2008): Analysis of the Soil Oscillation Law in the Example of the Open Pit „Kovilovača“, Podzemni radovi No.16, pp. 47-56, December 2008, RGF Belgrade.

[10] Savić M., (2000): Blasting at the Open Pits, Monograph, RTB Bor, Copper Institute Bor, Indok Center, Bor, pp. 317, (In Serbian).

INSTITUT ZA RUDARSTVO I METALURGIJU BOR
UDK: 622

ISSN: 2334-8836 (Štampano izdanje)
ISSN: 2406-1395 (Online)

UDK: 550.8.013:622.235(045)=163.41

doi:10.5937/MMEB1503053L

Suzana Lutovac[*], *Nebojša Vidanović*[*], *Čedomir Beljić*[*], *Zoran Gligorić*[*]

ODREĐIVANJE PARAMETARA ZAKONA OSCILOVANJA TLA UZ PRIMENU LAGRANŽOVE TEOREME NA PK „KOVILOVAČA“[**]

Izvod

Masovna miniranja, kao metoda eksploatacije mineralnih sirovina, imaju sve veću primenu, sa ciljem da se poveća količina odminirane mase i smanje troškovi proizvodnje. Povećanje količine odminirane mase zahteva upotrebu velikih količina eksploziva, što dovodi i do povećanja negativnih efekata miniranja. Pod negativnim efektima miniranja podrazumevamo seizmičko dejstvo miniranja, dejstvo vazdušnog talasa, zvučni efekat, razbacivanje odminirane stenske mase itd.

Za ocenu, kontrolu i planiranje seizmičkog dejstva miniranja, neophodno je utvrditi zakon oscilovanja tla u pravcu minsko polje – objekti koji se štite. Jedna od najčešće korišćenih je jednačina M.A. Sadovskog, koja definiše zakon promene brzine oscilovanja tla u zavisnosti od rastojanja, količine eksploziva, uslova izvođenja miniranja i geoloških karakteristika tla. Jednačina Sadovskog određuje se na osnovu probnih miniranja za konkretnu radnu sredinu.

U ovom radu posebna pažnja posvećena je seizmičkom dejstvu miniranja. U skladu sa tim izvršena je analiza metode za određivanje parametara zakona oscilovanja tla, koji je predložio ruski profesor M. A. Sadovski. Za određivanje parametara u jednačini Sadovskog, pored uobičajenog modela - metode najmanjih kvadrata, prikazan je još jedan model uz primenu Lagranžove teoreme. Pri tom je konstatovano da se oba modela mogu koristiti za izračunavanje brzine oscilovanja stenske mase.

Ključne reči: *radna sredina, miniranje, seizmičko dejstvo, brzina oscilovanja, zakon oscilovanja tla*

1. UVOD

Kao vezu između brzine oscilovanja tla i osnovnih parametara koji utiču na njenu veličinu, a to su: količina eksploziva, rastojanje od mesta miniranja, osobina stenskog materijala i način izvođenja miniranja, najčešće se koristi jednačina M. A. Sadovskog, gde je brzina oscilovanja v data u obliku:

$$v = K \cdot R^{-n},$$

gde R predstavlja redukovano tj. svedeno rastojanje, a parametri K i n uslovljeni su karakteristikama tla i uslovima miniranja. Pri tome je v opadajuća i konveksna funkcija promenljive R.

Primenom zakona oscilovanja stenske mase pri miniranju omogućava se da se za svako miniranje unapred odredi brzina oscilovanja tla, a miniranja se u pogledu seizmičkog dejstva stavljaju pod kontrolu, što pruža mogućnost da se veličina potresa za svako sledeće miniranje unapred planira [2]. Na taj način smanjuju se negativni efekti miniranja. Pod negativnim efektima mini-

---

[*] *Univerzitet u Beogradu, Rudarsko-geološki fakultet, Đušina 7, 11000 Beograd, Srbija, e-mail: suzana.lutovac@rgf.bg.ac.rs; nebojsa.vidanovic@rgf.bg.ac.rs; cedomir.beljic@rgf.bg.ac.rs; zoran.gligoric@rgf.bg.ac.rs;*

[**] *Rad je proistekao iz projekta broj 33025 i 33029 koji je finansiran sredstvima Ministarstva za prosvetu i nauku Republike Srbije, a čiji je realizator Rudarsko-geološki fakultet, Univerziteta u Beogradu*

ranja osim seizmičkog dejstva miniranja podrazumevamo i dejstvo vazdušnog talasa, zvučni efekat, razbacivanje odminirane stenske mase itd. Na taj način povećava se efikasnost proizvodnje i ujedno štite građevinski i rudarski objekti u okolini mesta miniranja, kao i životna sredina.

2. ZAKON OSCILOVANJA TLA

Za uspostavljanje korelacione veze između brzine oscilovanja i tri osnovna parametra koji utiču na njenu veličinu: količine eksploziva, osobine stenskog materijala i rastojanja, u svetu je razvijeno više modela. Jedan od najčešće korišćenih modela je jednačina Sadovskog, koja definiše zakon promene brzine oscilovanja tla u zavisnosti od rastojanja, količine eksploziva i načina izvođenja miniranja [10]. Tako definisan zakon pruža mogućnost da odredimo seizmičko dejstvo miniranja u pravcu nekog objekta ili naselja, pri čemu se koristi veza između brzine oscilovanja tla i posledica koje se mogu odraziti na objekte.

Jednačina M. A. Sadovskog data je u obliku:

$$v = K \cdot \left(\frac{r}{\sqrt[3]{Q}} \right)^{-n} \tag{1}$$

gde je:

v – brzina oscilovanja tla [cm/s],

K - koeficijent koji je uslovljen karakteristikama tla i uslovima miniranja, a određuje se terenskim merenjima,

n - eksponent koji je uslovljen karakteristikama tla i uslovima miniranja, a određuje se takođe terenskim merenjima,

r - rastojanje od mesta miniranja do mesta opažanja [m],

Q - količina eksploziva [kg].

2.1. Izvođenje jednačine zakona oscilovanja stenske mase

Jednačina Sadovskog izvedena je iz uslova: ako se radijus punjenja r_o i rastojanje od mesta izvođenja miniranja do mesta opažanja r povećavaju u istoj ili približno istoj razmeri brzina oscilovanja tla v ostaje ista [1], tj. da je:

$$v = K_v \cdot \left(\frac{r_o}{r} \right)^n , \tag{2}$$

Radijus eksplozivnog punjenja r_0 i količina eksploziva Q vezani su jednačinom:

$$Q = \frac{4}{3} \cdot \pi \cdot r_o^3 ,$$

odakle je:

$$r_o = \sqrt[3]{\frac{3 \cdot Q}{4 \cdot \pi}} . \tag{3}$$

Zamenom vrednosti r_o iz jednačine (3) u jednačini (2) dobijamo:

$$v = K_v \cdot \left(\frac{\sqrt[3]{\frac{3 \cdot Q}{4 \cdot \pi}}}{r} \right)^n = K_v \cdot \left(\sqrt[3]{\frac{3}{4 \cdot \pi}} \right)^n \cdot \left(\frac{\sqrt[3]{Q}}{r} \right)^n = K_v \cdot K_1 \cdot \left(\frac{r}{\sqrt[3]{Q}} \right)^{-n} = K \cdot \left(\frac{r}{\sqrt[3]{Q}} \right)^{-n} = K \cdot R^{-n}$$

gde je stavljeno:

$$\left(\sqrt[3]{\frac{3}{4 \cdot \pi}} \right)^n = K_1 ; \; K_v \cdot K_1 = K ; \; \frac{r}{\sqrt[3]{Q}} = R$$

i gde je:

R - redukovano rastojanje ili svedeno rastojanje koje predstavlja rastojanje od mesta miniranja do mesta opažanja svedeno na količinu eksploziva, a dato je u obliku $R = \frac{r}{r_0}$

Na taj način dobili smo zakon oscilovanja stenske mase tj. jednačinu Sadovskog u obliku:

$$v = K \cdot R^{-n} \tag{4}$$

2.2. Modeli određivanja parametara zakona oscilovanja tla

U jednačini (4) javljaju se dva parametra K i n, koje treba odrediti za konkretnu radnu sredinu i pri određenim uslovima miniranja. S obzirom na svojstvo zakona oscilovanja stenske mase, moguće je parametre K i n odrediti na više načina tj. modela, koristeći pri tome vrednosti dobijene eksperimentalnim merenjima.

♦ Određivanje parametara po modelu 1

Za dobijanje parametara (K) i (n) uglavnom se koristi metoda najmanjih kvadrata, koja predstavlja uobičajeni model [3].

♦ Određivanje parametara po modelu 2

U zakonu brzine oscilovanja stenske mase datog po jednačini (4) u obliku:

$$v = K \cdot R^{-n} \tag{4}$$

parametar n možemo odrediti uzastopnim aproksimacijama uz primenu Lagranžove teoreme [8].

Ako zakon brzine oscilovanja stenske mase dat jednačinom (4) diferenciramo po R dobićemo:

$$v' = -n \cdot K \cdot R^{-n-1},$$

tj.

$$v' = -\frac{n}{R} \cdot K \cdot R^{-n}. \tag{5}$$

Imajući u vidu (4), jednačina (5) se svodi na:

$$v' = -\frac{n \cdot v}{R}. \tag{6}$$

Iz (6) nalazimo:

$$n = -v' \cdot \frac{R}{v}. \tag{7}$$

Ako bismo našli izvod v' u nekoj tački R_c, onda iz jednačine (7) možemo da odredimo n. Vrednost izvoda v′ možemo odrediti pomoću neke od formula za numeričku diferencijaciju. U tu svrhu često se koristi formula Stirlinga za slučaj ekvidistantnih vrednosti za promenljivu R. Pri tome je potrebno da korak h bude mali broj što na primerima miniranja u rudarstvu nije slučaj.

Ranija ispitivanja su pokazala da se vrednost parametra n kreće uglavnom u intervalu od 1 do 3, najčešće u intervalu od 1 do 2.

Za određivanje parametra n koristićemo Lagranžovu teoremu koja glasi:

Neka je funkcija f(x) neprekidna na [a,b] i diferencijabilna u intervalu (a, b). Tada postoji bar jedno c,

$a < c < b$,

za koje je:

$$\frac{f(b) - f(a)}{b - a} = f'(c).$$

U našem slučaju, s obzirom da je brzina oscilovanja neprekidna, opadajuća i konveksna funkcija na $[R_1, R_s]$ i diferencijabilna u intervalu (R_1, R_s), za nju važi Lagranžova teorema:

$$\frac{v(R_s) - v(R_1)}{R_s - R_1} = v'(R_c),$$

$$R_1 < R_c < R_s. \tag{8}$$

Imajući u vidu formule (4) i (5), formula (8) se svodi na:

$$\frac{k \cdot R_s^{-n} - k \cdot R_1^{-n}}{R_s - R_1} = -k \cdot n \cdot R_c^{-n-1}, \tag{9}$$

tj. na:

$$\frac{R_s^{-n} - R_1^{-n}}{R_s - R_1} = -n \cdot R_c^{-n-1},$$

$$R_1 < R_c < R_s. \tag{10}$$

Iz jednačine (10) dobijamo:

$$R_c = \left(\frac{n \cdot (R_s - R_1)}{R_1^{-n} - R_s^{-n}} \right)^{\frac{1}{n+1}},$$

$R_1 < R_c < R_s$. (11)

U praksi se može uzeti da je R_1 najmanje redukovano rastojanje, a R_s najveće redukovano rastojanje koje je posmatrano prilikom miniranja tj. merenja.

U formuli (8) vrednosti $v(R_s)$, $v(R_1)$, R_s i R_1 uzimamo iz tabele eksperimentalnih podataka, tako da imamo:

$$\frac{v_s - v_1}{R_s - R_1} = v'(R_c). \qquad (12)$$

Na ovaj način nalazimo izvod $v'(R_c)$ u tački R_c, gde je R_c dato pomoću formule (11).

U praksi formulu (8) koristimo tako što vrednosti $v(R_s)$ i $v(R_1)$ uzimamo iz tabela dobijenih eksperimentalnih podataka za odgovarajuća redukovana rastojanja R_s i R_1, pri čemu za R_s uzimamo najveće redukovano rastojanje, a za R_1 najmanje redukovano rastojanje za svaku posmatranu tabelu.

Za nalaženje vrednosti $v'(R_c)$, u skladu sa formulom (8), koristićemo formulu:

$$v'(R_c) = \frac{v_s - v_1}{R_s - R_1} \qquad (13)$$

gde je:

- v_s - registrovana brzina oscilovanja stenske mase za najveće redukovano rastojanje R_s,
- v_1 - registrovana brzina oscilovanja stenske mase za najmanje redukovano rastojanje R_1.

Na ovaj način dobijamo $v'(R_c)$, a zatim R_c određujemo po formuli (11). U formuli (11) za određivanje vrednosti R_c javlja se parametar n. Za početnu približnu vrednost parametra n uzećemo da je:

$n = n_o = 1,5$.

Sada, prema formuli (11), za n = 1,5 dobijamo:

$$R_c = \left(\frac{1,5 \cdot (R_s - R_1)}{R_1^{-1,5} - R_s^{-1,5}} \right)^{\frac{1}{2,5}}, \qquad (14)$$

gde se dobijena vrednost R_c nalazi između vrednosti R_j i R_{j+1} datih u tabeli eksperimentalnih podataka, što znači:

$R_j < R_c < R_{j+1}$.

Sa ovako određenom vrednošću za R_c treba da odredimo vrednost $v_c = v(R_c)$, pri čemu je:

$v_j < v_c < v_{j+1}$.

Za nalaženje vrednosti $v_c = v(R_c)$ koristićemo interpolacionu formulu:

$$v_c = v_j + \frac{v_{j+1} - v_j}{R_{j+1} - R_j} \cdot (R_c - R_j). \qquad (15)$$

Sa ovako nađenom vrednošću v_c, u skladu sa formulom (7), dobijamo parameter n kao:

$$n = -v' \cdot \frac{R_c}{v_c}, \qquad (16)$$

koji ćemo označiti sa n_1, pa prema formuli (8) imamo:

$$n_1 = -v' \cdot \frac{R_c}{v_c}. \qquad (17)$$

Sada, sa ovako nađenom vrednošću n_1 koristimo formulu (11) za određivanje nove vrednosti R_c, gde umesto n stavljamo n_1, pri čemu nastavljamo prethodni postupak za nalaženje nove približne vrednosti n_2 parametra n.

U praksi, posle nekoliko iteracija dobija se zadovoljavajuća vrednost parametra n.

Vrednost parametra K dobijamo iz formule (4), pri čemu je:

$$K = v \cdot R^n \qquad (18)$$

U jednačini (18) za n uzimamo vrednost koju smo dobili na prethodni način.

Pri tome se koriste podaci za parove (R_m, v_m), m = 1,2,...,N, iz tabele eksperimentalnih podataka, tako da uzimamo:

$$K_1 = v_1 \cdot R_1^n$$

$$K_2 = v_2 \cdot R_2^n$$

$$\dots$$

$$K_N = v_N \cdot R_N^n ,$$

pri čemu za parametar K uzimamo njegovu aritmetičku sredinu tj:

$$K = \frac{K_1 + K_2 + \ldots + K_N}{N} . \qquad (19)$$

Na ovaj način odredili smo model rešavanja zakona oscilovanja stenske mase, uzimajući:

$$v = K \cdot R^{-n}$$

koji važi za datu sredinu gde je izvršeno miniranje.

3. DEFINISANJE STATISTIČKIH KRITERIJUMA

Za ocenu stepena povezanosti između registrovanih (izmerenih) i izračunatih podataka u ovom radu koristili smo *koeficijent linearne korelacije r* [5] između logaritama redukovanog rastojanja R i logaritama brzine oscilovanja v. Pored toga, uzimali smo u obzir i *indeks krivolinijske zavisnosti ρ* [4] između redukovanog rastojanja R i brzine oscilovanja v.

Ocena stepena povezanosti dve promenljive [8] prema vrednostima indeksa krivolinijske zavisnosti ρ data je u narednom pregledu:

0,0 < ρ < 0,2 nikakva ili veoma slaba veza,

0,2 < ρ < 0,4 slaba povezanost,

0,4 < ρ < 0,7 značajna povezanost,

0,7 < ρ < 1,0 jaka ili vrlo jaka povezanost.

Isto važi i za apsolutnu vrednost koeficijenta linearne korelacije r.

Kao mera pogodnosti dobijene funkcionalne veze za date eksperimentalne podatke koristili smo i kriterijum „3S“ [6]. Ovaj kriterijum koristi kvadrate razlika između dobijenih eksperimentalnih podataka i izračunatih podataka za brzine oscilovanja v. Ako su te razlike redom ε_1, ε_2 ... ε_N, tada je:

$$S = \sqrt{\frac{\varepsilon_1^2 + \varepsilon_2^2 + \ldots + \varepsilon_N^2}{N}} \qquad (20)$$

Prema ovom kriterijumu, za ocenu pogodnosti dobijene funkcionalne veze važe sledeći odnosi:

- ako je $|\varepsilon_{max}| \geq 3S$, odbacuje se dobijena funkcionalna veza kao nepovoljna,
- ako je $|\varepsilon_{max}| < 3S$, prihvata se funkcionalna veza kao dobra.

4. PRIKAZ MASOVNIH MINIRANJA NA PK „KOVILOVAČA“ - DESPOTOVAC

4.1. Opšte karakteristike površinskog kopa „Kovilovača"

Ležište krečnjaka "Kovilovača" ima izuzetno prostu geološku građu. Krečnjaci ove zone su masivni ili slojeviti, pri čemu su slojevi debljine 0,20–0,80 m, pravac pružanja im je SI-JZ i pad od oko 42° prema jugozapadu. Ove stene, u inženjersko-geološkom smislu pripadaju grupi vezanih stena, koje su ispucale i karstifikovane [7]. Dosadašnjim istražnim i eksploatacionom radovima u ležištu nisu konstatovane značajne rupturne deformacije, koje bi bitno uticale na proces istraživanja i eksploatacije. Jedino se posle miniranja javljaju blokovi stena od 0,50 m^3, koji bi se mogli pripisati uticaju manjih raseda i karstifikovanih pukotina u ležištu.

Ispitivanjem fizičko - mehaničkih osobina radne sredine dobijene su sledeće vrednosti:

- ugao unutrašnjeg trenja	$\varphi = 31^{o}\ 35'$
- kohezija	$C = 138{,}33\ [kN/m^2]$
- zapreminska težina	$\gamma\ = 26{,}26\ [kN/m^3]$
- čvrstoća na pritisak	$\sigma_p = 808{,}08\ [daN/cm^2]$
- čvrstoća na zatezanje	$\sigma_z = 75{,}90\ [daN/cm^2]$
- brzina longitudinalnih elastičnih talasa	$c_p = 6.661{,}00\ [m/s]$
- brzina transverzalnih elastičnih talasa	$c_s = 2.852{,}67\ [m/s]$
- dinamički modul elastičnosti	$E_{din} = 62{,}46\ [GN/m^2]$
- dinamički Poasonov koeficijent	$\mu_{din} = 0{,}39\ [GN/m^2]$

4.2. Način izvođenja miniranja

Merenja seizmičkih potresa na PK „Kovilovača“ obavljena su pri miniranjima koja se izvode radi eksploatacije ležišta [9]. Izvedena su dva miniranja.

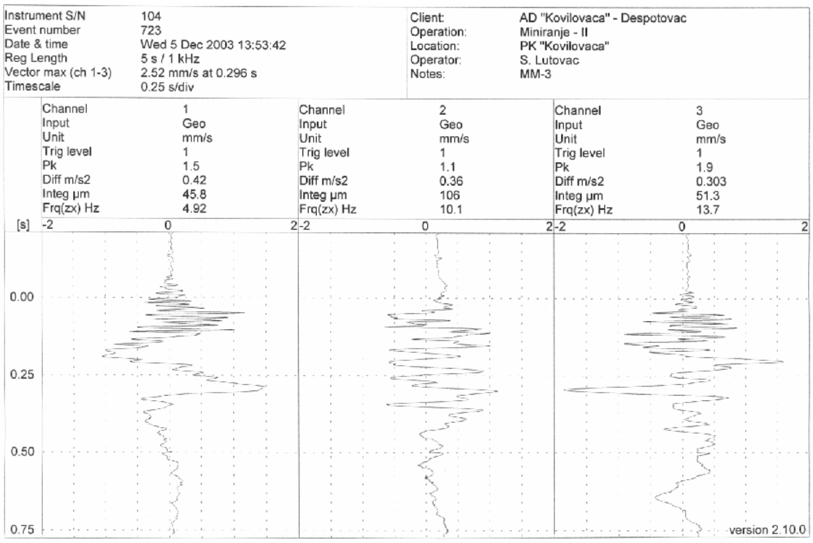
Kao eksploziv korišćen je balkanit 60/1500, i detonex 65/1500, kao i ANFO 70/1500. Aktiviranje eksploziva u bušotinama vršeno je nonel detonatorima i to sa usporenjima u bušotini od 500 ms, dok je usporenje između bušotina na površini bilo od 25 ms i 42 ms. Aktiviranje nonel cevčice izvršeno je električnim detonatorom.

Osnovni podaci vezani za broj bušotina N_b, ukupnu količinu eksploziva Q_{uk}, maksimalnu količinu eksploziva po intervalu usporenja Q_i, ukupnu dubinu bušotina L_{uk}, i prosečnu dužinu čepa $L_{pč}$, dati su u tabeli 1.

Tabela 1. *Prikaz parametara miniranja*

Miniranje	N_b	Q_{uk}[kg]	Q_i[kg]	L_{uk}[m]	$L_{pč}$[m]
I	34	3623,0	108,0	842,0	2,2
II	7	3264,0	92,0	918,0	2,2

Na slici 1. prikazan je snimak brzine oscilovanja tla za miniranje broj II - merno mesto broj 3.



Instrument S/N 104
Event number 723
Date & time Wed 5 Dec 2003 13:53:42
Reg Length 5 s / 1 kHz
Vector max (ch 1-3) 2.52 mm/s at 0.296 s
Timescale 0.25 s/div

Client: AD "Kovilovaca" - Despotovac
Operation: Miniranje - II
Location: PK "Kovilovaca"
Operator: S. Lutovac
Notes: MM-3

Channel	1	Channel	2	Channel	3
Input	Geo	Input	Geo	Input	Geo
Unit	mm/s	Unit	mm/s	Unit	mm/s
Trig level	1	Trig level	1	Trig level	1
Pk	1.5	Pk	1.1	Pk	1.9
Diff m/s2	0.42	Diff m/s2	0.36	Diff m/s2	0.303
Integ µm	45.8	Integ µm	106	Integ µm	51.3
Frq(zx) Hz	4.92	Frq(zx) Hz	10.1	Frq(zx) Hz	13.7

Sl. 1. *Snimak brzine oscilovanja tla za miniranje II – MM3*

4.3. Proračun parametara zakona oscilovanja tla

Vrednosti rastojanja od mesta miniranja do mesta opažanja r, količina eksploziva Q, izračunate vrednosti redukovanih rastojanja R, registrovane vrednosti brzina oscilovanja tla po komponentama v_t, v_v, v_l i rezultujuće brzine oscilovanja v_{rez} za miniranja I - II na ukupno deset mernih mesta MM date su u tabeli 2.

Tabela 2. *Prikaz parametara miniranja i rezultata merenja*

R.b.	Min. b.	MM	r [m]	Q [kg]	R	v_t [cm/s]	v_v [cm/s]	v_l [cm/s]	v_{rez}[cm/s]
1	I	MM–1	335,0	3.623,0	21,8117	0,1460	0,0517	1,2000	1,2100
2	I	MM–3	850,0	3.623,0	55,3430	0,0138	0,0270	0,0617	0,0687
3	I	MM–7	950,0	3.623,0	61,8540	0,0222	0,0422	0,0623	0,0785
4	I	MM–8	1.155,0	3.623,0	75,2014	0,0327	0,0317	0,0246	0,0518
5	II	MM–3	860,0	3.264,0	57,9760	0,1400	0,1010	0,1830	0,2516
6	II	MM–5	830,0	3.264,0	55,9536	0,0206	0,0133	0,0407	0,0475
7	II	MM–6	965,0	3.264,0	65,0545	0,0045	0,0337	0,0555	0,0651
8	II	MM–6a	970,0	3.264,0	65,3916	0,0202	0,0568	0,0711	0,0932
9	II	MM–7	960,0	3.264,0	64,7174	0,0174	0,0477	0,0708	0,0871
10	II	MM–9	855,0	3.264,0	57,6390	0,0200	0,1070	0,0245	0,1116
11	II	MM–10	880,0	3.264,0	59,3234	0,0729	0,0936	0,0156	0,1197
12	II	MM–10a	885,0	3.264,0	59,6614	0,0134	0,1530	0,0426	0,1594

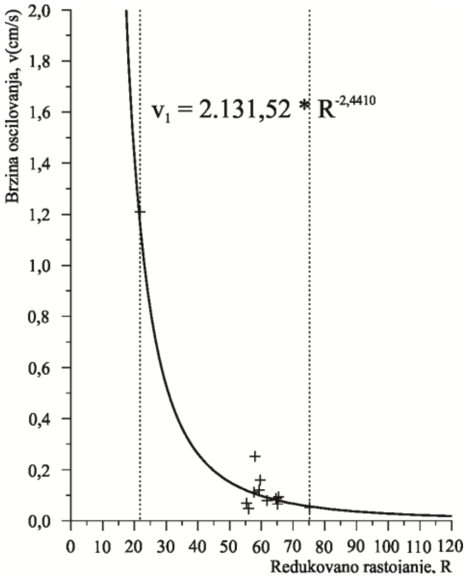
Na osnovu podataka datih u tabeli 2 izračunava se zakon oscilovanja tla po formuli (4) - po modelima 1 i 2. Proračun krive izvršen je za vrednosti redukovanih rastojanja od R = 21,8117 do R = 75,2014. Na taj način izračunati su parametri krive, koji omogućuju da se odredi jednačina oscilovanja tla u obliku:

♦ Model 1

$$v_1 = 2.131{,}52 \cdot R^{-2{,}4410} \qquad (21)$$

pri čemu je između log v i log R dobijena linearna zavisnost, izražena jednačinom (21) sa *koeficijentom linearne zavisnosti r* koji iznosi: r = -0,8613

Grafički prikaz zakona oscilovanja tla dat je na slici 2.



Sl. 2. *Grafički prikaz brzine oscilovanja tla na PK „Kovilovača“*

◆ **Model 2**

$$v_2 = 38{,}9387 \cdot R^{-1{,}4227} \qquad (22)$$

Na osnovu dobijenih jednačina oscilovanja tla (21) i (22), moguće je izračunati vrednosti brzina oscilovanja tla za odgovarajuća redukovana rastojanja za model 1 i 2.

U tabeli 3. dat je pregled redukovanih rastojanja R, registrovanih brzina oscilovanja tla v_r, izračunatih brzina oscilovanja tla v_{i1}, v_{i2}, kao i razlika između registrovanih i izračunatih brzina oscilovanja tla za model 1 i 2.

Tabela 3. *Prikaz registrovanih i izračunatih brzina oscilovanja tla za model 1 i 2*

Redni broj	R	v_r [cm/s]	v_{i1} [cm/s]	v_{i2} [cm/s]	$v_r - v_{i1}$	$v_r - v_{i2}$
1*	21,8117	1,2100	1,1507	0,4851	0,0593	0,7249
2	55,3430	0,0687	0,1185	0,1290	-0,0498	-0,0603
3	61,8540	0,0785	0,0904	0,1101	-0,0119	-0,0316
4	75,2014	0,0518	0,0561	0,0834	-0,0043	-0,0316
5	57,9760	0,2516	0,1058	0,1207	0,1458	0,1309
6	55,9536	0,0475	0,1154	0,1270	-0,0679	-0,0795
7	65,0545	0,0651	0,0799	0,1025	-0,0148	-0,0374
8	65,3916	0,0932	0,0789	0,1017	0,0143	-0,0085
9	64,7174	0,0871	0,0809	0,1032	0,0062	-0,0161
10	57,6390	0,1116	0,1073	0,1217	0,0040	-0,0101
11	59,3234	0,1197	0,1001	0,1168	0,0196	0,0029
12	59,6614	0,1594	0,0987	0,1159	0,0607	0,0435

Na osnovu podataka iz tabele 3. izvršena je statistička analiza i dobijene su sledeće vrednosti.

Model 1:

Indeks krivolinijske zavisnosti ρ_1 između redukovanog rastojanja R i brzine oscilovanja tla v, iznosi:

$\rho_1 = 0{,}9843$ (postoji *vrlo jaka povezanost* između R i v, data u formuli (22)).

Maksimalna razlika između registrovanih i izračunatih brzina oscilovanja tla $\left(\varepsilon_{max}\right) = \max\left|\varepsilon_i\right|$, iznosi:

$\varepsilon_{max1} = 0{,}1458$; $S_1 = 0{,}0552$;

$3S_1 = 0{,}1656$.

Pošto je $\varepsilon_{max1} < 3S_1$, pretpostavljena *funkcionalna veza se prihvata kao dobra*.

Model 2:

$\rho_2 = 0{,}8513$ – za 11 podataka (postoji *vrlo jaka povezanost* između R i v, data u formuli (22)).

$\varepsilon_{max2} = 0{,}1309$; $S_2 = 0{,}0577$;

$3S_2 = 0{,}1713$.

$\varepsilon_{max2} < 3S_2$ (pretpostavljena *funkcionalna veza prihvata se kao dobra*).

5. ZAKLJUČAK

Za uspostavljanje veze između brzine oscilovanja stenske mase i osnovnih parametara koji utiču na njenu veličinu, a to su: količina eksploziva, rastojenje od mesta miniranja, osobina stenskog materijala i način izvođenja miniranja, najčešće se koristi jednačina profesora M. A. Sadovskog.

U ovom radu parametri n i K u zakonu Sadovskog određivani su na dva načina – modela u datoj radnoj sredini. Prvi model predstavlja uobičajenu metodu najmanjih kvadrata, a drugi model je izveden uz primenu Lagranžove teoreme. Pri tome su dobijene odgovarajuće funkcije kojima su predstavljene brzine oscilovanja stenske mase u zavisnosti od redukovanog rastojanja. Izračunati odgovarajući indeksi krivolinijske korelacije pokazuju da između redukovanog rastojanja i brzine oscilovanja stenske mase postoji vrlo jaka krivolinijska veza izražena dobijenim funkcijama.

Upoređujući vrednosti registrovanih brzina oscilovanja stenske mase sa odgovarajućim izračunatim vrednostima, vidimo da one imaju približno iste vrednosti. Na osnovu dobijenih vrednosti koeficijenata krivolinijske zavisnosti i vrednosti koeficijenata linearne korelacije između logaritama redukovanog rastojanja i logaritama brzine oscilovanja zaključujemo da se oba modela mogu koristiti za izračunavanje brzine oscilovanja stenske mase.

LITERATURA

[1] Medvedev S. V. (1964): Seismika gornwh vzrwvov, Nedra, Moskva, str. 42-43.

[2] Trajković S., Slimak Š., Lutovac S,. (2005): Tehnika miniranja i potresi, RGF Beograd, str. 199.

[3] Simeunović D., (1985): Matematika, RGF – Rudarski odsek, Beograd, str. 102-103.

[4] Ivanović B., (1973): Teorijska statistika, Naučna knjiga, Beograd, str. 90.

[5] Simonović V., (1995): Uvod u teoriju verovatnoće i matematičku statistiku, TEKON - Tehnokonsalting, Beograd.

[6] Vukadinović S., (1970): Elementi računa verovatnoće i matematičke statistike, Tehnika za umnožavanje Biroa za građevinarstvo, Beograd, str. 329-331.

[7] Trajković S., Tokalić R., Lutovac S., (2004): Studija seizmičkih uticaja na okolne građevinske objekte kao posledica izvođenja miniranja na PK "Kovilovača" - Despotovac, RGF Beograd, str. 1-47.

[8] Lutovac S., (2010). Model određivanja parametara zakona oscilovanja stenske mase pri miniranju, Doktorska disertacija, RGF Beograd, str 1-240.

[9] Trajković S.; Lutovac S.; Tokalić R., (2008): Analiza zakona oscilovanja tla na primeru PK "Kovilovača", Časopis Podzemni radovi br. 16, str. 47-56, RGF Beograd.

[10] Savić M., (2000): Miniranje na površinskim kopovima, Monografija, RTB Bor Institut za bakar Bor, Indok centar, Bor, str. 317.

MINING AND METALLURGY INSTITUTE BOR
UDK: 622

ISSN: 2334-8836 (Štampano izdanje)
ISSN: 2406-1395 (Online)

UDK: 622.271:681.8:330.1(045)=111

doi:10.5937/MMEB1503073K

Daniel Kržanović[*], *Radmilo Rajković*[*], *Miomir Mikić*[*], *Milenko Ljubojev*[*]

ANALYSIS THE POSSIBILITY OF INCREASING CAPACITY OF COPPER ORE MINING AT THE OPEN PIT SOUTH MINING DISTRICT MAJDANPEK AT 11x10^6 TONS ANNUALLY[**]

Abstract

The paper analyzes the possibility of increasing capacity at the Open Pit South Mining District in terms of achieving maximum net present value. The analysis is based on the movement of discounted cash flow during exploitation period of 18 years. The modern approach of designing the open pits was used for this consideration using the software Whittle and Gemcom Gems.

The analysis showed a positive trend of discounted cash flow from the third year until the end of analyzed period in achieving the net present value in the amount of 596 252 546 $.

Keywords: *Open Pit South mining District Majdanpek, optimization of boundary of open pit, open pit development phase, net present value, software Whittle, Gemcom*

INTRODUCTION

Mining works at the open pit South Mining District, which were suspended in May 2009, continued in 2012 by stripping the deposit on location Andesite finger, on the basis of designed technical solutions by the experts from the Mining and Metallurgy Institute Bor from Bor [1], [2].

In accordance with the new strategic plan of development of copper production in RTB with the annual production capacity of 80-85 000 t of ore, it is necessary to increase the capacity of ore mining and processing at the open pit South Mining District from the existing capacity of 8.5 million tons to 11 million tons annually. Among others, this is one of the prerequisites for achieving the profitable mining and processing of copper ore.

The long-term designing of the open pit and solution to the problem of optimization was achieved by modeling the problems using software. Software, which were used, Whittle and Gems, their work based on an algorithm that is applied to a three-dimensional block model of the ore body South Mining District

Technical and economic analysis were carried out in software Whittle, while the deposit modeling and design of optimal contour of the open pit and development phase of the open pit development were carried out in software Gemcom Gems.

---

[*] *Mining and Metallurgy Institute Bor, e-mail: daniel.krzanovic@irmbor.co.rs*

[**] *This work is the result of the Project 33021 "Investigation and Monitoring the Changes of Stress-strain State in the Rock Mass "In-situ" around the Underground Rooms with Development a Model with Special Reference on the Tunel of the Krivelj River and Jama Bor", funded by the Ministry of Education, Science and Technological Development of the Republic of Serbia.*

PROBLEMS OF THE PRODUCTION SYSTEM AT THE OPEN PIT

The basic problem of the production system at the open pit South Mining District is:

- Deviation from designed calendar plan of excavation.
- Implementation of works out of designed boundaries of the open pit.
- Delay in revitalization and rehabilitation of mining machines and infrastructure facilities (transport system for overburden TS-1 crushing plant for ore).
- Pumping of mine water, which is of crucial importance for ore mining at the open pit, has not yet commenced. Also a problem is in defining an optimal technology for treatment of such waters, as well as the treatment plant.

Also, in the coming period it is necessary to carry out the relocation of capital infrastructural facilities in the coming period, as follows:

- A route of the state road M22 I B order.
- A part of the route of the existing power line 35 kV.
- The riverbed of the river Mali Pek.
- The town collector of waste water.

METHODOLOGY

Analysis of the possibility of increasing the capacity of mining was carried out on the basis of long-term planning of copper ore exploitation at the open pit South Mining District.

The conducted analysis in this paper, with the aim of maximizing the net present value is achieved by application the method of geostatistical modeling, method of long-term planning and optimization method for open pits.

The procedure is carried out through the following steps:

1) The first step presents a development of block model using the statistical methods for analysis and assessment. Deposit modeling was performed in the software Gemcom Gems.
2) The second step is optimization the final contours of the open pit. The basis for optimization is the block model. In this paper, optimization of the open pit of copper ore was carried out in the software Whittle that applied a modified Lerchs-Grossmann algorithm. Software for generating the nested pits and defining the pushbacks uses a technique of parameterization (Revenue Factors), and calculation is based on undiscounted cash values.
3) The third step is to define the development phases of the open pit. The main reason for planning the development phase of the open pit is of economic nature, i.e. maximization the net present value.

In defining the development phases of the open pit, the following requirements are satisfied [3]:

- There is a minimum allowable distance between the phase boundaries.
- There is a minimum working width of each phase bottom.
- NPV of each phase is positive.
- NPV for defined phases is maximum.

In addition to the economic, the practical importance of the phase open pit development is also considered, and it is applied to the problems caused by the excessive number of phases which can lead to [3]:

- increase in costs for maintenance of many sites,

- increase in costs due to the redevelopment of transport routes,
- insufficient width of the working platforms for operation of mechanization,
- increased number of the primary and auxiliary equipment, etc.

4) The fourth step defining the mining dynamics. The analysis is based on the Milawa algorithm, which is supported by the software Whittle, and it is specifically designed for defining the mining dynamics in long-term planning strategies of exploitation.

Modeling of deposit

Geological reserves of the copper deposit South Mining District Majdanpek were calculated by the method of mini blocks, whereby the dimensions of the blocks are 15×15×15 m. The basis for calculation the geological reserves is a digital block model of deposit which was formed in the software Gemcom using the geostatistical methods of analysis and assessment [4], [5].

Figure 1 shows a three dimensional view of the block model Cu in the deposit South Mining District.

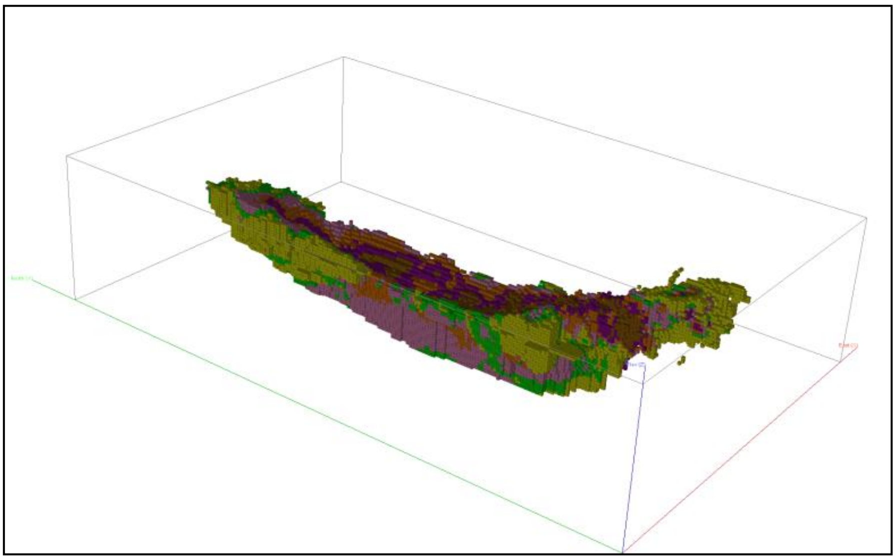


Figure 1 *Three dimensional view of the block model Cu in the deposit South Mining District*

Optimization of the open pit boundary

Optimization process was carried out on the basis of defining the selling price of metals, discount rate and costs and efficiency of excavation, flotation and metallurgical treatment.

Table 1 presents the starting parameters used to define the optimal contour of the open pit and defining the excavation phases.

Table 1 *Starting parameters for optimization the open pit boundary and defining the excavation phases*

Parameter	Unit	Value
Base metal prices		
– Copper	USD/t	6 000.00
– Gold	USD/kg	35 000.00
– Silver	USD/kg	650.00
Costs of ore mining	USD/t	1.50
Costs of overburden mining	USD/t	2.50
Costs of flotation ore processing	USD/t	3.20
Costs of metallurgical treatment of concentrate		
– Costs of copper production from concentrates	USD/t Cu cathode	600.00
– Costs of gold refining	USD/kg	150.00
– Costs of silver refining	USD/kg	15.00
Flotation copper recovery from ore	%	86.0
Metallurgical copper recovery from ore	%	98.5
Total recovery on gold	%	50.0
Total recovery on silver	%	50.0
Discount rate	%	10

Ore mining capacities are limited by years, based on assessment the possibility of increasing the capacity of flotation processing.

The planned value of ore mining capacity at annual level is as follows:

1. In the 1st and 2nd year
   6 000 000 t of ore
- In the 3rd year
  8 500 000 t of ore
- in the 4th year to the end of the exploitation period
  11 000 000 t of ore

Overburden mining is limited by the capacity of the transport system for waste TS-1 (27 million tons per year) and capacity of the external waste dumps (Table 2 and Figure 2). Due to this reason, maximum designed capacity of waste is 32 million tons per year.

Table 2 *View the capacities of the external waste dumps*

Capacities of the outer waste dumps				**Total**
Kovej	Andesite finger	Bugarski potok	Dump	
1 995 000	8 000 000	13 000 000	23 500 000	**46 495 000**

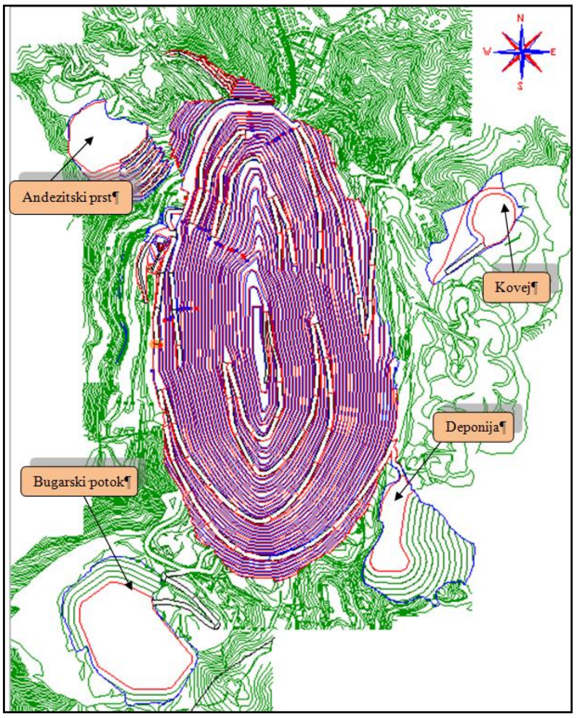


Figure 2 *View of the truck dumps*

The optimum boundary of excavation the open pit was obtained using the software for optimization and strategic planning of the open pits Whittle [6], [7].

Figure 3 graphically shows the results of optimization for the base copper price of 6000 USD/t, on the basis of which the optimal contour of the open pit and development phases of the open pit are selected.

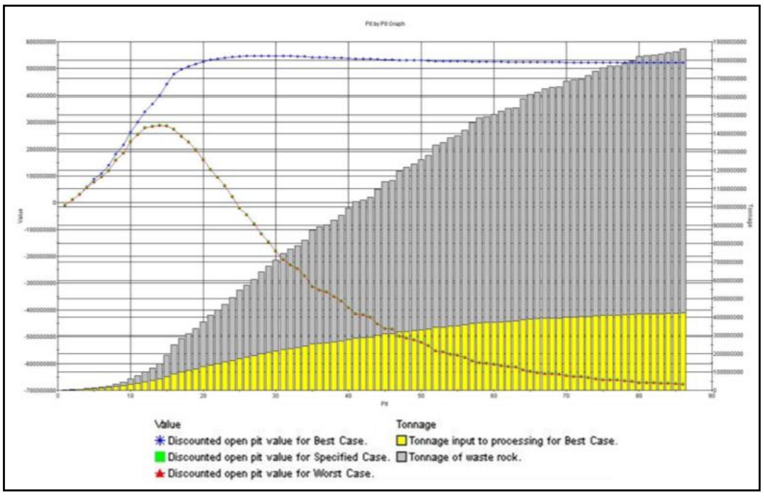


Figure 3 *Graphical presentation of optimization results (Pit by pit graph)*

It can be seen from graph that, for the adopted technical-economic parameters the open pit No. 25 was chosen as the optimal one. The selected open pit has total of 549,837,135 t excavation, out of which 175,536,668 t of ore and 374,300,467 t of overburden. Overburden coefficient is 2.13 t/t.

Defining the development phases of the open pit (Pushbacks)

After determining the final borders of mining, the next step in the process of designing the open pits is to define the excavation phases.

Simulations and DCF analysis are carried out in this step to obtain the most favorable variant, or determine the number of phases that affect the maximization of net present value for long-term planning of open pits.

Based on the results of optimization, which is graphically shown in Figure 3, the excavation phases are defined and those are the open pits Nos. 18 and 22. Based on a need of providing the quantities of ore by the mining dynamics, according to the request of the Investor, with minimum quantity of overburden, it is necessary to split the open pit No. 18 into four phases, whereby the northern part is the Phase 1, the eastern phase is the Phases 2 and 3, and the southern and western part are designated as the Phase 4. Pursuant to the adopted rule of labeling the phases, the open pits Nos. 22 and 25 are defined as the Phase 5 and Phase 6, respectively (Figure 4).

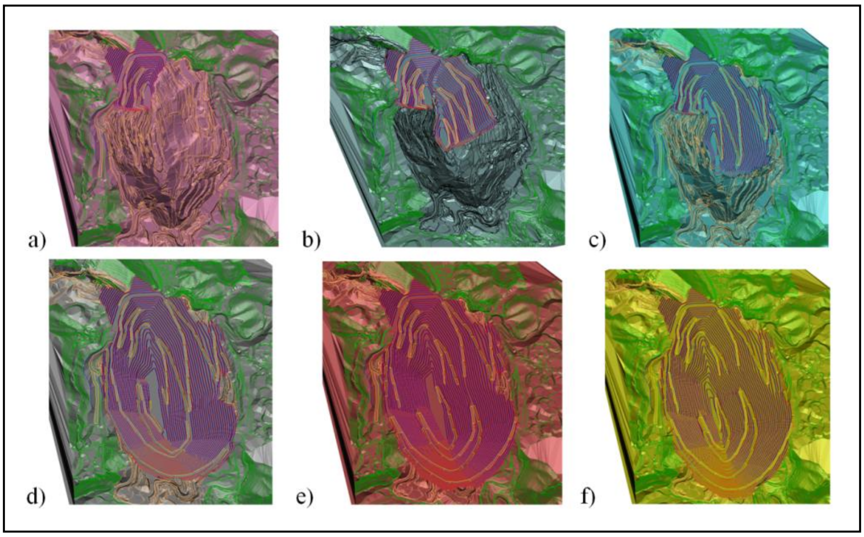


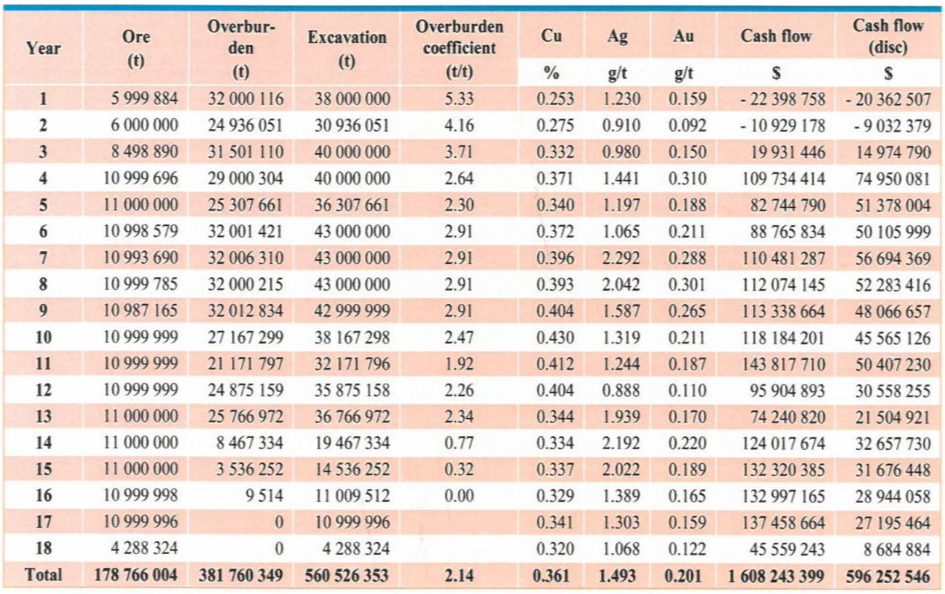
Figure 4 *View of the final contour (3D view)*
a) Phase 1; b) Phase 2; c) Phase 3; d) Phase 4; e) Phase 5; f) Phase 6

Optimization of mining dynamics

Mining dynamics by years of exploitation was obtained in Whittle software. To optimize the mining dynamics, the used software was Milawa algorithm for balancing regime (Milawa Balanced) [8].

Results of optimization the mining dynamics are shown in Table 3.

Table 3 *Mining dynamics by years and periods of exploitation*



Year	Ore (t)	Overbur-den (t)	Excavation (t)	Overburden coefficient (t/t)	Cu	Ag	Au	Cash flow	Cash flow (disc)
					%	g/t	g/t	$	$
1	5 999 884	32 000 116	38 000 000	5.33	0.253	1.230	0.159	- 22 398 758	- 20 362 507
2	6 000 000	24 936 051	30 936 051	4.16	0.275	0.910	0.092	- 10 929 178	- 9 032 379
3	8 498 890	31 501 110	40 000 000	3.71	0.332	0.980	0.150	19 931 446	14 974 790
4	10 999 696	29 000 304	40 000 000	2.64	0.371	1.441	0.310	109 734 414	74 950 081
5	11 000 000	25 307 661	36 307 661	2.30	0.340	1.197	0.188	82 744 790	51 378 004
6	10 998 579	32 001 421	43 000 000	2.91	0.372	1.065	0.211	88 765 834	50 105 999
7	10 993 690	32 006 310	43 000 000	2.91	0.396	2.292	0.288	110 481 287	56 694 369
8	10 999 785	32 000 215	43 000 000	2.91	0.393	2.042	0.301	112 074 145	52 283 416
9	10 987 165	32 012 834	42 999 999	2.91	0.404	1.587	0.265	113 338 664	48 066 657
10	10 999 999	27 167 299	38 167 298	2.47	0.430	1.319	0.211	118 184 201	45 565 126
11	10 999 999	21 171 797	32 171 796	1.92	0.412	1.244	0.187	143 817 710	50 407 230
12	10 999 999	24 875 159	35 875 158	2.26	0.404	0.888	0.110	95 904 893	30 558 255
13	11 000 000	25 766 972	36 766 972	2.34	0.344	1.939	0.170	74 240 820	21 504 921
14	11 000 000	8 467 334	19 467 334	0.77	0.334	2.192	0.220	124 017 674	32 657 730
15	11 000 000	3 536 252	14 536 252	0.32	0.337	2.022	0.189	132 320 385	31 676 448
16	10 999 998	9 514	11 009 512	0.00	0.329	1.389	0.165	132 997 165	28 944 058
17	10 999 996	0	10 999 996		0.341	1.303	0.159	137 458 664	27 195 464
18	4 288 324	0	4 288 324		0.320	1.068	0.122	45 559 243	8 684 884
Total	**178 766 004**	**381 760 349**	**560 526 353**	**2.14**	**0.361**	**1.493**	**0.201**	**1 608 243 399**	**596 252 546**

CONCLUSION

The performed analysis the possibilities for increasing the capacity at the open pit South Mining District was carried out using the software for optimization and strategic planning of the open pits Whittle, which is based on an analysis of trends the discounted cash flow during its service period, or the net present value, and that is an indicator of the achieved economic results of exploitation the deposit South Mining District for the given initial conditions. Deposit modeling and design of optimal contour of the open pit and the phases of development the open pit are carried out in the software Gemcom Gems

On the basis of performed analysis, the following is concluded:

1) There is a possibility to increase the capacities of copper ore excavation at the open pit South Mining District Majdanpek, which is realized in the 4th year for the analyzed period.
2) Service life of the open pit mining is 18 years.
3) Movement in cash flow is positive throughout the whole period of exploitation, except in the first and second year of the analyzed period.
4) The net present value is achieved in the amount of **596,252,546 $**.

REFERENCES

[1] D. Kržanović et al., Feasibility Study on Mining the South Mining District Deposit in the Copper Mine Majdanpek (MMI Bor, 2011.), (in Serbian)

[2] D. Kržanović et al. Additional Mining Design of Copper Ore Mining from the South Mining District Deposit in the Copper Mine Majdanpek (MMI Bor), (in Serbian)

[3] D. Kržanović, R. Rajković, M. Mikić, M. Ljubojev: Effect of Stage Development of Mining Operations on Maximization the Net Present Value in Long-Term Planning of Open Pits, Mining and Metallurgy Engineering Bor, 4/2014, pp. 33-40;

[4] D. Kržanović, M. Žikić, R. Pantović: Important Improvement of Utilization the Available Geological Reserves of the South Mining District Deposit in Majdanpek in the New Defined Optimum Contour of the Open Pit Using the Whittle and Gemcom Software, Mining Engineering, Mining and Metallurgy Institute Bor, 2012, pp. 29-36

[5] D. Kržanović, M. Žikić, Z. Vaduvesković: Innovated Block Model of the Copper Ore Deposit South Mining District-Majdanpek As a Basis for Analysis the Optimum Development of Open Pit Using the Software Packages Whittle and Gemcom, Mining Engineering, Mining and Metallurgy Institute Bor, 2011, pp 69-76

[6] G. Whittle, W. Stange and N. Hanson, Optimising Project Value and Robustness, Project Evaluation Conference, Melbourne, Vic, 19 - 20 June 2007, pp. 1-10;

[7] D. Kržanović, R. Rajković, M. Mikić: The Effect of Open Pit Slope Design on Net Present Value for Long Term Planning, The 46th International October Conference on Mining and Metallurgy, Bor Lake, Serbia, 2014;

[8] D. Kržanović, R. Rajković, M. Mikić, M. Ljubojev: Effect of Stage Development of Mining Operations on Maximization the Net Present Value in Long-Term Planning of Open Pits.

INSTITUT ZA RUDARSTVO I METALURGIJU BOR
UDK: 622
ISSN: 2334-8836 (Štampano izdanje)
ISSN: 2406-1395 (Online)

UDK: 622.271:681.8:330.1(045)=111
doi:10.5937/MMEB1503073K

Daniel Kržanović[*], *Radmilo Rajković*[*], *Miomir Mikić*[*], *Milenko Ljubojev*[*]

ANALIZA MOGUĆNOSTI POVEĆANJA KAPACITETA OTKOPAVANJA RUDE BAKRA NA POVRŠINSKOM KOPU JUŽNI REVIR MAJDANPEK NA 11x10^6 TONA GODIŠNJE[**]

Izvod

U radu je izvršena analiza mogućnosti povećanja kapaciteta na površinskom kopu Južni revir sa aspekta ostvarivanja maksimizacije neto sadašnje vrednosti. Analiza se bazira na kretanju diskontovanog novčanog toka tokom eksploatacionog perioda od 18 godina. Za ovo sagledavanje korišćen je savremeni pristup projektovanju površinskih kopova primenom softvera Whittle i Gemcom Gems.

Analiza je pokazala pozitivno kretanje diskontovanog novčanog toka od treće godine do kraja analiziranog perioda, pri čemu se ostvaruje neto sadašnja vrednost u iznosu od ***596.252.546 $.***

Ključne reči: *površinski kop Južni revir Majdanpek, optimizacija granice kopa, fazni razvoj kopa, neto sadašnja vrednost, softver Whittle, softver Gemcom Gems*

UVOD

Rudarski radovi na površinskom kopu Južni revir, koji su obustavljeni maja 2009. godine, nastavljeni su 2012. godine, raskrivanjem ležišta na lokaciji Andezitskog prsta, na osnovu projektovanih tehničkih rešenja od starne stručnjaka iz Instituta za rudarstvo i metalurgiju Bor iz Bora [1], [2].

U skladu sa novim strateškim planom razvoja proizvodnje bakra u RTB-u sa godišnjim kapacitetom proizvodnje od 80-85.000 t rude, neophodno je povećanje i kapaciteta otkopavanja i prerade rude na površinskom kopu Južni revir sa postojećeg kapaciteta od 8,5 miliona tona na 11 miliona tona na godišnjem nivou. Pored ostalih, ovo je jedan od preduslova za ostvarenje profitabilne eksploatacije i prerade rude bakra.

Dugoročno projektovanje površinskog kopa i rešenje problema optimizacije ostvareno je modeliranjem problema primenom softvera. Softveri koji su korišćeni, Whittle i Gems, svoj rad baziraju na algoritmu koji se primenjuje na trodimenzionalnom blok modelu rudnog tela Južni revir.

Tehničko-ekonomska analiza izvršena je u sofveru Whittle, dok je modeliranje ležišta i konstrukcija optimalne konture kopa i faza razvoja kopa izvršena u softveru Gemcom Gems.

---

[*] *Institut za rudarstvo i metalurgiju Bor, e-mail: daniel.krzanovic@irmbor.co.rs*

[**] *Ovaj rad je proistekao kao rezultat projekta 33021 „Istraživanje i praćenje promena naponsko deformacijskog stanja u stenskom masivu „in-situ“ oko podzemnih prostorija sa izradom modela sa posebnim osvrtom na tunel Kriveljske reke i Jame Bor“, koga finansira Ministarstvo prosvete, nauke i tehnološkog razvoja Republike Srbije*

PROBLEMATIKA PROIZVODNOG SISTEMA NA KOPU

Osnovna problematika proizvodnog sistema na površinskom kopu Južni revir jeste:

- Odstupanje od projektovanog kalendarskog plana otkopavanja.
- Izvođenje radova van projektovanih granica kopa.
- Kašnjenje u revitalizaciji i sanaciji rudarskih mašina i infrastukturnih objekata (transportni sistem za jalovinu TS-1, drobilično postrojenje za rudu).
- Ispumpavanje rudničkih voda, što je od presudnog značaja za otkopavanje rude na kopu, nije započeto. Problem je i definisanje optimalne tehnologije prečišćavanja tih voda, kao i samog postrojenja za prečišćavanje.

Takođe, u narednom periodu neophodno je da se izvrši izmeštanje kapitalnih infrastukturnih objekata i to:

- trase državnog puta M22 I B reda,
- dela trase postojećeg dalekovoda 35 kV,
- korita reke Mali Pek,
- gradskog kolektora otpadnih voda.

METODOLOGIJA

Analiza mogućnosti povećanja kapaciteta otkopavanja sprovedena je na osnovu dugoročnog planiranja eksploatacije rude bakra na površinskom kopu Južni revir.

Sprovedena analiza u ovom radu sa ciljem postizanja maksimalne neto sadašnje vrednosti, ostvarena je primenom metoda geostatističkog modeliranja, metoda dugoročnog planiranja i metoda optimizacije površinskih kopova.

Procedura je sprovedena je kroz sledeće korake:

1) Prvi korak predstavlja izradu blok modela primenom geostatističkih metoda za analizu i procenu. Modeliranje ležišta izvršeno je u softveru Gemcom Gems.
2) Drugi korak je optimizacija završne konture površinskog kopa. Osnova za optimizaciju jeste blok model. U ovom radu optimizacija površinskog kopa rude bakra izvršena je u softveru Whittle, koji primenjuje modifikovani Lerchs-Grossmann algoritam. Softver za generisanje ugnježdenih kopova i definisanje pushback-ova koristi tehniku parametrizacije (Revenue Factors), a proračun se zasniva na nediskontovanim novčanim vrednostima.
3) Treći korak je definisanje faza razvoja površinskog kopa. Osnovni razlog za planiranje faznog razvoja kopa jeste ekonomske prirode, odnosno maksimizacija neto sadašnje vrednosti.

Kod definisanje faza razvoja kopa zadovoljeni su sledeći zahtevi [3]:

- postoji minimalno dozvoljeno rastojanje između granica faza,
- postoji minimalna radna širina dna svake faze,
- NPV svake faze je pozitivna,
- NPV za definisane faze je maksimalna.

Pored ekonomskog, uvažen je i praktičan značaj faznog razvoja kopa, a odnosi se na problematiku uzrokovanu prevelikim brojem faza što može da dovede do [3]:

- povećanja troškova zbog održavanja više radilišta,
- povećanja troškova zbog ponovne izrade transportnih puteva,

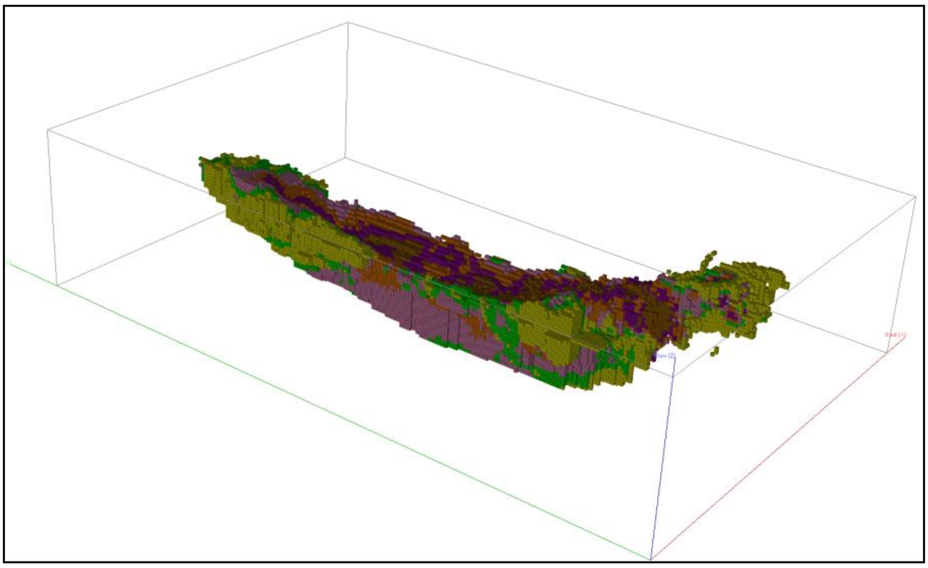
  - nedovoljne širina radnih platoa za rad mehanizacije,
  - povećanog broj osnovne i pomoćne opreme i dr.

4) Četvrti korak predstavlja definisanje dinamike otkopavanja. Analiza se bazira na Milawa algoritmu, koji podržava softver Whittle, a specifično je namenjen za definisanje dinamike otkopavanja kod strategije dugoročnog planiranja eksploatacije.

Modelovanje ležišta

Geološke rezerve ležište bakra Južni revir Majdanpek sračunate su metodom mini blokova, pri čemu su dimenzije blokova 15×15×15 m. Osnova za za proračun geoloških rezervi jeste digitalni blok model ležišta koji je formiran u softveru Gemcom, primenom geostatističkih metoda analize i procene [4], [5].

Na slici 1 prikazan je trodimenzionalni izgled blok modela Cu u ležištu Južni revir.



Sl. 1. *Trodimenzionalni izgled blok modela Cu u ležištu Južni revir*

Optimizacija granice površinskog kopa

Proces optimizacije sproveden je na osnovu definisane prodajne cene metala, diskontne stope i troškova i iskorišćenja otkopavanja, flotacijske i metalurške prerade.

U tabeli 1 dati polazni parametri koji su poslužili za definisanje optimalne konture kopa i definisanje faza otkopavanja.

Tabela 1. *Polazni parametri za optimizaciju granice kopa i definisanje faza otkopavanja*

Parametar	Jedinica	Vrednost
Bazne cene metala		
– Bakra	USD/t	6 000,00
– Zlata	USD/kg	35 000,00
– Srebra	USD/kg	650,00
Troškovi otkopavanja rude	USD/t	1,50
Troškovi otkopavanja jalovine	USD/t	2,50
Troškovi flotacijske prerade rude	USD/t	3,20
Troškovi metalurške prerade koncentrata		
– Troškovi proizvodnje bakra iz koncentrata	USD/t Cu katode	600,00
– Troškovi rafinacije zlata	USD/kg	150,00
– Troškovi rafinacije srebra	USD/kg	15,00
Flotacijsko iskorišćenje bakra iz rude	%	86,0
Metalurško iskorišćenje bakra iz rude	%	98,5
Ukupno iskorišćenje na zlatu	%	50,0
Ukupno iskorišćenje na srebru	%	50,0
Diskontna stopa	%	10

Kapaciteti otkopavanja rude limitirani su po godinama, na osnovu procene mogućnosti povećanja kapaciteta flotacijske prerade.

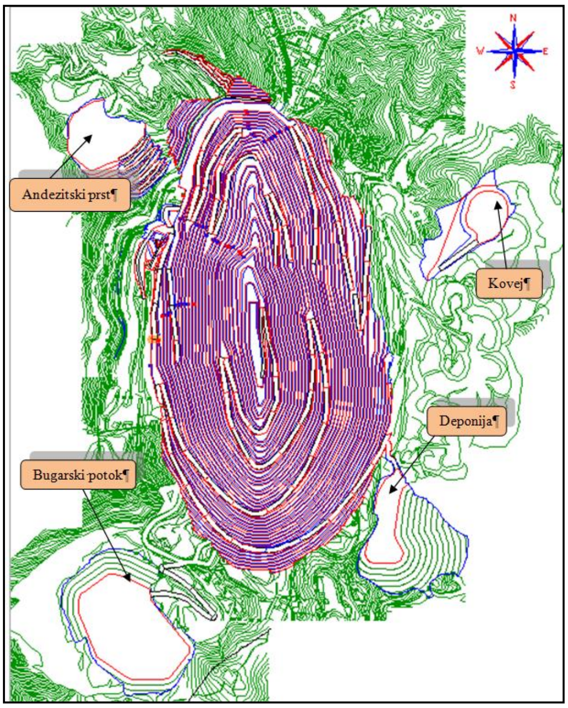
Planirana vrednost kapaciteta otkopavanja rude na godišnjem nivou sledeća:

- ➢ u 1. i 2. godini
  6.000.000 t rude
- ➢ u 3. godini
  8.500.000 t rude
- ➢ u 4. godini do kraja eksploatacionog perioda
  11.000.000 t rude

Otkopavanje jalovine ograničena je kapacitetom transportnog sistema za jalovinu TS-1 (27 miliona tona godišnje) i kapacitetom spoljašnjih odlagališta jalovine (tabela 2 i slika 2). Iz tog razloga maksimalni projektovani kapacitet jalovine iznosi 32 miliona tona godišnje.

Tabela 2. *Prikaz kapaciteta spoljašnjih odlagališta jalovine*

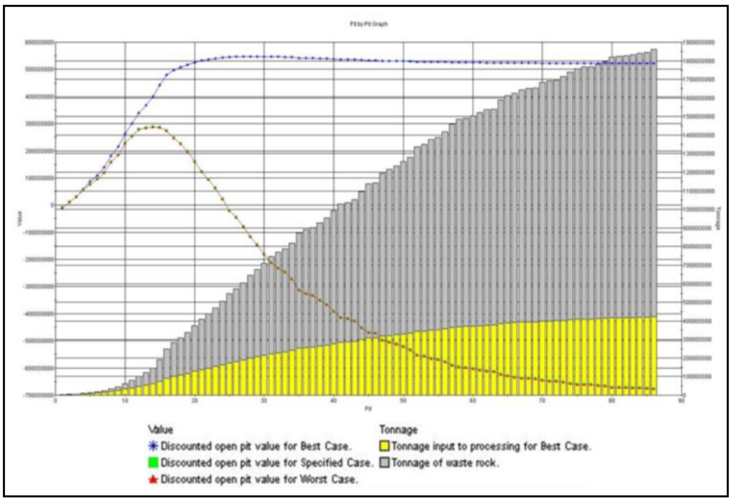
Kapaciteti spoljašnjih odlagališta jalovine				Ukupno
Kovej	Andezitski prst	Bugarski potok	Deponija	
1 995 000	8 000 000	13 000 000	23 500 000	**46 495 000**



Sl. 2. *Prikaz lokacija kamionskih odlagališta*

Optimalna granica otkopavanja površinskog kopa dobijena je korišćenjem softvera za optimizaciju i strateško planiranje površinskih kopova Whittle [6], [7].

Na slici 3 grafički su prikazani rezultati optimizacije za baznu cenu bakra od 6.000 USD/t, na osnovu čega se vrši izbor optimalne konture kopa i faze razvoja kopa.



Sl. 3. *Grafički prikaz rezultata optimizacije (Pit by pit graf)*

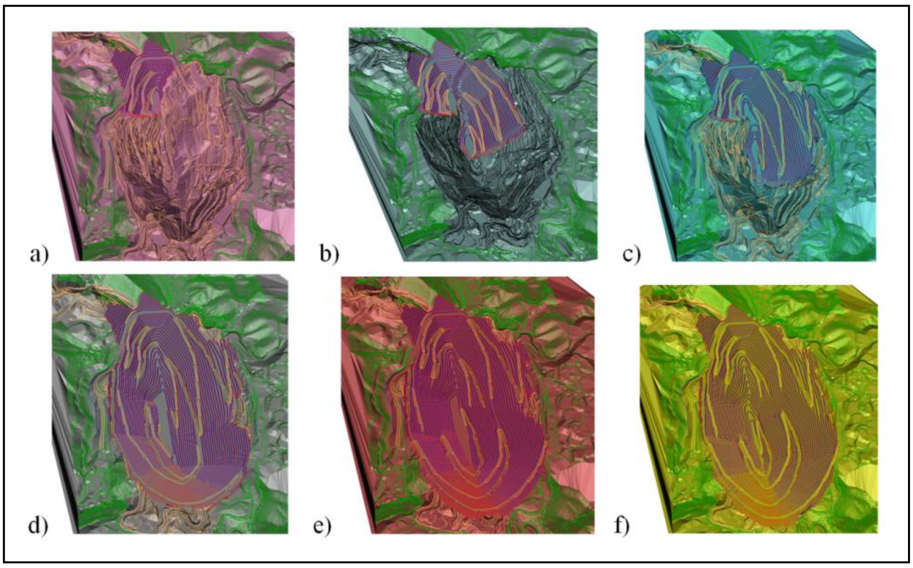
Sa grafika može se videti da je, za usvojene tehno-ekonomske parametre kao optimalan izabran kop broj 25. Izabrani kop ima ukupno 549.837.135 t iskopina, od čega 175.536.668 t rude i 374.300.467 t otkrivke. Koeficijent otkrivke iznosi 2,13 t/t.

Definisanje faza razvoja kopa (pushbacks)

Nakon određivanja konačne granice otkopavanja, sledeći korak u procesu dizajniranja površinskih kopava jeste definisanje faza otkopavanja.

U ovom koraku sprovodi se simulacija i DCF analiza da bi se dobila najpovoljnija varijanta, odnosno odredio broj faza koji utiče na maksimizaciju neto sadašnje vrednosti kod dugoročnog planiranja kopova.

Na osnovu rezultata optimizacije koja je grafički prikazana na slici 3, definisane su i faze otkopavanja i to su kopovi 18 i 22. Na osnovu potrebe da se dinamikom otkopavanja obezbede potrebne količine rude shodno zahtevu Investitora, uz minimalne količine otkrivke neophodno je da se i kop broj 18 podeli na četiri faze, pri čemu njegov severni deo predstavlja Fazu 1, istočni Fazu 2 i 3, a južni i zapadni deo su označeni kao Faza 4. Shodno usvojenom pravilu označavanja faza, kopovi 22 i 25 definisani su kao Faza 5 i Faza 6, respektivno (slika 4).



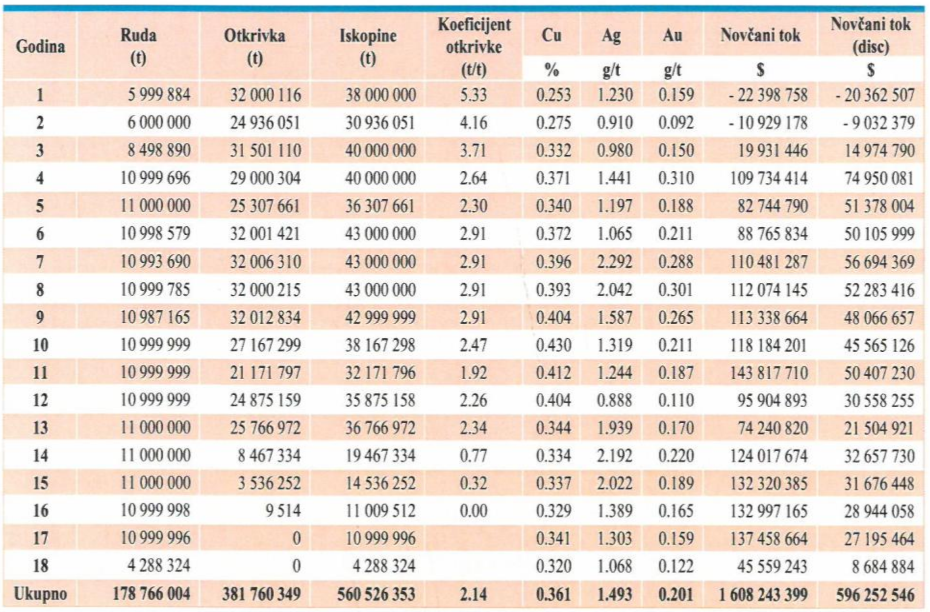
Sl. 4. *Izgled završne konture (3D prikaz)*
a) Faza 1; b) Faza 2; c) Faza 3; d) Faza 4; e) Faza 5; f) Faza 6

Optimizacija dinamike otkopavanja

Dinamika otkopavanja po godinama eksploatacije dobijena je u softveru Whittle. Za optimizaciju dinamike otkopavanja softver korišćen je Milava algoritam, za režim balansiranja (Milawa Balanced) [8].

Rezultati optimizacije dinamike otkopavanja prikazani su u tabeli 3.

Tabela 3. *Dinamika otkopavanja po godinama i periodima eksploatacije*



Godina	Ruda (t)	Otkrivka (t)	Iskopine (t)	Koeficijent otkrivke (t/t)	Cu	Ag	Au	Novčani tok	Novčani tok (disc)
					%	g/t	g/t	$	$
1	5 999 884	32 000 116	38 000 000	5.33	0.253	1.230	0.159	- 22 398 758	- 20 362 507
2	6 000 000	24 936 051	30 936 051	4.16	0.275	0.910	0.092	- 10 929 178	- 9 032 379
3	8 498 890	31 501 110	40 000 000	3.71	0.332	0.980	0.150	19 931 446	14 974 790
4	10 999 696	29 000 304	40 000 000	2.64	0.371	1.441	0.310	109 734 414	74 950 081
5	11 000 000	25 307 661	36 307 661	2.30	0.340	1.197	0.188	82 744 790	51 378 004
6	10 998 579	32 001 421	43 000 000	2.91	0.372	1.065	0.211	88 765 834	50 105 999
7	10 993 690	32 006 310	43 000 000	2.91	0.396	2.292	0.288	110 481 287	56 694 369
8	10 999 785	32 000 215	43 000 000	2.91	0.393	2.042	0.301	112 074 145	52 283 416
9	10 987 165	32 012 834	42 999 999	2.91	0.404	1.587	0.265	113 338 664	48 066 657
10	10 999 999	27 167 299	38 167 298	2.47	0.430	1.319	0.211	118 184 201	45 565 126
11	10 999 999	21 171 797	32 171 796	1.92	0.412	1.244	0.187	143 817 710	50 407 230
12	10 999 999	24 875 159	35 875 158	2.26	0.404	0.888	0.110	95 904 893	30 558 255
13	11 000 000	25 766 972	36 766 972	2.34	0.344	1.939	0.170	74 240 820	21 504 921
14	11 000 000	8 467 334	19 467 334	0.77	0.334	2.192	0.220	124 017 674	32 657 730
15	11 000 000	3 536 252	14 536 252	0.32	0.337	2.022	0.189	132 320 385	31 676 448
16	10 999 998	9 514	11 009 512	0.00	0.329	1.389	0.165	132 997 165	28 944 058
17	10 999 996	0	10 999 996		0.341	1.303	0.159	137 458 664	27 195 464
18	4 288 324	0	4 288 324		0.320	1.068	0.122	45 559 243	8 684 884
Ukupno	**178 766 004**	**381 760 349**	**560 526 353**	**2.14**	**0.361**	**1.493**	**0.201**	**1 608 243 399**	**596 252 546**

ZAKLJUČAK

Sprovedena analiza mogućnosti povećanja kapaciteta na kopu Južni revir obavljena je korišćenjem softvera za optimizaciju i strateško planiranje površinskih kopova Whittle, a koja se zasniva na analizi kretanja diskontovanog novčanog toka tokom eksploatacionog perioda, odnosno ostvarene neto sadašnje vrednosti, i koja je pokazatelj postignutih ekonomskih rezultata eksploatacije ležišta Južni revir za zadate početne uslove. Modeliranje ležišta i konstrukcija optimalne konture kopa i faza razvoja kopa izvršena u softveru Gemcom Gems

Na osnovu sprovede analize zaključuje se sledeće:

1) Postoji mogućnost povećanja kapaciteta na otkopavanju rude bakra na površinskom kopu Južni revir Majdanpek, koji se ostvaruje u 4. godini za analizirani period
2) Vek eksploatacije kopa iznosi 18 godina.
3) Kretanje novčanog toka je pozitivno tokom celog perioda eksploatacije, sem u prvoj i drugoj godini analiziranog perioda.
4) Ostvaruje se neto sadašnja vrednost u iznosu od **596.252.546 $**.

LITERATURA

[1] D. Kržanović i drugi, Studija izvodljivosti eksploatacije ležišta Južni revir u Rudniku bakra Majdanpek (IRM Bor, 2011. godina)

[2] D. Kržanović i drugi, Dopunski rudarski projekat otkopavanja rude bakra iz ležišta Južni revir u Rudniku bakra Majdanpek (IRM Bor)

[3] D. Kržanović, R. Rajković, M. Mikić, M. Ljubojev: Effect of stage develop-

ment of mining operations on maximization the net present value in long-term planning of open pits, Mining and Metallurgy Engineering Bor, 4/2014, pp. 33-40

[4] D. Kržanović, M. Žikić, R. Pantović: Important improvement of utilization the available geological reserves of the South mining district deposit in Majdanpek in the new defined optimum contour of the open pit using the Whittle and Gemcom softwares, Rudarski radovi – Mining Engineering, Institut za rudarstvo i metalurgiju Bor, 2012, pp 29-36.

[5] D. Kržanović, M. Žikić, Z. Vaduvesković: Innovated block model of the copper ore deposit South mining district-Majdanpek as a basis for analysis the optimum development of open pit using the software packages Whittle and Gemcom, Rudarski radovi – Mining Engineering, Institut za rudarstvo i metalurgiju Bor, 2011, pp 69-76

[6] G Whittle, W Stange and N Hanson, Optimising Project Value and Robustness, Project Evaluation Conference, Melbourne, Vic, 19 - 20 June 2007, pp. 1-10

[7] D. Kržanović, R. Rajković, M. Mikić: The effect of open pit slope design on net present value for long term planning, The 46th International October Conference on Mining and Metallurgy, Borsko jezero, Serbia, 2014

[8] D. Kržanović, R. Rajković, M. Mikić, M. Ljubojev: Effect of stage development of mining operations on maximization the net present value in long-term planning of open pits

ISSN: 2334-8836 (Štampano izdanje)
ISSN: 2406-1395 (Online)

UDK: 628.51:504.06(045)=111
doi:10.5937/MMEB1503089M

Vesna M. Marjanović[*], *Aleksandra T. Ivanović*[*]

SELECTION THE STABILIZATION/SOLIDIFICATION PROCESS AND SELECTION THE BINDERS AND REAGENTS DEPENDING ON THE TYPE OF WASTE MATERIAL IN THE FUNCTION OF ENVIRONMENTAL PROTECTION[**]

Abstract

This paper presents the overview and method of selection the stabilization/solidification process, considering that a very long time suitable for treatment the hazardous waste in order to protect the environment. Selection the method for stabilization/solidification (S/S) the hazardous waste depends on the type of waste, content of hazardous and harmful components and it is applied as the method of pre-treatment the hazardous waste before disposal into landfill. Also, in this paper, the data are systemized that related to the process of stabilization and solidification, the basic concepts relating to these processes, as well as the phase of collecting the information on processing and verification the process S/S.

This paper provides the possibilities of selection the additives depending on the type of waste material. Using the technological process of stabilization/solidification (S/S) and corresponding additives, the waste material is transformed into inert material independently of the individual values of metal solubility or components in waste. Also the fact of great importance is that some physical or chemical parameters of solidified waste material (permeability, resistance to compression) can be easily controlled by selection of chemical additive and its share in the mixture (waste/additives). The process of S/S has a reasonable use in liquid waste or waste with a high content of liquid phase with impossible disposal on the landfills without prior treatment.

These processes can be performed in-situ - on the location of hazardous waste and ex-situ - in the facilities that are designed for that purpose.

Keywords: *stabilization/solidification, environmental protection, hazardous waste, additives*

1 INTRODUCTION

Stabilization/solidification processes have been in use since 1950, when they were applied for the treatment of radioactive and hazardous waste. Today, these processes and technologies are used for treatment and remediation of contaminated soil and waste originated from the technological processes of metals, purification of drinking water and others.

Stabilization/solidification (S/S) process is used to remove a wide range of pollutants from different materials and contaminated waste, particularly those contaminated with substances classified as "dangerous". The treatment involves mixing a binding agent with medium or contaminated waste [1].

The treatment involves mixing a binding agent with medium or contaminated waste, so the hazardous substances contained in it are immobilized and their mobilization in the environment is prevented [2].

---

[*] *Mining and Metallurgy Institute Bor*

[**] *This work is the result of the Project TR 33038: Improvement the Technology of Exploitation and Processing of Copper Ore with Monitoring the Environment in RTB Bor Group, funded by the Ministry of Education, Science and Technological Development of the Republic of Serbia.*

Stabilization and solidification are processes which include a wide range of technologies, which closely related to the chemical and/or physical processes of reduction the potential negative impacts on the environment (soil, surface and ground water) and indirectly on the wildlife and human health [2].

2 CONCEPT OF STABILIZATION AND SOLIDIFICATION

Stabilization refers to the techniques for reduction the potential hazards of waste and transforms the pollutants into less soluble, mobile, or toxic form using the chemical processes. The physical characteristics of waste have not to be changed in the course of stabilization.

Solidification refers to the techniques that encapsulate the waste, forming a solid material, and doing so there are no chemical interactions between the pollutants and additives used for fixing. Solidification is achieved by a chemical reaction between the waste and specific reagents or mechanical processes. The product of waste solidification may be a monolithic block, clay-like material, granular particles, or another other physical form that is usually considered a "solid substance".

Solidification is divided into the micro-encapsulation (particles up to 2 mm) and macro-encapsulation (particles larger than 2 mm), depending on the grain size distribution of material to be treated [3]. Migration of impurities is often limited by reduction the surface area exposed to the leaching and/or coating material waste with small permeability.

The combined processes of solidification /stabilization mixed waste, soil and sludge, and treatment by the certain agents constitute the hazardous ingredients in them physically and chemically fixed. These technologies are not considered as the destructive techniques, but they just eliminate or prevent (complicate) the mobility of pollutants [3].

Stabilization and solidification processes cover a wide range of technologies, which are closely associated with chemical and/or physical processes to reduce the potential negative impacts on the environment (soil, surface and groundwater) and indirectly on the wildlife and human health (ITRC). The S/S is an important technological process which allows transforming of wastes into inert material, regardless the value of individual solubility of metals, or the components in the waste. Also, the fact is of great importance that some physical or chemical parameters of solidified waste material (permeability, resistance to compression) can easily control the selection of chemical additives and their share in the mixture (waste/additives) [4].

3 SELECTION THE STABILIZATION/SOLIDIFICATION PROCESS DEPENDING ON THE TYPE OF WASTE MATERIAL

Selection process is primarily dependent on the type of waste material and its further treatment. Based on the type of waste is the identification of S/S technology as the Best Demonstrated Available Treatment Technology - BDAT, and Figure 1 shows the phase of collecting the information on technological process, and Figure 2 shows the manner in which the technological checking of stabilization/solidification process is carried out [5].

Based on the preliminary characterization, it is necessary to perform the waste sampling, after which it is necessary to do the additional characterization on the basis of which it is decided whether the waste is acceptable for laboratory research or not. If so, a detailed characterization of waste is carried out, then the physical, chemical and microstructural testing the S/S waste, and based on this information the facility characteristics are given, in the ex-situ case of S/S, Figure 1, [5].

Checking the technology of the S/S process in-situ begins studying the characteristics of terrain and waste, and field sampling. After that, setting the performance targets, and then it is needed to develop a feasibility study in which it is decided whether the process S/S is aviable option. If the answer is no, it is needed to check whether the best analytical and technical solutions are selec-ted, and if the answer is negative again, the conclusion is made that the process S/S would be unsuccessful.

When the feasibility study produces the positive results, the literature is checked to select the best combination of waste/binder, and laboratory analyses and testing. In the case of positive test results, testing in the site or pilot plant is carried out based on which a positive or negative decision will be made on the process of S/S waste materials, Figure 2 [5].

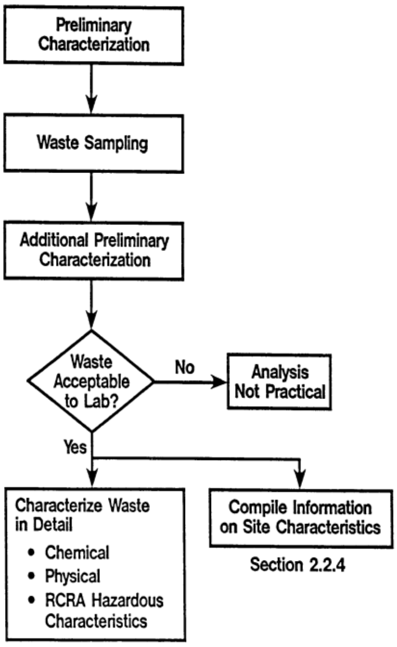


Figure 1 *Information collection steps in the technology-screening process [5]*

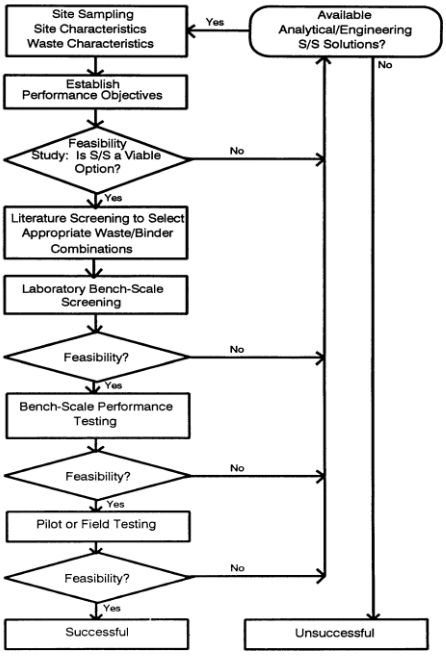


Figure 2 *Solidification/stabilization technology screening [5]*

4 SELECTION OF ADDITIVES ACCORDING TO THE TYPE OF WASTE

Selection the S/S method of hazardous waste depends on the type of waste, content of hazardous and harmful components, and is applied as a method of pre-treatment of hazardous waste before disposal to a landfill.

A large influence on the efficiency of the process has a selection of additives used in the process of S/S, which depend on the type of waste and conditions of aging the product of S/S process. The efficiency of the S/S process is done by determining the mobility of hazardous and harmful components, and compressive strength, after the solidification/stabilization process.

Additives which are used as binders in the processes S/S can be of inorganic and organic origin or a combination thereof. The most commonly applied additives are of inorganic origin such as: cement, ash, lime, soluble silicates, pozzolans, bentonite, clays, blast furnace slag and other materials, and the organic additives are asphalt, epoxide, polyester and polyethylene. Inorganic binders are used in more than 90% of the process S/S. In general, inorganic binders are cheaper and easier to use than organic. Organic binders are generally used for solidification of radioactive waste or specific volatile organic compounds [6].

4.1 Inorganic binders as additives

In order to facilitate the selection of additives, depending on the type of waste, the paper of the authors *Fleri M. A., et al., (2007)* [7] provides an overview of additives used in the processes of S/S. Based on the results obtained by the analytical methods of processing a sample and criteria to be met by the S/S waste material, a preliminary selection of additives is carried out.

The most commonly used additive is *Portland cement (PC),* which can meet a variety of physical and chemical conditions [8] *(ASTM C150, 2003).* During testing, the Portland cement is usually combined with other reagents to form a mixture that meets the required criteria. The additives of primary importance are pozzolans, bentonite and chemicals that reduce leaching and dilution of pollutants.

Pozzolans are supplements that contain fly ash, silica fumes and other fine-ground cement substances that increase the strength, density and durability. In the field of environmental protection is commonly used pozzolana including fly ash and slag from blast furnaces. The ashes can be classified into two main classes, as specified in the standard ASTM C618 [9].

Another significant pozzolan is the blast furnace slag, which is defined as a "non-metallic product that is essentially composed of silicate, alumino-silicates and calcium base that is developed in a molten condition simultaneously with iron in a blast furnace." Three types of slag used in production cement, and they are air-cooled, expanded and granulated slag. The main feature of these types of slag is durability and use as an add-cement product. Due to its affordability and accessibility, blast furnace slag is selected for use in a mixture with fly ash [7].

4.2 Efficiency of additives for different types of waste material

The success of the process of S/S primarily depends on the selection of additives and their efficiency. Table 1 shows the additives that are commonly used and their application depending on the type of waste material.

Table 1 *Recommended process of S/S depending on type of waste* [4]

Process of S/S	Application
Solidification with cement	Sludges, contaminated land
Solidification with lime	Waste from the desulfurization of waste gases, other inorganic waste
Solidification with thermoplastic materials	Radioactive waste
Encapsulation	Sludges, liquids
Vitrification	Extremely hazardous waste, radioactive waste

In such cases, it is efficient use of cement as an additive for binding the liquid phase, because the cement reacts with water, chemically binding the water in e hydrated cement product. Free liquid phase when adding cement binds it more often chemical bonds, and less is absorbed, and therefore the resistance to compression of at least 0.34 MPa (50 psi) [4].

In the case of implementation the remediation process as the sustainability process of land, S/S is often the only solution and the available technology for remediation of large amounts of soil contaminated with heavy metals, sludge or sediment. In this case, the cement is recommended, because it reduces the mobility of metal ions, forming a hardly soluble metal hydroxide, carbonate or silicate. During the process of S/S, metal transforms from ionic forms into mineral structure and physical encapsulation. Also, pre-treatment can reduce the toxicity of some metals changing the valence state [4].

Applying the combined process of stabilization and solidification of waste containing heavy metals, the transformation of form of the heavy metals occurs to a large degree and they usually transform into heavy soluble hydroxides in which the mobility of heavy metal ions is reduced.

Solidification further reduces the mobility of heavy metals from the newly created heavy soluble forms, Figure 3.

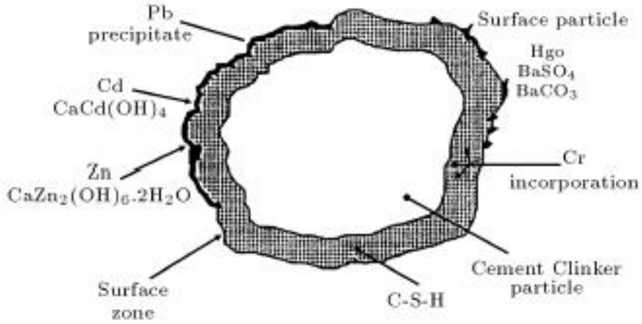


Figure 3 *Solidification and stabilization of heavy metals by hydrates of Portland cement* [11]

Treatment of materials containing mostly organic pollutants is also possible using the cement as an additive. In the process of S/S, the material hardening occurs through changes in physical properties of cement. They are highly recommended if the waste or material contains free water, which enters in the hydration process, producing with cement high physically integrated material monolith. The process has demonstrated a high efficiency in reducing the mobility of hazardous and harmful substances from waste containing semi volatile and heavy volatile polycyclic aromatic hydrocarbons (PAHs), polychlorinated biphenyls (PCBs), pesticides, organic cyanides and others.

Disadvantage of S/S applying of cement is in the cases when the waste has a high content of fats and oils, when the process of cement hydration is disabled. The cement particles are coated with oils or fats, thus inhibiting a contact between cement and water. Some organic components affecting the binding time of cement, thus the whole process of solidification can be extended considerably. For these reasons, it is necessary before selection of additives to carry out a complete qualitative and quantitative chemical analysis of waste, thereby preventing the adverse effects on the ground. Also, using the quicklime, as additive, results into an exothermic reaction during the hydration process and thereby liberating a significant amount of energy. If the waste includes volatile hazardous and harmful components, the same, during the S/S, will to be emitted into the atmosphere. If there is no other alternative to quicklime as an additive in the process of S/S, it is necessary to provide the facilities for collection and treatment of gases/air [4].

4.3. Selection of additives, depending on the type of waste

In order to facilitate the selection of additives depending on type of waste, the investigation were carried out by the author *Chan B. K. C. et al. (2008)* [14]. Tested materials for development a model for selection of additives were as follows: JR –waste with higher levels of hazardous components, OMW - fine-grained, Fe- and Ca-rich neutralization precipitates from bioleaching with relatively low levels of hazardous components. Tested additives are: SS – silica sand, PC – commercially available cement, FA – fly ash and L - lime. Table 2 shows the test results of stabilization the hazardous waste with different content of harmful components using different additives and with different proportions.

Table 2 *Material formulation for CLSM mix design [12]*

MIX	Dry solids/%						Ratio of water to solid
	PC	FA	SS	OMW	JR	L	
5PC-FA	5	15	80	-	-	-	0.20
5PC-FA-OMW	5	15	70	10	-	-	0.30
5PC-FA-JR	5	15	70	-	10	-	0.25
10PC-FA-JR	10	15	65	-	10	-	0.30
10L-FA-JR	-	15	65	-	10	10	0.43
5PC-FA-L-JR	5	15	65	-	10	5	0.41

JR – with higher levels od hazardous components, OMW – fine-grained, Fe- and Ca-rich neutralization precipitates from bioleaching with relatively low levels of hazardous components, SS – silica sand, PC - a commercially available cement, FA –fly ash and L - lime.

Concentrations of heavy elements As, Cd, Co, Cu, Mn, Mo and Ni in waste after pretreatment, obtained by implementation of the prescribed test procedures of hazardous and toxic waste characteristics, were below the allowable values for groundwater and soil, even from the waste samples with increased content of hazardous components. Figure 4 shows the concentration of Pb and Zn from various additives, and with which it can be seen that the concentrations of Pb and Zn, with a combination of additive 5PC-5L-JR are above the intervention value. In tested sample JR, the concentrations of Pb and Zn were above the allowable limit. Testing of contaminated soil with a lower content of hazardous components, and after the procedure of pretreatment, gave the satisfactory results [12].

Adsorption on hydrated iron (III) oxide, which was present in samples has reduced the mobility of arsenic, Figure 5.

4.4 Correct selection of reagents

For the stabilization of waste containing heavy metals and a large amount of water, which was a result of mining activities, the process recommended lime neutralization of creation the hardly soluble hydroxide in alkaline conditions.

Further, in the process of solidification can occur on the grain surface, in the presence of silicon and aluminum, a liquid barrier, calcium silicate gel, or calcium-aluminate gel, thereby increasing the efficiency of the process [13]. Curve hydroxide solubility of heavy metals, depending on the pH of the environment, is illustrated in Figure 6 (a), which clearly shows the influence of pH value on mobility of heavy metals [4].

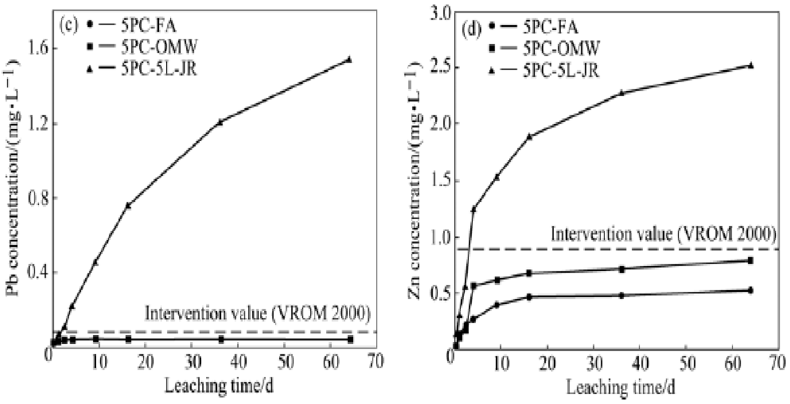


Figure 4 *Pb and As concentrations with the addition of various additives [12]*

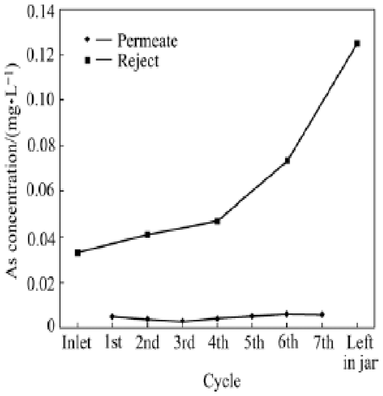
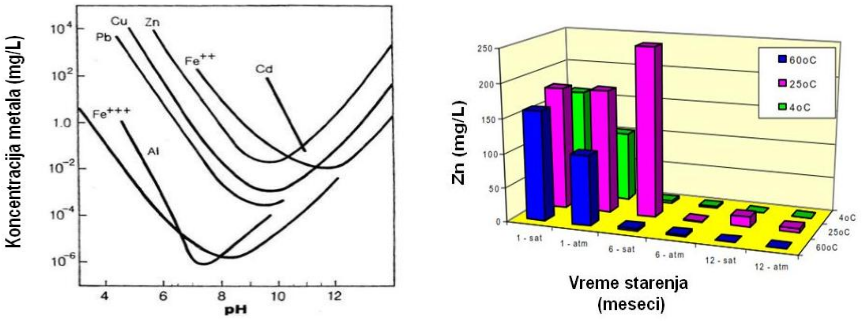


Figure 5 *Concentration of arsenic with and without the addition of additives (Fe_2O_3) to the initial concentration As of 0.03 mg/L [12]*

Treatment of the resulting product after the solidification process and stabilization of waste material can have a significant effect on the efficiency of process.

Figure 6 (b) shows the effect of temperature and drying conditions and aging time on the mobility of zinc ions in the sludge.



(a) *(b)*

Figure 6 *(a) Solubility curve of heavy metal hydroxide depending on the pH and (b) The effect of temperature, drying conditions and aging time on the mobility of zinc ions in the sludge [4]*

Figure 6 clearly shows that the aging of 6 months at temperature of 25°C, at atmospheric conditions, reduces the mobility of zinc to less than 10 mg/L, [4].

5 PROCESSES OF STABILIZATION/SOLIDIFICATION IN-SITU AND EX-SITU

Processes and technology of stabilization /solidification in-situ are popular for treatment and remediation of contaminated soil, particularly at the location where the buildings already exist or are abandoned. The process of S/S contributes to the sustainable development such as the contaminated material can be treated in site and thus reused without fuel consumption for transport and reduction the risk to the environment [1].

In-situ stabilization/solidification or deep soil mixing is a widely accepted technique in the field of environmental protection, which is used for immobilization of pollutants, thus preventing further spreading of pollution through the soil and groundwater. S/S is used for the ecological treatment of various industrial waste materials from contaminated sites. In any case, the treated material can be reused in-situ or at another location, which significantly reduces costs and protects the human health and environment [1].

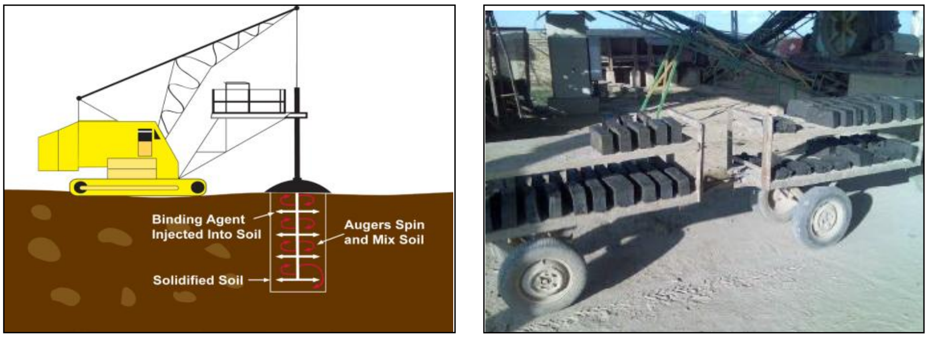
The most common in-situ stabilization process involves mixing the contaminated soil or waste with cement as additive or other materials that have similar chemical and physical properties (fly ash, etc.) that have a high adsorption capacity, thus reducing the mobility of hazardous and harmful components [14].

Processes S / S used for remediation are intended to reduce the passage of pollutants from soil, sediment, sludge and waste that is washed (leach) from a source of pollution to the environment, within the acceptable criteria listed in order of remediation.

Technology S/S can be applied for a wide range of pollutants. The successful implementation of this technology begins with the testing locations. Subsequently, on the basis of the collected data, the treatability study (TS) and pilot studies (PS) are performed which show the required amount and impact of binders on soil as well as the soil geochemistry. To determine the potential efficiency of the S/S technology, the parameters should be collected that related to the tests and criteria used for development of the S/S treatment that meets the objectives of the remediation. These specifications are intended to: (1) guidance and evaluation the feasibility studies and (2) establishing a minimum number of field operations and compliance the characteristics of material in the laboratory conditions. Improving the technology - the project S/S is done by monitoring the life cycle of process, from the research of site to the completion of remediation, as the evidence of technology sustainability. Well done the feasibility study might reduce the number and type of additives to be used in the pilot study, which also allows a correct pricing, delivery and availability of additives and binders, as well as to better understand the physical and chemical properties of the contaminated waste. The selection of additives and binders must be carried out systematically on the basis of physical and chemical properties of the waste, and then based on the best supplier of additives and most widespread and most cost effective binder because the additive costs can amount to 30-50% of the stabilization costs [7].

When the remediation is implemented – realized, the long-term natural resource management programs are needed that are typically used to check whether the project is still in effect, and as such whether it protects the human health and the environment (ITRC).

Fleri M.A. et al. (2007) showed a number of projects in which the technologies of stabilization involving injecting a binding agent into the soil. In fact, the technology of deep mixing of soil becoming a common choice of remediation technologies, Figure 7, because it reduces the amount of excavated soil (off-site), and thus saving the benefits and costs of removal and subsequent filling; reduces unpleasant smells while performing remediation and the total remediation costs are significantly lower than the other remediation technologies such as the thermal desorption and in-situ chemical oxidation for removal of contaminated materials.



(a) *(b)*

Figure 7 *S/S process in-situ (a) and ex-situ (S/S waste material) (b)*

The S/S *ex-situ* processes are applied in plants that have been designed for these processes and are used for different types of sludge and other waste materials containing "hazardous" substances, such as heavy metals; the S/S waste material is shown in Figure 7[17].

6 CONCLUSION

In the process of stabilization/solidification (S/S) has been proven to be effective for the treatment of waste containing dangerous substances. The most important step in the process of S/S waste material represents a qualitative and quantitative analysis of waste material, based on which it can make a choice of binder and additives.

Physical and chemical methods are carried out tests with S/S products, on the basis of which is made of his categorization. By changing the physical character of waste using stabilization/solidification process, prevent the occurrence of a large amounts of leachate at the landfill with a high content of hazardous and harmful components; thus achieving a double effect, protects the environment on the one hand and on the other hand reduces the process costs of hazardous waste disposal because there is no need for the installation and operation the system for waste/leachate water from the landfill.

REFERENCES

[1] Wilk C. M. (A), Applying Solidification/Stabilization for Sustainable Redevelopment of Contaminated Property [Internet]. LEHP, QEP, LEED AP Program Manager, Waste Treatment Portland Cement Association; http://www.pollutionengineering.com/ext/resources/PE/Home/Files/PDFs/PCA_S-S_Whitepaper.pdf?1354286601

[2] ITRC, [Internet]. Washington: Intersta-te Technology & Regulatory Council, http://www.itrcweb.org/ Team/Public?teamID=15

[3] EPA, 1999., [Internet]. Solidification/stabilization resource guide, EPA/542-B-99-002 (1999), http://epa.gov/tio/download/remed/solidstab.pdf

[4] Zinck J., [Internet]. Canada: Review of Disposal, Repro-Cessing and Reuse Options for Acidic Drainage Treatment Sludge, The Mining Association of Canada, MEND and CENMET Mining and Mineral Scienties Laboratories, MEND Report 3. 42. 3, 2005: 3, http://mend-nedem.org/wp-content/uploads/2013/01/3.42.3.pdf

[5] EPA 1993., [Internet]. Technical Resource Document, Solidification/Stabilization and its Application to Waste Materials, June 1993, p. 1-5. p. 2-6. (A), p. 2-2. (B)

[6] EPA, 2000., [Internet]. Solidification/Stabilization Use of Superfund Sites, EPA-542-R-00-010, Septembar 2000, http://www.epa.gov/tio/download/remed/ss_sfund.pdf

[7] Fleri M. A., Whetstone G. T., In situ stabilisation/solidification: Project lifecycle, J. Hazard. Mater. 2007; 141: 441–456.

[8] ASTM C150, Standard Specification for Portland Cement, vol. 4.01, American Society for Testing Materials, West Conshohocken, Pennsylvania, 2003, pp. 150– 153.

[9] ASTM C618, Standard Test Method for Coal Fly Ash and Raw or Calcined Natural Pozzolan for Use in Concrete, vol. 4.02, American Society for Testing Materials, West Conshohocken, Pennsylvania, 2003, pp. 319–321.

[10] Black Hills Bentonite, LLC. 2009., [Internet]. Wyoming, http://www.bhbentonite.com/minchar.htm

[11] Ganjidoust H., Hassani A., Rajabpour Ashkiki, Cement-Based Solidification/Stabilization of Heavy Metal Contaminated Soils with the Objective of Achieving High Compressive Strength for the Final Matrix, Sharif University of Technology, Transaction A: Civil Engineering, 2009; 16: 107-115, http://www.sid.ir/en/VEWSSID/J_pdf/95520092A05.pdf

[12] Chan B. K. C., Bouzalakos S., Dudeney A. W. L., Integrated Waste and Water Management in Mining and Metallurgical Industries, Trans. Nonferrous Met. Soc. China. 2008; 18: 1497-1505

[13] Bakstrom M. Baltic Sea Region Programe, Orebro University, Sweden: Compendium of Mining and Processing Waste Management Technologies, Project: MINNOVATION Mining and Mineral Processing Waste Management Innovation Network, Baltic Sea Region Programe, 2013: 214, http://www.minnovation.eu/uploads/compendium%20of%20Mining %20and%20Processing%20Waste%20Management%20Technologies.pdf

[14] Gardić V., Obradović Lj., Filipović S., Review of Solidification and Stabilization Methods of Hazardous Waste, MME Bor. 2013; 4: 93-100.

[15] Krčmar D., Stabilization/Solidification of Sludge Rich with Arsenic. http://www.arsenicplatform.pmf.uns.ac.rs/pdf/10_Solidifikacija.pdf

UDK: 628.51:504.06(045)=163.41 doi:10.5937/MMEB1503089M

Vesna M. Marjanović[*], *Aleksandra T. Ivanović*[*]

IZBOR PROCESA STABILIZACIJE/SOLIDIFIKACIJE I IZBOR VEZIVNIH SREDSTVA I REAGENASA U ZAVISNOSTI OD VRSTE OTPADNOG MATERIJALA U FUNKCIJI ZAŠTITI ŽIVOTNE SREDINE[**]

Izvod

U radu je dat pregled i način izbora procesa stabilizacije/solidifikacije s obzirom da se veoma dugo upotrebljavaju za tretman opasnog otpada u cilju zaštite životne sredine. Izbor metode stabilizacije/solidifikacije (S/S) opasnog otpada zavisi od vrste otpada, sadržaja opasnih i štetnih komponenti, i primenjuje se kao metoda predtretmana opasnog otpada pre odlaganja na deponiju. Takođe, ovom radu sistematizovani su podaci vezani za procese stabilizacije i solidifikacije, osnovni pojmovi koji se odnose na ove procese, kao i faze prikupljanja informacija o tehnološkom procesu i provera procesa S/S.

U radu su date mogućnosti izbora aditiva u zavisnosti od vrste otpadnog materijala. Primenom tehnološkog postupka stabilizacije/solidifikacije (S/S) i odgovarajućih aditiva otpadni materijal se transformiše u inertni materijal nezavisno od pojedinačnih vrednosti rastvorljivosti metala, odnosno komponente u otpadu. Takođe, od velike je važnosti činjenica da se neki fizički ili hemijski parametari solidifikovanog otpadnog materijala (propustljivost, otpor na kompresiju) mogu lako kontrolisati izborom hemijskog aditiva i njegovog udela u mešavini (otpad/aditivi). Proces S/S nalazi opravdanu primenu kod otpada u tečnom stanju ili otpada sa velikim sadržajem tečne faze, čije odlaganje na deponije bez prethodnog tretmana nije moguće.

Ovi procesi se mogu vršiti in-situ - na lokaciji na kojoj se nalazi opasan otpada i ex-situ - u pogonima koji su projektovani za tu namenu.

Ključne reči: *proces stabilizacije/solidifikacije, zaštita životne sredine, opasan otpad, aditivi*

1. UVOD

Procesi stabilizacije/solidifikacije su u upotrebi od 1950. godine, kada su primenjeni za tretman radioaktivnog i opasnog otpada; danas se ovi procesi i tehnologije koriste za tretman i remedijaciju kontaminiranog zemljišta i otpada koji potiče iz tehnoloških procesa prerade metala, prečišćavanja voda za piće i dr.

Stabilizacija/solidifikacija (S/S) je proces koji se koristi za odstranivanje širokog spektara zagađujućih supstanci iz različitih materijala i kontaminiranih otpada, posebno onih koji su kontaminirani sa supstancama koje su klasifikovane kao „opasne“. Tretman podrazumeva mešanje vezivnog sredstva sa medijimom ili kontaminiranim otpadom [1].

Tretman podrazumeva mešanje vezivnog sredstva sa medijimom ili kontaminiranim otpadom, na taj način se opasne materije koje se nalaze u njemu imobilizuju i sprečava se njihova mobilizacija u životnu sredinu [2].

---

[*] *Institut za rudarstvo i metalurgiju Bor*

[**] *Ovaj rad je rezultat projekta TR 33038 "Usavršavanje tehnologije eksploatacije i prerade rude bakra sa monitoringom životne i radne sredine u RTB-BOR grupa", koji je finansiran od strane Ministarstva prosvete, nauke i tehnološkog razvoja Republike Srbije.*

Stabilizacija i solidifikacija su procesi koji obuhvataju širok spektar tehnologija, koje su usko povezane sa hemijskim i/ili fizičkim procesima smanjenja potencijalnih negativnih uticaja na životnu sredinu (zemljište, površinske i podzemne vode) i posredno na živi svet i zdravlje ljudi [2].

2. POJAM STABILIZACIJE I SOLIDIFIKACIJE

Stabilizacija se odnosi na tehnike kojima se hemijski postupcima smanjuju potencijalne opasnosti otpada i pretvaraju zagađujuće materije u manje rastvorljive, mobilne, ili toksične oblike. Fizičke karakteristike otpada ne moraju da se menjaju u toku stabilizacije.

Solidifikacija se odnosi na tehnike koje enkapsuliraju otpad, formiraju čvrst materijal, a da pri tome ne mora doći do hemijske interakcije između zagađujuće materije i aditiva koji služe za učvršćivanje. Solidifikacija se postiže hemijskom reakcijom između otpada i određenog reagensa ili meha-

otpada, može biti monolitni blok, materijal sličan glini, granulirane čestice, ili neki drugi drugi fizički oblik koji se obično smatra „čvrstom supstancom“.

Solidifikacija se deli na mikroenkapsulaciju (čestice do 2 mm) i makroenkapsulaciju (čestice veće od 2 mm) u zavisnosti od granulacije materijala koji se tretira [3]

-

njenjem površine koja je izložena luženju i/ili oblaganjem otpada sa materjalom male propustljivosti.

Kombinovani procesi solidifikacije/stabilizacije mešanog otpada, zemljišta i mulja, i tretman određenim sredstvima čine opasne sastojke u njima fizički i hemijskim nepo-

eliminišu ili sprečavaju (otežavaju) mobilnost zagađujućih materija [3].

Stabilizacija i solidifikacija su procesi koji obuhvataju širok spektar tehnologija, koje su usko povezane sa hemijskim i/ili fizičkim procesima smanjenja potencijalnih negativnih uticaja na životnu sredinu (zemljište, površinske i podzemne vode) i posredno na živi svet i zdravlje ljudi *(ITRC).* S/S je važan tehnološki postupak koji omogućava transformaciju otpada u inertni materijal, nezavisno od pojedinačnih vrednosti rastvorljivosti metala, odnosno komponente u otpadu. Takođe je od velike važnosti činjenica da se neki fizički ili hemijski parametari solidifikovanog otpadnog materijala (propustljivost, otpor na kompresiju) mogu lako kontrolisati izborom hemijskog aditiva i njegovog udela u mešavini (otpad/aditivi) [4].

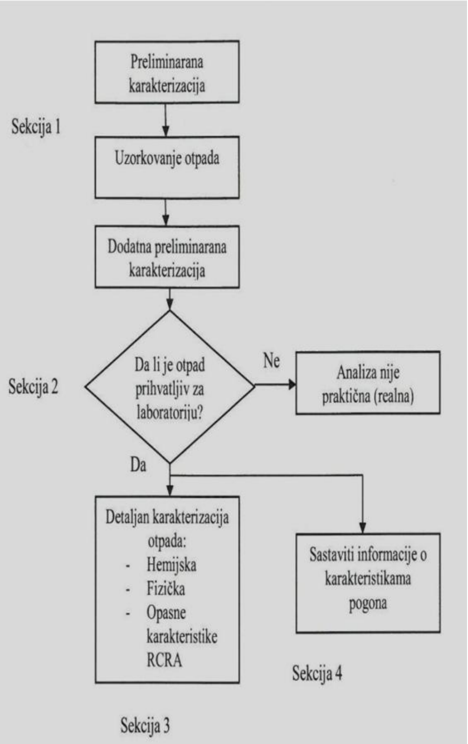
3. IZBOR PROCESA STABILIZACIJE/SOLIDIFIKACIJE U ZAVISNOSTI OD VRSTE OTPADNOG MATERIJALA

Izbor procesa pre svega zavisi od vrste otpadnog materijala i njegovog daljeg tretmana. Na osnovu vrste otpada vrši se identifikacija S/S tehnologije kao *Best Demonstrated Avialable Treatment Tehnology - BDAT*, i na slici 1. prikazane su faze prikupljanja informacija o tehnološkom procesu, a na slici 2. prikazan je način na koji se vrši tehnološka provera procesa stabilizacije/solidifikacije [5].

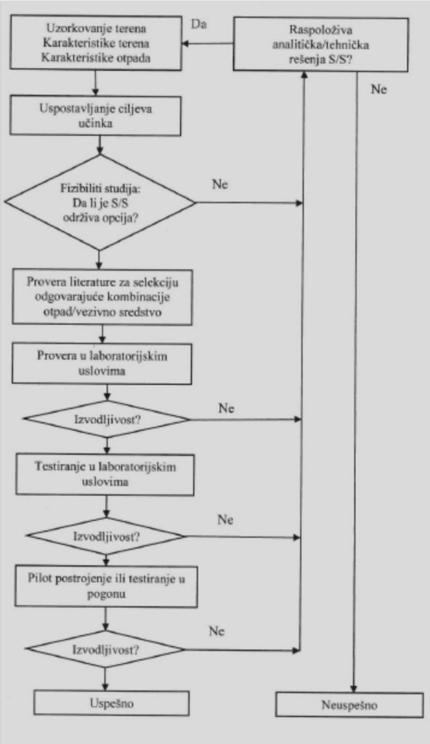
Na osnovu preliminarne karakterizacije potrebno je izvršiti uzorkovanje otpada, posle čega je potrebno uraditi dodatnu karakterizaciju na osnovu koje se donosi odluka da li je otpad prihvatljiv za laboratorijska istraživanja ili nije. Ukoliko jeste, vrši se detaljna karakterizacija otpada, zatim fizička, hemijska i mikrostrukturalna ispitivanja S/S otpada, i na osnovu ovih informacija daju se karakteristike pogona, u slučaju S/S ex-situ, slika 1, [5].

Provera tehnologije procesa S/S in-situ počinje proučavanjem karakteristika terena i otpada, i uzorkovanjem terena. Nakon toga postavljaju se ciljevi učinka, a zatim je potrebno uraditi fizibiliti studiju u kojoj se odlučuje da li je proces S/S održiva opcija. Ukoliko je odgovor negativan potrebno je proveriti da li su izabrana najbolja analitička i tehnička rešenja, i ukoliko je odgovor opet negativan, dolazi se do zaključka da bi proces S/S bio neuspešan.

Kada fizibiliti studija daje pozitivne rezultate vrši se provera literature za odabir najbolje kombinacije otpad/vezivno sredstvo, i laboratorijska ispitivanja i testiranja. U slučaju pozitivnih rezultata vrši se testiranje u pogonu ili pilot postrojenju na osnovu čega se donosi pozitivna ili negativna odluka o procesu S/S otpadnih materijala, slika 2, [5].



Sl. 1. *Faze prikupljanja informacija o tehnološkom procesu [5]*



Sl. 2. *Provera procesa stabilizacije/solidifikacije [5]*

4. IZBOR ADITIVA U ZAVISNOSTI OD VRSTE OTPADA

Izbor metode S/S opasnog otpada zavisi od vrste otpada, sadržaja opasnih i štetnih komponenti, i primenjuje se kao metoda predtretmana opasnog otpada pre odlaganja na deponiju.

Veliki uticaj na efikasnost procesa ima izbor aditiva koji se koriste u procesu S/S, a koji zavise se od vrste otpada i uslova starenja produkta procesa S/S. Efikasnost S/S procesa vrši se određivanjem mobilnosti opasnih i štetnih komponenti, i pritisnom čvrstoćom, nakon postupka solidifikacije/stabilizacije.

Aditivi koji se primenjuju kao veziva u procesima S/S mogu biti neorganskog, organskog porekla, ili njihova kombinacija. Najčešće primenjeni aditivi su neorganskog porekla i to: cement, pepeo, kreč, rastvorljivi silikati, pocolani, bentonit, glina, šljaka visokih peći i drugi materijali, a organski aditivi su asfalt, epoksid, poliestar i polietilen. U više od 90% procesa S/S koriste se neorganska veziva. U principu, neorganska vezi-

-

skih. Organska veziva se obično koriste za solidifikaciju radioaktivnog otpada ili specifičnih i opasnih organskih jedinjenja [6].

4.1. Neorganska vezivna sredstva kao aditivi

U cilju lakšeg izbora aditiva, u zavisnosti od vrste otpada, u radu autora *Fleri M. A., i sar., (2007),* [7] dat je pregled aditiva koji se koriste u procesima S/S. Na osnovu rezultata dobijenih analitičkim metodama obrade uzorka i kriterijuma koje treba da ispuni S/S otpadni materijal vrši se preliminarna selekcija aditiva.

Najčešće korišćen aditiv je *portland cement (PC)*, koji može da zadovolji razne fizičke i hemijske uslove [8]. Tokom testiranja, portland cement se obično kombinuje sa drugim reagensima za formiranje smeše koja zadovoljava potreban kriterijum. Dodaci od primarnog značaja su pocolani, bentonit i hemikalije koje smanjuju luženje i razređivanje zagađujućih materija.

Pocolani su dodaci koji sadrže leteći pepeo, silicijumove pare i druge fino mlevene supstance koje cementu povećavaju čvrstoću, gustinu i izdržljivost. U oblasti zaštite životne sredine najčešće se koriste pocolani koji uključuju leteći pepeo i šljaku iz visoke peći. Pepeo se može podeliti u dve glavne klase, kao što je navedeno u ASTM C618 standardu [9].

Drugi značajan pocolan je *šljaka* visoke peći, koji se definiše kao „nemetalni proizvod koji se u suštini sastoji od silikata, alumino-silikata kalcijuma i osnove koja se razvija u istopljenom stanju istovremeno sa gvožđem u visokoj peći.“ Tri vrste šljake se koriste u proizvodnji cementa, i to su vazdušno hlađena, ekspandirana i granulisana šljaka. Osnovna osobina ovih vrsta šljaka je trajnost i upotreba kao dodatak cementnim proizvodima. Zbog svoje pristupačne cene i dostupnosti, šljaka visoke peći je izabrana za upotrebu u smeši sa letećim pepelom [7].

Bentonit je obrađen glineni materijal koji se sastoji uglavnom od minerala montmorilonita. On ima veliki afinitet prema vodi i, kada je hidratisan, povećava svoju zapreminu više od 7 puta [10]. Bubrenje i mala propustljivosti su svojstva zbog kojih je upotreba bentonita široko rasprostranjena u projektima zaštite životne sredine. Smanjenje propustljivosti donjeg dela zemljišta može se postići malim dodacima bentonita; dodavanjem samo 0,75% bentonita propustljivost se smanjuje dva puta.

4.2. Efikasnost aditiva za različite vrste otpadnog materijala

Uspešnost procesa S/S pre svega zavisi od izbora aditiva i njihove efikasnosti. U tabeli 1. dati su aditivi koji se najčešće koriste i njihova primena u zavisnosti od vrste otpadnog materijala.

Tabela 1. *Preporučene procesi S/S u zavisnosti od vrste otpada* [4]

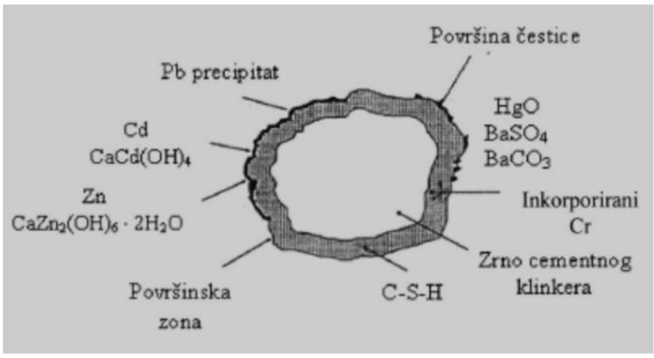
Proces S/S	Primena
Solidifikacija sa cementom	Muljevi, kontaminirana zemljišta
Solidifikacija sa krečom	Otpad od desulfurizacije otpadnih gasova, drugi neorganski otpad
Solidifikacija sa termoplastičnim materijalima	Radioaktivni otpad
Inkapsulacija	Muljevi, tečnosti, određene materije
Vitrifikacija	Ekstremno opasan otpad, radioaktivni otpad

U ovakvim slučajevima efikasna je primena cementa kao aditiva za vezivanje tečne faze, jer cement reaguje sa vodom, hemijski vezujući vodu u hidratisani cementni proizvod. Slobodna tečna faza pri dodavanju cementa vezuje se za njega češće hemijskim vezama, a ređe biva adsorbovana, i zbog toga je otpor na kompresiju najmanje 0,34 MPa (50 psi) [4].

U slučaju sprovođenja remedijacije, kao postupka održivosti zemljišta, S/S je često jedino rešenje i dostupna tehnologija za remedijaciju velike količine zemljišta kontaminirane teškim metalima, mulja ili taloga. U ovom slučaju kao se preporučuje cement, jer smanjuje mobilnost metalnih jona, formiranjem teško rastvornih hidroksida metala, karbonata ili silikata. U toku procesa S/S dolazi do prelaska metala iz jonskog oblika u mineralnu strukturu i fizičke inkapsulacije. Takođe, predtretmanom se može smanjiti toksičnost nekih metala promenom valentnog stanja [4].

Primenom kombinovanog postupka stabilizacije i solidifikacije otpada koji sadrži teške metale, u velikoj meri dolazi do transformacije oblika u kome se teški metali nalaze i najčešće prelaze u teško rastvorne hidroksidi u kojima je smanjena mobilnost jona teških metala.

Solidifikacijom se dodatno smanjuje mobilnost teških metala iz novonastalih teško rastvornih oblika, slika 3.



Sl. 3. *Proizvod procesa stabilizacije i solidifikacije opasnog otpada koji sadrži teške metale, primenom Portland cementa kao aditiva* [11].

Tretman materijala koji sadrži pretežno organske zagađujuće materije moguć je takođe primenom cementa kao aditiva. U toku procesa S/S dolazi do očvršćavanja materijala, kroz promene fizičkih osobina cementa. Naročito se preporučuje ukoliko otpad ili materijal sadrži slobodnu vodu, koja ulazi u proces hidratacije, stvarajući sa cementom visoko fizički integrisan materijal, monolit. Postupak je pokazao visoku efikasnost u smanjenju mobilnosti opasnih i štetnih materija iz otpada koji sadrži polu i teško isparljive policiklične aromatične ugljovodonike (PAH), polihlorovane bifenile (PCB), pesticide, organske cijanide i dr.

Nedostatak S/S primenom cementa je u slučajevima kada otpad ima visoki sadržaj masti i ulja, kada je onemogućen proces hidratacije cementa. Čestice cementa bivaju obložene uljima ili mastima, čime je onemogućen kontakt između cementa i vode. Neke organske komponente utiču na vreme vezivanja cementa, čime ceo postupak solidifikacije može znatno da se produži. Iz navedenih razloga, neophodno je pre izbora aditiva uraditi kompletnu kvalitativnu i kvantitativnu hemijsku analizu otpada, čime se sprečava nastanak neželjenih efekata na samom terenu. Takođe, upotrebom negašenog kreča kao aditiva dolazi do egzotermne reakcije tokom procesa hidratacije, čime se oslobađa znatna količina energije. Ako su u otpadu prisutne lako isparljive opasne i štetne komponente, iste će tokom procesa S/S biti emitovane u atmosferu. Ako ne postoji druga alternativa negašenom kreču kao aditivu u procesu S/S, neophodno je obezbediti uređaje za sakupljanje i tretman gasova/vazduha [4].

4.3. Izbor aditiva u zavisnosti od vrste otpada

U cilju lakšeg izbora aditiva u zavisnosti od vrste otpada rađena su istraživanja od strane autora *Chan B. K. C. i sar. (2008),* [14]. Ispitivani materijali za izradu modela za izbor aditiva bili su sledeći: JR – otpad sa najvećim sadržajem opasnih komponenti, OMW - fino granulisani otpad sa niskim sadržajem opasnih komponenti. Testirani aditivi su: SS - kvarcni pesak, PC - komer-cijalno dostupni Portland cement, FA - leteći pepeo i L - kreč. U tabeli 2. prikazani su rezultati ispitivanja stabilizacije opasnog otpada sa različitim sadržajem opasnih komponenti primenom različitih aditiva i sa različitim udelom.

Tabela 2. *Rezultati ispitivanja stabilizacije opasnog otpada sa različitim sadržajem opasnih komponenti primenom različitih aditiva [12]*

MEŠAVINA	% Osušenog kontaminiranog zemljišta/otpada						Udeo voda/otpad
	PC	FA	SS	OMW	JR	L	
5PC-FA	5	15	80	-	-	-	0,20
5PC-FA-OMW	5	15	70	10	-	-	0,30
5PC-FA-JR	5	15	70	-	10	-	0,25
10PC-FA-JR	10	15	65	-	10	-	0,30
10L-FA-JR	-	15	65	-	10	10	0,43
5PC-FA-L-JR	5	15	65	-	10	5	0,41

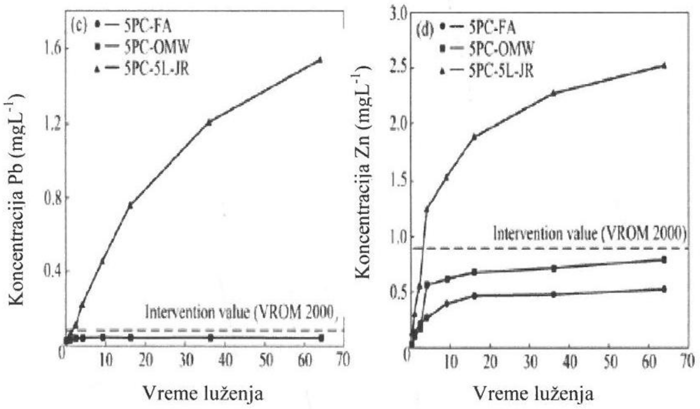
JR - otpad sa najvećim sadržajem opasnih komponenti, OMW - fino granulisani otpad sa niskim sadržajem opasnih komponenti, SS - kvarcni pesak, PC - komercijalno dostupni Portland cement, FA - leteći pepeo i L - kreč

Koncentracije teških elemenata As, Cd, Co, Cu, Mn, Mo i Ni u otpadu posle predtretmana, dobijene sprovođenjem propisanih procedura ispitivanja opasnih i toksičnih karakteristika otpada, bile su ispod granice dozvoljenih vrednosti za podzemne vode i zemljište, čak i iz uzoraka otpada koji ima povećani sadržaj opasnih komponenti. Na slici 4 su prikazana koncentracije Pb i Zn sa različitim aditivima, i sa kojih se vidi da su koncentracija Pb i Zn sa kombinacijom aditiva 5PC-5L-JR iznad dozvoljenih granica. U ispitivanom uzorku JR koncentracije Pb i Zn su bile iznad dozvoljenih granica. Rezultati ispitivanja kontaminiranog zemljišta sa manjim sadržajem opasnih komponenti, a nakon sprovedenog postupka predtretmana, dali su zadovoljavajuće rezultate [12]. Adsorpcija na hidratisanom gvožđe(III)-oksidu, koji je bio prisutan u uzorcima smanjila je mobilnost jona arsena, slika 5.

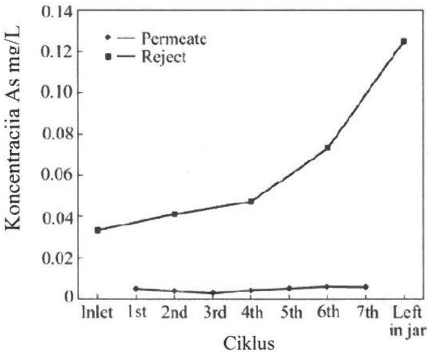
4.4. Pravilan izbor reagensa

Za stabilizaciju otpada koji sadrži teške metale i veliku količinu vode, a koji je nastao kao posledica rudarskih aktivnosti, postupak koji se preporučuje je neutralizacija krečom iz razloga stvaranja teško rastvornih hidroksida u alkalnim uslovima.

Dodatno, u postupku solidifikacije može nastati po površini zrna, u prisustvu silicijuma i aluminijuma, nepropusna barijera, kalcijum-silikatni gel ili kalcijum-aluminatni gel, čime se povećava efikasnost postupka [13]. Kriva rastvorljivosti hidroksida teških metala u zavisnosti od pH vrednosti sredine prikazana je na slici 6. (a), čime se jasno uočava uticaj pH vrednosti na mobilnost teških metala [4].

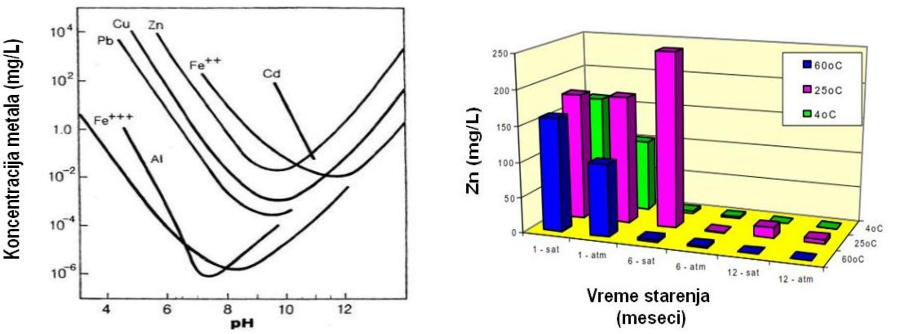


Sl. 4. *Koncentracije Pb i As uz dodatak različitih aditiva [12]*



Sl. 5. *Koncentracija As bez i sa dodatkom aditiva (Fe_2O_3) sa početnom koncentracijom As od 0,03 mg/L [12]*

Tretman nastalog produkta nakon procesa solidifikacije i stabilizacije otpadnog materijala može imati značajni efekat na efikasnost postupka. Na slici 6. (b) prikazan je uticaj temperature i uslova sušenja i vremena starenja na mobilnost cinkovih jona u mulju.



(a) *(b)*

Sl. 6 *(a) Kriva rastvorljivosti hidroksida teških metala u zavisnosti od pH vrednosti i (b) Uticaj temperature, uslova sušenja i vremena starenja na mobilnost cinkovih jona u mulju [4]*

Sa slike 6. se jasno uočava da starenje od 6 meseci pri temperaturi od 25°C, pri atmosferskim uslovima, smanjuje mobilnost jona cinka na ispod 10 mg/L [4].

5. PROCESI STABILIZACIJE/SOLIDIFIKACIJE IN-SITU I EX-SITU

Procesi i tehnologija stabilizacije/solidifikacije in-situ popularni su za tretman i remedijaciju kontaminiranog zemljišta, posebno na lokaciji na kojoj objekat već postoji ili je napušten. Proces S/S doprinosi održivom razvoju, tako što se kontaminirani materijal može tretirati na licu mesta i na taj način ponovo koristiti, bez potrošnje goriva za transport i smanjenja rizika za okolinu [1].

In-situ stabilizacija/solidifikacija, odnosno dubinsko mešanje zemljišta, je široko prihvaćen tehnika u oblasti zaštite životne sredine, koja se koristi za imobilizaciju zagađujućih materija, čime se sprečava dalje širenje zagađenja kroz zemljište i podzemne vode. S/S se koristi za ekološko tretiranje raznih industrijskih otpadnih materijala na kontaminiranim lokacijama. U svakom slučaju, tretiran materijal može se ponovo upotrebiti na licu mesta ili na drugoj lokaciji, što značajno smanjuje troškove, i štiti zdravlje ljudi i životnu sredinu [1].

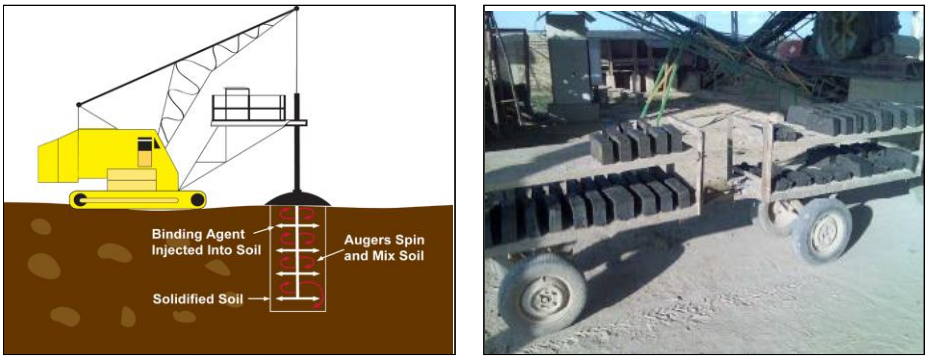
Najzastupljenija *in-situ* proces stabilizacije podrazumeva mešanje kontaminiranog zemljišta ili otpada sa cementom kao aditivom ili drugim materijalima koji imaju slične hemijske i fizičke osobine (leteći pepeo i sl.), koji imaju veliku sposobnost adsorbcije, time smanjuju pokretljivosti opasnih i štetnih komponenti [14].

Procesi S/S koji se koriste za remedijaciju imaju namenu da smanje prolazak zagađujućih materija iz zemljišta, taloga, mulja i otpada koji se ispira (luži) iz izvora zagađenja u okolinu, u okviru prihvatljivih kriterijuma navedenih u cilju remedijacije.

Tehnologija S/S se može primeniti za širok spektar zagađujućih materija. Uspešna primena ove tehnologije počinje ispitivanjem lokacije. Nakon toga, i na osnovu prikupljenih podataka, vrši se izrada tehnoekonomske studije (TS – *Treatibility Study*) i pilot studije (PS – *Pilot Study*) iz kojih se vidi potrebna količina i uticaj veziva na zemljište, kao i geohemija zemljišta. Da bi se utvrdila potencijalna efikasnost S/S tehnologije treba prikupiti parametre koji se odnose na testove i kriterijume, koji se koriste za razvoj S/S tretmana koji zadovoljava ciljeve remedijacije. Ove specifikacije imaju za cilj: (1) usmeravanje i procenu fizibiliti studije, i (2) uspostavljanje minimalnog broja operacija na terenu i usklađenost karakteristika materijala u laboratorijskim uslovima. Unapređenje tehnologije – projekta S/S vrši se praćenjem životnog cilkusa procesa, od istraživanja lokacije do potpunog završetka remedijacije, kao dokaz održivosti tehnologije. Dobro urađena fizibiliti studija može smanjiti broj i vrstu aditiva koje je potrebno koristiti u pilot studiji, koja takođe omogućava pravilno određivanje cena, isporuku i dostupnost aditiva i vezivnih sredstava, kao i da se bolje razumeju fizičke i hemijske osobine kontaminiranih otpada. Izbor aditiva i veziva mora se vršiti planski, na osnovu fizičkih i hemijskih osobina otpada, zatim na osnovu najboljeg isporučioca aditiva, a i najrasprostranijeg i najisplativijeg vezivnog sredstva, jer troškovi za aditive mogu da iznose 30-50 % od troškova za stabilizaciju [7].

Kada je remedijacija implementirana – realizovana, potrebni su dugoročni programi upravljanja prirodnim resursima koji se obično koriste za proveru da li je projekat i dalje na snazi, i kao takav da li štiti zdravlje ljudi i životnu sredinu *(ITRC).*

Fleri M. A. i sar.(2007) [7] prikazali su niz projekata u kojima je prikazana tehnologija stabilizacije koji uključuju injektiranje vezivnog sredstva u zemljiste. U stvari, tehnologija dubinskog mešanja zemljišta postaje čest izbor remedijacione tehnologije, slika 7., jer se smanjuje količina iskopanog zemljišta (off-site), i na taj način štede naknade i troškovi uklanjanja i naknadnog popunjavanja; smanjuju se neprijatni mirisi za vreme vršenja sanacije okoline i ukupni remedijacioni troškovi su znatno niži od drugih remedijacijonih tehnologija, kao što termička desorpcija i in-situ hemijska oksidacija za otklanjanja kontaminiranih materijala.



(a) *(b)*

Sl. 7. *S/S proces in-situ (a) i ex-situ (S/S otpadni materijal) (b)*

Procesi S/S *ex-situ* se primenjuju u pogonima koji su projektovani za te procese, a koriste se za različite vrste muljeva, i druge otpadne materije koje sadrže „opasne“ supstance, kao što su teški metali, S/S otpadni materijal dat je na slici 7 [15].

6. ZAKLJUČAK

Za procese stabilizacije/solidifikacije (S/S) je dokazano da su efikasni za tretman otpada koji sadrži opasne materije. Najvažniji korak u procesu S/S otpadnog materijala predstavlja kvalitativna i kvantitativna analiza otpadnog materijala, na osnovu koje se može izvršiti izbor vezivnog sredstva i aditiva. Fizičkim i hemijskim metodama vrše se ispitivanja S/S proizvoda, na osnovu kojih se vrši njegova kategorizacija.

Promenom fizičkog karaktera otpada primenom procesa stabilizacije/solidifikacije, sprečava se nastanak velike količine procednih voda na deponiji sa visokim sadržajem opasnih i štetnih komponenti; čime se postiže dvostruki efekat, štiti se životna sredina sa jedne strane, a sa druge strane smanjuju se troškovi procesa zbrinjavanja opasnog otpada, jer nema potrebe za instalacijom i radom sistema za prečišćavanje otpadnih/procednih voda sa deponije.

LITERATURA

[1] Wilk C. M. (A), Applying Solidification/Stabilization for Sustainable Redevelopment of Contaminated Property [Internet]. LEHP, QEP, LEED AP Program Manager, Waste Treatment Portland Cement Association; http://www.pollutionengineering.com/ext/resources/PE/Home/Files/PDFs/PCA_S-S_Whitepaper.pdf?1354286601

[2] ITRC, [Internet]. Washington: Interstate Technology & Regulatory Council, http://www.itrcweb.org/ Team/Public?teamID=15

[3] EPA, 1999., [Internet]. Solidification/stabilization resource guide, EPA/542-B-99-002 (1999), http://epa.gov/tio/download/remed/solidstab.pdf

[4] Zinck J., [Internet]. Canada: Review of Disposal, Repro-Cessing and Reuse Options for Acidic Drainage Treat

ment Sludge, The Mining Association of Canada, MEND and CENMET Mining and Mineral Scienties Laboratories, MEND Report 3. 42. 3, 2005: 3, http://mend-nedem.org/wp-content/uploads/2013/01/3.42.3.pdf

[5] EPA 1993., [Internet]. Technical Resource Document, Solidification/Stabilization and its Application to Waste Materials, June 1993, p. 1-5. p. 2-6. (A), p. 2-2. (B)

[6] EPA, 2000., [Internet]. Solidification/Stabilization Use of Superfund Sites, EPA-542-R-00-010, Septembar 2000, http://www.epa.gov/tio/download/remed/ss_sfund.pdf

[7] Fleri M. A., Whetstone G. T., In situ stabilisation/solidification: Project lifecycle, J. Hazard. Mater. 2007; 141: 441–456.

[8] ASTM C150, Standard Specification for Portland Cement, vol. 4.01, American Society for Testing Materials, West Conshohocken, Pennsylvania, 2003, pp. 150– 153.

[9] ASTM C618, Standard Test Method for Coal Fly Ash and Raw or Calcined Natural Pozzolan for Use in Concrete, vol. 4.02, American Society for Testing Materials, West Conshohocken, Pennsylvania, 2003, pp. 319–321.

[10] Black Hills Bentonite, LLC. 2009., [Internet]. Wyoming, http://www.bhbentonite.com/minchar.htm

[11] Ganjidoust H., Hassani A., Rajabpour Ashkiki, Cement-Based Solidification/Stabilization of Heavy Metal Contaminated Soils with the Objective of Achieving High Compressive Strength for the Final Matrix, Sharif University of Technology, Transaction A: Civil Engineering, 2009; 16: 107-115, http://www.sid.ir/en/VEWSSID/J_pdf/95520092A05.pdf

[12] Chan B. K. C., Bouzalakos S., Dudeney A. W. L., Integrated Waste and Water Management in Mining and Metallurgical Industries, Trans. Nonferrous Met. Soc. China. 2008; 18: 1497-1505

[13] Bakstrom M. Baltic Sea Region Programe, Orebro University, Sweden: Compendium of Mining and Processing Waste Management Technologies, Project: MINNOVATION Mining and Mineral Processing Waste Management Innovation Network, Baltic Sea Region Programe, 2013: 214, http://www.minnovation.eu/uploads/compendium%20of%20Mining %20and%20Processing%20Waste%20Management%20Technologies.pdf

[14] Gardić V., Obradović Lj., Filipović S., Review of Solidification and Stabilization Methods of Hazardous Waste, MME Bor. 2013; 4: 93-100.

[15] Krčmar D., Stabilizacija/solidifikacija mulja bogatog arsenom. http://www.arsenicplatform.pmf.uns.ac.rs/pdf/10_Solidifikacija.pdf

MINING AND METALLURGY INSTITUTE BOR	ISSN: 2334-8836 (Štampano izdanje)
UDK: 622	ISSN: 2406-1395 (Online)

UDK: 622.79:658.567(045)=111	doi:10.5937/MMEB1503109B

Kenzhaliyev Bagdaulet[*], *Berkinbayeva Ainur*[*]

RECOVERY OF PRECIOUS AND NON-FERROUS METALS FROM THE REBELLIOUS COMPLEX OF MINERAL RAW MATERIALS

Abstract

The results of comprehensive researches aimed to develop the advanced technology of rebellious refractory minerals and ore processing are given in this paper. Some ways in solving the most challenging technological problems associated with complex ores enrichment and hydrometallurgical processing to recover precious and non-ferrous metals, biochemical leaching inclusive, as well as recommendations on processing of leaching solutions aimed at valuable components recovery are proposed. Effects of reagent X on dissolving the non-ferrous and precious metals as well as the associated elements from refractory ore, concentrates and metallurgical production wastes are shown.

Reagent X promotes metal leaching through a control of oxygen regime of leaching process. Reagent X, capable to form readily soluble metals hetero-complexes, plays a prominent part. Beneficial effects of reagent X on the mineral polarizing processes in alkali-cyanides media were found. Reagent X pretreatment enhances metals recovery into solution by 20-30 % depending on the process time.

Process of Au, Cu, Zn etc., dissolving from rebellious gold-bearing raw materials was studied through the use of unique microorganisms strain; there are identified chemo-physical regularities of chemical leaching process, and the innovation technology of chemical leaching of gold-containing materials was developed.

***Keywords**: precious metals, non-ferrous metals, refractory ores, hydrometallurgy, sorption*

INTRODUCTION

Complex mineralogical compositions of the ore are responsible for considerable engineering difficulties and lead to inadmissibly reduced recovery of principal metals in the enrichment processes. Many problems occur both in the ore processing and beneficiation of produced concentrates. Default of generalized criteria to evaluate the metamorphozation degree of the ore, default of assessment particular chemo-physical features through differences of homonymic minerals of the ore, effects of mentioned differences on associated interactions with minerals of enclosing rocks result in considerable metals losses in such ore processing by the applied technologies for many years.

So, for example, referred to [1], over 100 tons of mineral raw materials are annually mined and processed per capita, out of which 95% go to waste. The annual volume of industrial waste overgrows one billion tons. So far, mentioned data prove an urgent necessity to diversify productions in mining and smelting industries provided that there are developed scientific concepts of resource-saving and environmentally sound technologies. Numerous engineering solutions are developed and implemented in the world industrial practice.

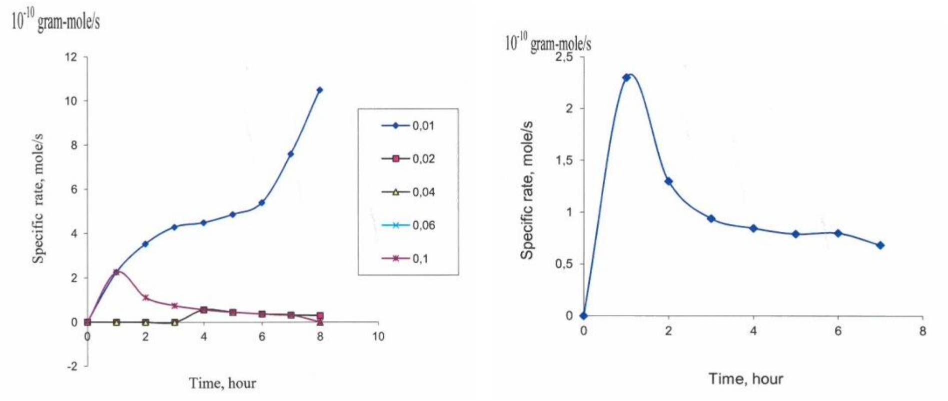
---

[*] *Kazakh-British Technical University, Almaty City, Republic of Kazakhstan,
e-mail:bagdaulet_k@mail.ru, Phone+727-3334175, Fax: +727-2723368*

EXPERIMENTAL PART

In [2-6] it was shown that the amino acids may be used as the ore metal solvents combined with oxidants and salting-out agents in the sorption and heap leaching processes. At that individual reagents “X” among the amino acids capable to form readily soluble metals hetero-complexes are of crucial importance.

It was shown that cysteine at 0.01 g E/dm^3 concentrations had the utmost effect on gold recovery from flotation concentrates. Up to 22.57 % recovery rates were achieved that is about twice as compared to the benchmarks (13.7%). Specific rate of gold dissolving increased over time and it reached 10^{-9} mole/s for eight hours. At higher amino acids concentrations this regularity was not observed (Fig. 1, a). Comparison of this value with the alternative variant without cysteine (Fig.1, b) revealed a substantial advantage to introduce 0.01 gE/dm^3 cysteine into pulp before leaching start-up.



a *b*

Figure 1 *Specific rate of gold dissolving in the process of flotation concentrate chemical leaching in the presence of cysteine (a) and Control (b)*

Similar effects of cysteine are observed in copper leaching process. Increasing cysteine concentration promotes recovery of such associated elements as iron and arsenic (Fig. 2).

It was shown that concentration of oxygen, which provides an oxidizing trend of processes, occurred in pulp, increases with cysteine introduction. In course of leaching process, the oxygen concentration in pulp substantially decreases at all studied cysteine concentrations, in particular, during first five hours of leaching. In further running of leaching process, the oxygen concentration again increases.

It was found that electric conductivity of pulp increases only at higher cysteine concentrations (0.06–0.1 gE/dm^3). Leaching process itself is characterized by increased electric conductivity as compared to the initial values for 2 – 5 times at 0.01–0.04 gE/dm^3 and remains higher in all course of leaching process, where jump fluctuations of electric conductivity are observed at higher concentrations.

Detailed analysis of all parameters for the first five leaching hours revealed substantial decrease of oxygen concentration in the first process hour associated with rated-down gold dissolving and stabilized electric conductivity. Near to 6th hour, the pattern varied: rate of gold recovery into solution increased concurrently with a sharp increase of oxygen concentration.

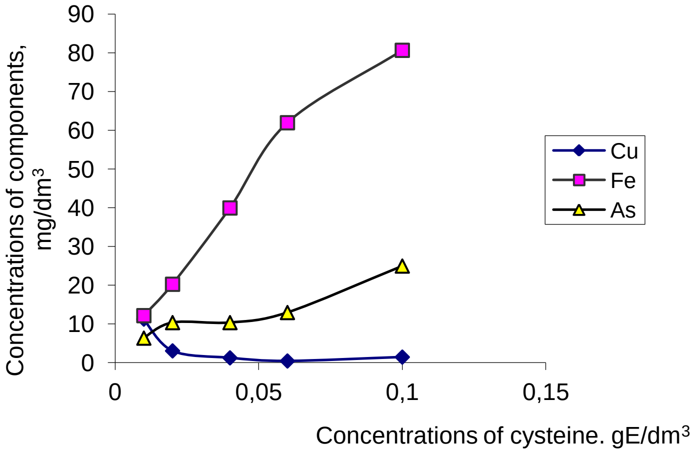


Figure 2 *Dependences of copper, iron and cyanic recovery on cysteine concentrations at 20ºC*

Probably this five-hour inhibition of gold dissolving was due to intense yield of other elements into solution, in particular, the iron yield which concentration increased only in the first leaching hours.

With temperature increasing (from 20ºC to 30ºC), the rate of gold recovery at lower cysteine values increased pro rata to the increased process time duration. Quantity of dissolved oxygen decreased in course of eight-hour experiment and generally electric conductivity increased approximately by 2%.

Increasing of mill rotation speed from 200 rpm to 400 rpm resulted in the increased gold yield by twice or more at 0.01 gE/dm^3 of cysteine concentration showing dependence in a direct proportion. With increasing the amino acids concentration trend to increased gold recovery into solution remains, however at substantially lower level. Increasing of mill rotation speed at 0.02 gE/dm^3 cysteine in pulp resulted in substantially increased oxygen concentration in pulp. At that, pulp electric conductivity remains practically unvaried. We controlled cysteine concentrations in pulp during the whole leaching process. It was found that in the process of concentrate leaching amino acid was not consumed rather it affected only the leaching process performance.

Experimental data proved that in the presence of reagent "X" in leaching pulp lead to 50% saving of cyanic acid. Quantum-chemical computations of potential chemical reactions in pulp allow assuming high probability of hetero-complex (amino acid-Au-cyanide) formation. This complex, as well as $Au(CN)_2^-$, is negatively charged that is critically important to analyze chemistry of leaching processes. The initial metal fixation with amino acid makes easier further cyanide-ion addition. In case of cysteine, there is possible presence of complex as (amino acid-Au-amino acid) due to cyanide deficiency.

Introduction of 0.01 gE/dm^3 cysteine into leaching solution provided 22.57% gold recovery rendering beneficial effects on gold dissolving rate. However, in the first five hours of leaching process some adverse events occurred, probably due to intensive recovery of such associated elements as iron, arsenic and antimony into solution. Concentrations of amino acid subjected to temporal fluctuations remained by the end of leaching process at their initial level, that is, cysteine was not consumed. Temperature factor and agitation rate render beneficial effects equalizing initial 5-hours inhibition of gold leaching process. Increasing of oxygen concentration and electric conductivity in presence of cysteine evidences intensified oxidizing processes in pulp. Quantum-chemical computations confirm involvement of cysteine in leaching process, which probably, promotes formation of gold heterocomplex compounds.

By similar way, the leucine effects were studied on leaching process. In presence of leucine with increasing its concentrations from 0.01 gE/dm^3 to 0.06 gE/dm^3, the gold recovery increased from 57.04 % to 71.42%, respectively. At that, the specific rate of metal recovery into solution increased (Fig. 3). Metal content in solution reached 8.9 mg/dm^3. Equilibrium gold concentration reached the steady state in three leaching hours practically to the full extent. Reaction order defined through the Van’t Hoff diagram method was equal to 0.34.

The addition of 0.01 - 0.02 gE/dm^3 leucine into leaching solution affects no oxygen regime of pulp. Further increasing leucine concentrations leaded to somewhat decreased oxygen concentrations. In leaching process at 0.01 gE/dm^3 leucine the oxygen concentration sharply increased, especially, in the first leaching hours. At extended time of leaching process, the oxygen content in pulp jumped. At higher concentrations, oxygen content in pulp was stable.

Electric conductivity was substantially increased only when 0.1 gE/dm^3 of amino acid were added. In leaching process, as a rule, it increased, with exception of alternative of 0.1 gE/dm^3 leucine.

Rate of copper recovery into solution rose with increasing amino acid concentrations up to 0.06 gE/dm^3. Arsenic and iron recovery increasing up to 0.04 gE/dm^3 (Fig. 4) was observed with increased concentrations of leucine.

As it seen from experimental data, the best results by gold recovery into solution were achieved in presence of 0.04-0.06gE/dm^3 leucine. Data follow-up by oxygen regime, electric conductivity and variations of leucine quantity in pulp allowed revealing that oxygen concentrations during practically the whole leaching period remained at level of 6 mg/dm^3.

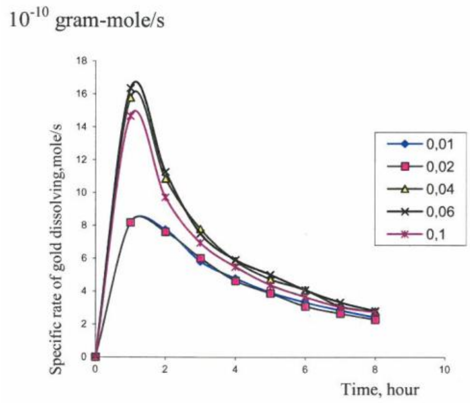


Figure 3 *Specific rates of gold dissolving in the process of biochemical leaching of flotation concentrate in the presence of leucine (0.01-0.1 gE/dm^3)*

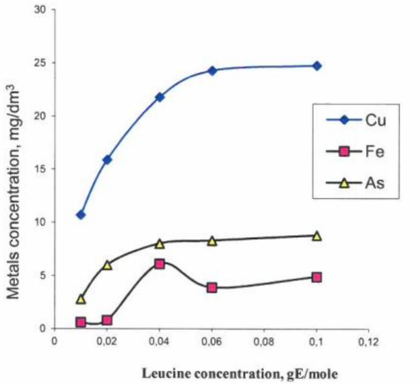


Figure 4 *Dependence of copper, iron and arsenic recovery on leucine concentration 20ºC*

Electric conductivity progressively increased from 3 mCm/cm to 7 mCm/cm in the first 4 hours, and then it remained at this level by the end of leaching process. Con centration of leucine after jumped variations, remained at its initial level, this is, similarly to cysteine alternative, the amino acid was not consumed in leaching process.

The gold recovery/temperature dependences were studied at different leucine concentrations. It was found that at 0.01 gE/dm^3 leucine concentration, the rate of gold recovery into solution practically does not depend on temperature, only the rate of equilibrium concentration reaching was intensified. At higher leucine concentrations (0.02; 0.04 gE/dm^3) with increasing temperatures (from 20ºC to 30ºC), the gold recovery into solution increased. The same behavior pattern was observed in copper leaching, while for iron and arsenic there was observed the contrary: increasing temperature leaded to decreased iron and arsenic recovery into solution. Optimal temperature of gold leaching was 30°C. At this temperature the 4-hours leaching provided 88.35 % gold recovery into solution where leucine content in solution reached 0.04 gE/dm^3 and at rate of mill rotation up to 300 rpm. Energy of activation of gold dissolving reaction at optimal leucine concentration (0.04 gE/dm^3) reached 45.43 kJ/mole.

Intensified pulp agitation rendered beneficial effects on gold and copper recovery only at 0.01 gE/dm^3 leucine in pulp. Specific gold dissolving rate increased with increasing mill rotation rate up to 400 rpm providing 80.15 % gold recovery in 7 leaching hours. Inverse correlation was observed at increasing amino acid concentration. Iron and arsenic recovery increased with increasing of mill rotation rate.

With intensified pulp agitationthe oxygen content in pulp increased during first 2-3 leaching hours. Pulp electric conductivity increased, then equalized and remained at higher level by the end of experiment.

Leucine used in concentrations ranging from 0.01 gE/dm^3 to 0.06 gE/dm^3 gave rise to gold recovery from 57.04% to 71.42%. In leaching process at 0.01 gE/dm^3 leucine, the oxygen content and solution electric conductivity increased, in particular, in first leaching hours. Gold and copper recovery into solution increased at 0.02 gE/dm^3 and 0.04 gE/dm^3 leucine concentrations with temperatures increasing, while, on the contrary, iron and arsenic recovery decreased. As with cysteine, leucine was not consumed in 8-hours leaching process.

Quantum-chemical computations proved that amino- and acid groups interact in the leucine. Effects of electron-accepting carboxy group and electron-donating oxygen atom of hydroxyl group on amine groups determine acidity degree and are characterized by proton affinity. Leucine showed the highest Eн+c (considering sign) and, hence, the lowest hydration energy (Table 1). Exactly leucine showed the lowest energy of complexes formation in solutions.

In estimating energy of multicomponent systems formation, as with cysteine, there was preferred formation of gold complex, firstly, with leucine anion, then bonding second ligand – cyanide ion. Leucine anion as the first ligand in solution showed higher reaction capacity as compared to cysteine, while, on contrary, by its activity as the second ligand (E3 рсм), it was weaker (Table 1).

Table 1 *Complexing energy at different sequence of ligands addition, kcal/mole*

	E1, kcal/m	E1pcm, kcal/m	E2, kcal/m	E2рсм, kcal/m	E3, kcal/m	E3pcm, kcal/m
Leucine- + Au$^+$ + CN$^-$	-296.183	-112.560	-121.894	-72.848	-66.259	-28.798

Notes: E1 – cyanide-ion and amino acid are concurrently combined with gold;
E1=E(AminAuCN) – E (Au) - E(Amin-) - E(CN)
E2 - at first, gold interacts with amino acid, then the second ligand adjoins: cyanide -ion E2=E(AminAuCN) - E(AuAmin) – E (CN$^-$)
E3 - at first, gold interacts with cyanide-ion, then amino acid adjoins E3=E(AminAuCN) – E (AuCN) - E(Amin-)

It was found that the serine at concentration 0.01 mg/dm^3 provides up to 65.8 % gold recovery into solution in seven hours of chemical leaching. With increased serine content up to 0.04 gE/dm^3, the gold recovery increased up to 66.78%. Presence of 0.06 gE/dm^3 amino acid in pulp stepped up the metal recovery.

Specific gold dissolving rate increased with increasing serine content in pulp from 0.01 gE/dm^3 to 0.06 gE/dm^3. In leaching process it evenly decreased (Fig. 5). Reaction order defined through the Van't Hoff diagram method was equal to 1.04.

It should be noted a more efficient cyanide use in leaching process. Its residual concentration in pulp decreased with increasing serine content in solution.

Increasing leaching process temperature up to 30-40°C was the most efficient for serine concentration 0.1 gE/dm^3. At 30°C gold was recovered into solution by 14.9% and at 40°C by 42.6% and more as compared to leaching conditions at 20°C. In the whole, 8-hours leaching at addition of 0.1 gE/dm^3 serine in pulp allowed to recover up to 98.7% gold in solution. By a similar way copper content in solution increased, while iron and arsenic concentrations decreased. Increasing serine content from 0.01 gE/dm^3 to 0.1 gE/dm^3 concurrently with increasing temperature resulted in sharp decreasing of antimony concentration (from 65.7 mg/dm^3 at 0.01 gE/dm^3 serine up to 12.7-23.5 mg/dm^3 at 0.06-0.1 gE/dm^3 amino acid).

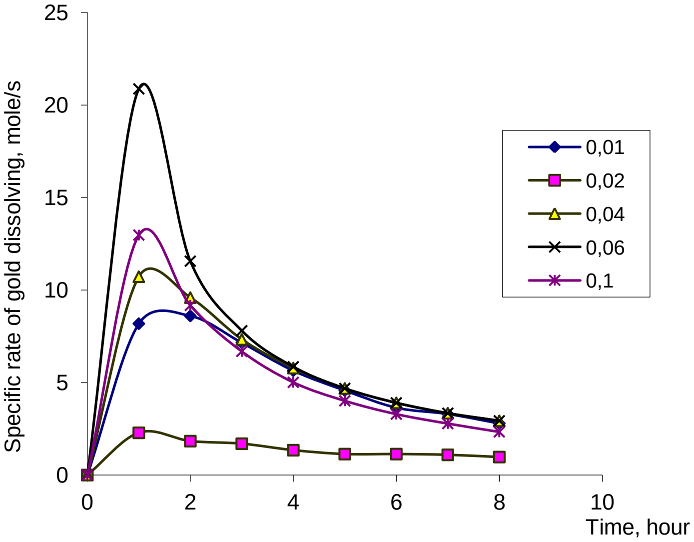


Figure 5 *Changes in specific gold dissolving rates (at different initial quantity of serine, gE/dm^3) in process of the Akbakay flotation concentrate leaching*

With increased temperature up to 30°C oxygen content in leaching pulp decreased while electric conductivity increased (in particular, at 0.01 gE/dm^3 and 0.1 gE/dm^3). Energy of gold dissolving reaction activation reached 21.72 kJ/mole.

Oxygen regime at minimal serine concentration in pulp was improved with increased agitation rate, while this parameter got worse with increased serine concentration. Electric conductivity was not subjected to somewhat significant modifications.

Quantum-chemical study of potential serine/gold complexing in process of flotation concentrate leaching proved that the serine shows lower Eн+ c (considering sign) as compared to leucine and, hence, higher hydration energy. This evidences higher reaction capacity of amino acid. Complexing energy of serine in solution was higher as compared to the leucine.

Probably, in the complexing process, as with other amino acids, gold cation is coordinated concurrently by two atoms: O and N. In case of leucine and serine molecules with optimal complex configuration the binding is coordinated towards to the carbonyl. Nevertheless, in compact serine molecule carbonyl oxygen and electron-donating oxygen atom of second hydroxyl group are also involved in Au binding that substantially promotes complex strengthening. Estimative analysis of multi-component systems formation energy/ligand bonding order dependences proved that the serine and leucine by their activity as first ligand in solution are closely equal**,** at that, serine anion in solution is the weakest second ligand.

RESULTS AND DISCUSSION

It was found that the leucine substantially enhances gold recovery into solution in process of flotation concentrate biochemical leaching. Direct correlation of gold recovery with increased amino acid concentration supplied up to 0.6 gE/dm^3. As judged by leaching process itself, as well as conforming to data of quantum-chemical computations, leucine generates bound with gold, coordinated towards to carbonyl that substantially enhance binding energy and makes easy formation the heterocomplex compounds of amino acid-gold-cyanide type. As result, flotation concentrate leaching in presence of leucine is not associated with complicating effects observed where leaching process runs in presence of cysteine.

It was found that serine promotes gold and copper recovery, improves oxygen regime and pulp electric conductivity. Increased leaching temperature up to 40^{o}C concurrently with increased serine concentration up to 0.1 gE/dm^3 provides 98.7% gold recovery. As with cysteine and leucine, the serine in leaching process is not consumed.

Estimation of different amino acids effects on metals dissolving features in process of flotation concentrate leaching allowed stating that the leucine and serine turned out to be very effective for gold and copper, especially in complex with temperature and agitation. Cysteine within studied range of factors variations promoted iron and arsenic yield. In terms of quantum-chemical study, serine is more active in liquid phase regarding to gold cation and gold cyanide as compared to leucine, at that it forms stronger comple-xes of amino acid-gold-cyanide type as compared to studied amino acids.

Experimental data give grounds to conclude that the amino acids formed in chemical leaching process act as catalysts for chemical reactions of gold dissolving. So, chemical leaching process efficiency may be monitored through changes in amino acid concentrations in leaching solutions and varied amino acids ratios depending on mineral compositions of process raw materials. In this case integrated processing technologies render beneficial effects.

CONCLUSION

Research data on kinetics of anodic oxidation process of chalcopyrite and sphalerite sulfide minerals obtained by the potentiometric method allowed identifying beneficial effects of reagents “X” in the processes of minerals polarizing in alkali-cyanides media. Reagent “X”-assisted minerals pretreatment result in intensified dissolving processes through increase the polarizing current density in the process of anodic minerals oxidation in solutions of pH-9. Within potentials range of 0.3-2.0 V metals recovery increases by 20-30% depending on treatment time duration.

It was found that the serine, leucine and phenylalanine at temperature t = $30^{o}C$ - $40^{o}C$ and agitation intensity up to 300-400 rpm render ultimate effects on gold and non-ferrous metals recovery into solution providing over 90 % gold recovery in 6-8 hours or more of treatment process. At that, oxygen solubility in leaching solutions increases. Values of redox potentials defined for amino acid solutions confirmed functions of serine and leucine in generation of overvoltage at the electrodes providing favorable conditions to recover gold and non-ferrous metals into solutions.

Quantum-chemical computations confirmed the amino acids functions in metals complexing in solution. Stability and consistency of complexes with amino acids and cyanide ion for atoms, having d-open shells, increase in series Fe >Zn>Cu>Au.

Chemo-physical regularities of Au, Cu, and Zn dissolving from rebellious gold-containing raw materials in presence of reagents are identified, kinetic performances of mentioned process are specified and theoretical backgrounds of metals dissolving from rebellious ores are built up, innovative technology of chemical leaching is developed.

REFERENCES

[1] Zhanbatyrov A., LLP “Frontier Mining Ltd”, (2010), pp. 167-170;

[2] James B., Biooxidation in Gold Heap Leaching from Lean Sulfide and Carbonate-Sulfide Ores. USA Patent No. 5246486, Newmont Gold Co., Publication: 21.09.1993;

[3] James B., Biooxidation Process for Recovery of Valued Metals from Brome/Sulfur Containing Raw Materials. USA Pat. No. 5332559. Newmont Gold Co., Publication: 26.07.1994;

[4] Rojas-Chapana I.A., Hydrometallurgy, 59 (2001) 291-300;

[5] Torma A.E., Int. Mater. Rev, 37 (1992) 187-193;

[6] Iguchi T., Ohsawa Emulsifying Factor of Hydrocarbon Produced by Hydrocarbon - Assimilating Yeast, (1969) 1657-1658.

MINING AND METALLURGY INSTITUTE BOR
UDK: 622

ISSN: 2334-8836 (Štampano izdanje)
ISSN: 2406-1395 (Online)

UDK: 669.22:537.311.1(045)=111

doi:10.5937/MMEB1503117M

Aleksandra Milosavljević[*], Ana Kostov*[*], Radiša Todorović*[*]*

CHANGES IN ELECTRICAL CONDUCTIVITY OF THE Ag-In-Sn-Cu ALLOYS AS INFLUENCE OF DIFFERENT TEMPERATURE REGIMES[**]

Abstract

Among ecological solders the SIAC (silver-indium-tin-copper) alloys seemed to be the promising because of their properties. In this paper the results of Ag-In-Sn-Cu electrical conductivity measurements are performed as well as polynomial regression of the same. These results are obtained for different temperature regimes and conditions.

Keywords: *Ag-In-Sn-Cu alloys, electrical conductivity, polynomial regression*

INTRODUCTION

The currently used lead-based solders are under way to be replaced by lead-free alloys due to the environmental and health concerns. In that purpose, various physical, chemical and mechanical properties of the candidate alloy, as well as the economic aspect have been considered. A significant part of work is to find a substitute for common Pb-Sn solder alloy, which has become complex and widely discussed [1-12]. The proper alloy must have the certain characteristics to satisfy:

- Availability
- No Toxicity
- Melting temperature range
- Wettability
- Other process conditions

The solder chosen for a particular use should have a low enough melting temperature that the melted solder does not damage any temperature-sensitive components that are to be joined. However, the melting temperature should also be high enough that the joint formed will not be affected by the operating temperature of the device or by subsequent soldering operations. In modern electronic applications, the temperature sensitivity of microelectronic components requires the use of solders at relatively low temperatures. In comparison, solders for joining and sealing pipes in plumbing operations are generally applied at much higher working temperatures because the components are not as temperature sensitive.

Solders with small pasty ranges are also important in certain "step-soldering" operations where components are added to a device sequentially. These operations are also dependent upon solders with specific melting temperatures. In step soldering, the first components are joined using a relatively

---

[*] *Mining and Metallurgy Institute Bor, Zeleni bulevar 35, 19210 Bor, Serbia e-mail: aleksandra.milosavljevic@irmbor.co.rs*

[**] *The research presented in this paper was done in the frame of the projects: "Development of Ecological Knowledge-Based Advanced Materials and Technologies for Multifunctional Application" No. 34005 financed by the Ministry of Education, Science and Technological Development of the Republic of Serbia*

high melting temperature solder. When later components are joined, a lower melting temperature solder is used so that the earlier-soldered joints are not affected by the soldering operation. Further components may then be added using solder with an even lower melting temperature. The availability of solders with different melting points is critical to such step-soldering processes. It is also important, if several soldering steps are to be performed, for the melting ranges of the solders to be small.

The question about melting temperature is one of the most difficult problems in the lead-free soldering transition, but not the only one. Ecological solder alloys must satisfy more requests in order to completely replace the standard solder alloys. Because of specific properties, there is not drop-in replacement yet.

However, the most promising ecological solder alloys, such as Sn-Ag or Sn-Ag-Cu have higher melting temperatures than conventional tin-lead solder. Because of that, in practice the temperature during electronic assembling must be raised by 30-40°C which reduces reliability and functionality of electronic components. Low processing temperature is desirable for preventing damage of electronic devices during soldering. An attractive solution for melting temperature decrease is theaddition of indium [9], so the indium based multicomponent solder alloys might have the appropriate characteristics.

Some of the alloys based on indium such as In-Sn, are mainly used in the process of cold soldering. The only faults of these alloys are high price of cost, but ductility, good lubricate and fatigue resistance are the qualities necessary for a good solders. Likewise, the alloys which possess some application in practise are Sn-In-Ag and Sn-In-Cu alloys.

Considering two suitable systems Sn-Ag-Cu and Sn-In-Ag and their properties as potential replacement for standard solder alloys, they can be combined for multicomponent alloy based on tin and indium, with the addition of silver and copper which might have better properties. In that case, there is the SIAC alloy (Sn-In-Ag-Cu). When indium is added to the ternary Sn-Ag-Cu alloys, it reacts with tin, silver and copper, and these reactions play an important role in defining microstructure and determining mechanical properties of the alloy.

A large number of researchers around the world as a part of international projects (e.g. COST531 [10]) work on establishing the thermodynamic, mechanical and structural properties of lead-free solders. Their results are reflected in the created databases that contain information about the melting point, density, viscosity, electrical and microstructural properties and phase diagram, starting from the binary and multicomponent alloys. In this way, for a certain type of process and specific requirements the optimum composition of the elements can be predicted, and the optimum alloy that could replace lead solder.

To contribute to the knowledge of ecological solder systems based on tin and indium, the results of the Ag-In-Sn–In–Cu system investigation are presented in this paper.

EXPERIMENTAL PART

Electrical conductivity of all prepared samples was measured at the room temperature using the standard apparatus SIGMATEST 2.069 (Foerster) eddy current instrument for measurements of electrical conductivity of non-ferromagnetic metals based on complex impedance of the measuring probe with diameter of 8 mm.

The Ag-In-Sn-Cu alloys with molar ratio In:Ag:Cu=7:2:1 and within the mole fraction of 0.5 to 0.95 for Sn were experimentally investigated. All samples were prepared from Ag, Cu, In and Sn of 99.99% purity. The chosen samples were investigated in two series A and B with the same compositions and various thermal conditions. The samples from A group, having masses approximately 2 g, were prepared by the induction melting under argon atmosphere, and the procedure was repeated several times to improve homogeneity, while the B samples were melted in electrical furnace up to 873K in argon atmosphere, annealed at 473K one hour, and slowly cooled with the furnace to the room temperature. In both cases, the mass loss of samples was less than 1 %.

Prepared samples were investigated by the standard apparatus in order to obtain the electrical conductivity for all samples.

RESULTS AND DISCUSSION

Twenty tin rich alloys with compositions along cross section with molar ratio In:Ag:Cu=7:2:1 have been experimentally investigated. Ten compositions were chosen from wide concentration area in Ag-In-Sn-Cu system, due to the previous investigations [1-12].

The compositions for both series A and B were the same and are given in Table 1.

Table 1 *The compositions of Ag-In-Sn-Cu samples*

Alloy	Xi			
	Sn	In	Ag	Cu
A1,B1	0.5	0.35	0.1	0.05
A2,B2	0.55	0.315	0.09	0.045
A3,B3	0.6	0.28	0.08	0.04
A4,B4	0.65	0.245	0.07	0.035
A5,B5	0.7	0.21	0.06	0.03
A6,B6	0.75	0.175	0.05	0.025
A7,B7	0.8	0.14	0.04	0.02
A8,B8	0.85	0.105	0.03	0.015
A9,B9	0.9	0.07	0.02	0.01
A10,B10	0.95	0.035	0.01	0.005

Electrical conductivity of all twenty samples was measured in three series and than the average values were calculated in order to obtain the dependence from composition. The results of measured values for Ag-In-Sn-Cu alloys are given in Tables 2 and 3.

Table 2 *Electrical conductivity measured values for the Ag-In-Sn-Cu alloys – A*

Alloy	Electrical conductivity MS/m			
	I	II	III	Average
A1	7,933	8,030	7,946	7,970
A2	8,451	8,515	8,378	8,448
A3	3,120	3,179	3,074	3,124
A4	4,806	5,004	4,756	4,855
A5	4,808	5,107	4,872	4,929
A6	8,668	8,794	8,806	8,756
A7	6,299	6,563	6,437	6,433
A8	8,562	8,555	8,570	8,562
A9	8,690	8,833	8,673	8,732
A10	5,555	5,709	5,575	5,613

Table 3 *Electrical conductivity measured values for the Ag-In-Sn-Cu alloys – B*

Alloy	**Electrical conductivity MS/m**			
	I	**II**	**III**	**Average**
B1	2,544	2,603	2,602	2,583
B2	2,867	2,720	2,657	2,748
B3	1,552	1,650	1,623	1,608
B4	1,590	1,645	1,648	1,628
B5	3,138	3,215	3,161	3,171
B6	1,726	1,848	1,552	1,709
B7	2,802	2,815	2,703	2,773
B8	3,283	3,169	3,361	3,271
B9	1,655	1,800	1,604	1,686
B10	1,300	1,613	1,591	1,501

All measured electrical conductivity values for A and B series showed many deviations. Rapidly changes which are observed are influenced by various intermetallic compounds in microstructure [12], so there could not be precisely defined increasing or decreasing curve as it was in the Ag-In-Sn or Cu-In-Sn alloys [7].

The differences in obtained measured values for A and B samples were obviously consequences of various thermal conditions. All alloys were not exposed to the same temperature regime. In contribution to this, there were differences in the structure and micro-hardness too [12].

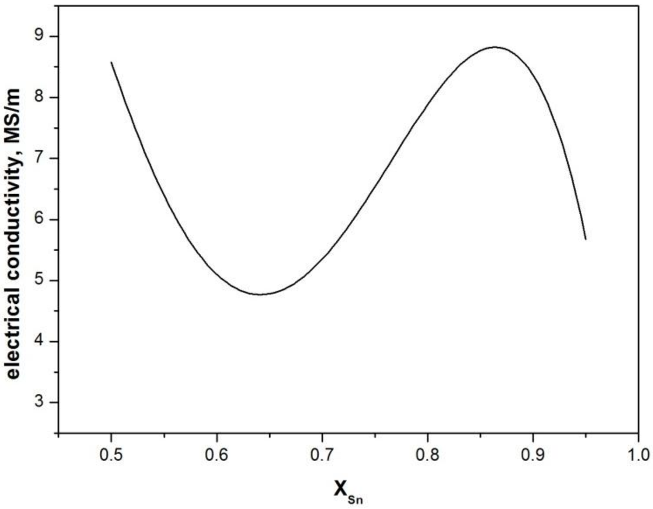


Figure 1 *σ(MS/m) = f (XSn) for Ag-In-Sn-Cu alloys – A*

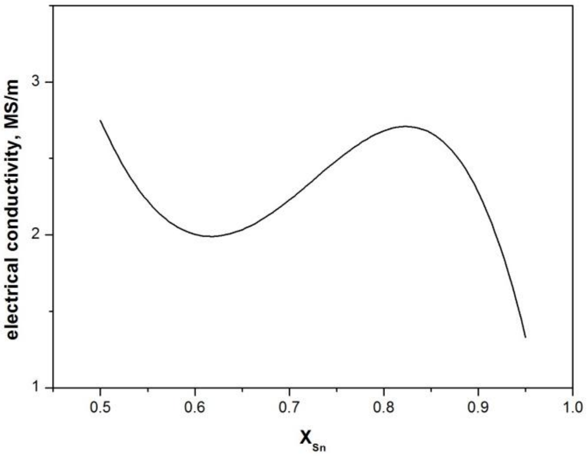


Figure 2 *σ(MS/m) = f (XSn) for Ag-In-Sn-Cu alloys – B*

In order to decrease the number of future experiments in the field of the best substitute for common Pb-Sn solder alloy, the regression model was applied. Polynomial regression was used to get an equation or dependence of electrical conductivity vs. composition with the following expression:

$$Y=A_0+A_1*X+A_2*X^2+A_3*X^3+\ldots+A_n*X^n + R \qquad (1)$$

where R is error which is normally distributed.

The results of electrical conductivity polynomial regression model are equations based on dependency of tin content in the alloy. These functions are shown in Figures 1 and 2. Therefore, equation (2) is for Ag-In-Sn-Cu alloys - A, and (3) is for Ag-In-Sn-Cu alloys - B. Both of expressions are polynomial of fourth order.

$$\sigma(MS/m) = -1210.58275*X^4 + 2907.51671*X^3 -2420.34324*X^2 + 794.10808*X -71.17413 \qquad (2)$$

$$\sigma(MS/m) = -138.36823*X^4 + 235.40618*X^3 -74.94735*X^2 - 46.37578*X + 23.89535 \qquad (3)$$

CONCLUSIONS

The results of electrical conductivity measurement and polynomial regression model of chosen alloys from the Ag-In-Sn-Cu system were presented in this paper, enabling better understanding of these types of alloys. The application of this type of regression model is in calculation of electrical conductivity for these alloys in any point, so the number of necessary experiments could be decreased. Also, the influence of thermal regime on obtained electrical conductivities was pointed out through results for two series of alloys.

As a potential candidate for ecological solder alloy, Ag-In-Sn-Cu alloys need to be well investigated, so the findings from this paper enable expansion of the existing database for this type of alloys.

REFERENCES

[1] Korhonen T. M., Kivilahti J. K., JEM, 27(1998)149

[2] Ohnuma I., Cui Y., Liu X.J., et al., JEM, 29(2000)1113

[3] Liu X. J., Inohana Y., Takaku Y., Ohnuma I., al., JEM, 31(2002)1139

[4] Moser Z., Gasior W., Pstrus J., et al., JEM, 30(2001)1120

[5] S. K. Lin, C. F. Yang, S. H. Wu, S.W.Chen, JEM, 37 (2008) 498

[6] X. J. Liu, H. S. Liu, I. Ohnuma, et. Al., JEM, 30 (2001) 1093

[7] Milosavljević A., Živković D., Manasijević D., Talijan N., Ćosović V., Grujić A. International Journal Materials and Product Technology 39 (1-2) (2010) 95.

[8] A. T. Dinsdale, A. Watson, A. Kroupa, J. Vrestal, A. Zemanova, J. Vizdal, Cost Action 531-Atlas of Phase Diagrams for Lead-free Soldering, 2008.

[9] www.indium.com (Indium Corporation of America, askus@indium.com)

[10] http://resource.npl.co.uk/mtdata/cost531.htm

[11] Popović A., Bencze L., International Journal of Mass Spectrometry 257 (2006) 41

[12] Milosavljević A., Doctoral Dissertation, Bor, 2010

MINING AND METALLURGY INSTITUTE BOR
UDK: 622

ISSN: 2334-8836 (Štampano izdanje)
ISSN: 2406-1395 (Online)

UDK: 669.35:536.7(045)=111

doi:10.5937/MMEB1503123M

Aleksandra Milosavljević[*], *Ana Kostov*[*]

THERMODYNAMIC CALCULATIONS IN THE Cu-In-Sn SYSTEM[**]

Abstract

Tin based alloys with addition of indium and copper are well discussed from the point of phase diagrams, but there are still properties which are not measured or calculated. Therefore, in this paper some calculations were performed in order to obtain the thermodynamic properties by prediction methods. The integral and partial molar excess Gibbs energies, as well as activities of tin in temperature range 873 – 1673 K were obtained for four sections In:Cu=1:1, 1:4, 4:1 and 9:1 in the Cu-In-Sn system.

Keywords: *thermodynamic properties, prediction methods, copper, indium, tin.*

INTRODUCTION

Although the Cu-In-Sn system has been studied a lot and there are the phase diagrams which have been calculated [1-6], there always is a need for more investigations and calculations in order to expand the existing data.

Phase equilibria for the system Cu-In-Sn was investigated by Liu et al. [6], who used the experimental results (differential scanning calorimetry and optical microscopy) and optimized values for binary systems. The liquidus projection for the Cu-In-Sn system and 8 isotermal sections at 110-900°C were given by them [6]. Contribution to the phase equilibria in this ternary system was also given by Milosavljević et al. [7], who determined the phase diagram of section with Cu:In = 1 : 9 in the Sn–In–Cu ternary system, based on thermal analysis and scanning electron microscopy with the energy dispersive X-ray data and applied calculation of phase diagrams method (CALPHAD).

A. T. Dinsdale and A. Watson systematized the results obtained for various solder systems in the atlas of phase diagrams [8], and the Cu-In-Sn as one as potential of ecological solder systems is among them, too. The thermodynamic prediction of the Cu-In-Sn system is performed based on parameters for constitutive binary systems which are included in large COST531 database [9].

THEORETICAL FUNDAMENTALS

Knowledge of the thermodynamic properties of a system has practical and scientific significance. On the basis of thermodynamic values, behaviour of components can be defined in the test system. Due to these reasons, in order to predict the thermodynamic properties of multicomponent system, the

---

[*] *Mining and Metallurgy Institute Bor, Zeleni bulevar 35, 19210 Bor, Serbia
e-mail: aleksandra.milosavljevic@irmbor.co.rs*

[**] *The research presented in this paper has been done in the frame of the projects: "Development of Ecological Knowledge-Based Advanced Materials and Technologies for Multifunctional Application" No. 34005 financed by the Ministry of Education, Science and Technological Development of the Republic of Serbia*

mathematical models were developed based on the characteristics of the elements or components of the system. Also, the adequacy of the applied mathematical models is possible to determine by comparative analysis of the calculated values, with no experimental measurements to test the system.

Basic mathematical interpretation of these models is based on the Gibbs energy for the multicomponent system calculated in dependence of the Gibbs energy of the binary system. In this way, at any point in the isothermal section of the multicom-ponent system an excess of the integral molar Gibbs energy can be determined using values of integral molar excess Gibbs energy for constitutive binary systems. There are usually two kinds of models which are popular for description of ternary systems. These are geometrical models symmetric [10] and asymmetric [11] models.

The basic equations of these predicting models are given as follows:

Toop model:

$$\begin{aligned}\Delta G_{123}^{xs} = {} & \frac{X_2}{1-X_1}\Delta G_{12}^{xs}\left(X_1;1-X_1\right) + \frac{X_3}{1-X_1}\Delta G_{13}^{xs}\left(X_1;1-X_1\right) \\ & + \left(X_2+X_3\right)^2 \Delta G_{23}^{xs}\left(\frac{X_2}{X_2+X_3};\frac{X_3}{X_2+X_3}\right)\end{aligned} \qquad (1)$$

Kohler model:

$$\begin{aligned}\Delta G_{123}^{xs} = {} & \left(X_1+X_2\right)^2 \Delta G_{12}^{xs}\left(\frac{X_1}{X_1+X_2};\frac{X_2}{X_1+X_2}\right) + \left(X_2+X_3\right)^2 \Delta G_{12}^{xs}\left(\frac{X_2}{X_2+X_3};\frac{X_3}{X_2+X_3}\right) \\ & + \left(X_3+X_1\right)^2 \Delta G_{12}^{xs}\left(\frac{X_3}{X_1+X_3};\frac{X_1}{X_1+X_3}\right)\end{aligned} \qquad (2)$$

In both equations corresponds to the integral molar excess Gibbs energy for ternary system, while X_1, X_2, X_3 correspond to the mole fraction of components in investigated system. Integral molar excess Gibbs energies for constitutive binary systems, ΔG_{ij}^{XS} (i,j=1,2,3) are obtained using Redlich-Kister parameters from COST531 Database [9].

RESULTS AND DISCUSSION

In this paper, the thermodynamic properties for the ternary Cu-In-Sn system are calculated for the sections with constant molar ratio In:Cu=1:1, 1:4, 4:1 and 9:1 at 873K up to 1673 K and by different models Kohler [10] [11].

In order to present all calculated values for integral and partial molar excess of the Gibbs energies, as well as activities of tin, the results of this thermodynamic properties are given in form of diagrams in Figures 1-3 for the Kohler method, and Figures 4-6 for the Toop method. Basic data for the thermodynamic calculation were the values of integral molar excess Gibbs energies for constitutive binary systems ΔG_{ij}^{XS}, which are calculated using the Redlich-Kister parameters from COST531 database [9]. These calculated values are given in Tables 1 – 3.

The R-K parameters for the constitutive binary systems are:

- System In-Sn:

PARAMETER G(LIQUID,IN,SN;0) 298.15 -828.54+0.76018*T-0.1211767*T*LOG(T); 3000 N !
PARAMETER G(LIQUID,IN,SN;1) 298.15 -115.59-1.39997*T; 3000 N !

- System In-Cu:

PARAMETER G(LIQUID,CU,IN;0) 298.15 -41564.79+238.616*T-29.827*T*LN(T); 6000.00 N !
PARAMETER G(LIQUID,CU,IN;1) 298.15 -76057.785+371.306*T-44.944*T*LN(T); 6000.00 N !
PARAMETER G(LIQUID,CU,IN;2) 298.15 -42076.516+192.395*T-23.281*T*LN(T); 6000.00 N !

- System Sn-Cu:

$PARAMETER G(LIQUID,CU,SN;0) 298.15 -9002.8-5.8381*T; 3000 N !
$PARAMETER G(LIQUID,CU,SN;1) 298.15 -20100.4+3.6366*T; 3000 N !
$PARAMETER G(LIQUID,CU,SN;2) 298.15 -10528.4; 3000 N !

Table 1 *Calculated values for , J/mol using the Redlich-Kister parameters [9]*

Alloy		**ΔG^{xs}_{In-Sn}, J/mol**								
X_{In}	**X_{Sn}**	**873K**	**973K**	**1073K**	**1173K**	**1273K**	**1373K**	**1473K**	**1573K**	**1673K**
1	0	0	0	0	0	0	0	0	0	0
0.9	0.1	53	67	80	93	106	119	132	145	158
0.8	0.2	52	71	90	109	128	146	165	184	202
0.7	0.3	12	31	50	69	88	107	125	144	162
0.6	0.4	-50	-35	-20	-5	9	24	39	53	67
0.5	0.5	-119	-110	-102	-93	-85	-77	-68	-60	-52
0.4	0.6	-178	-177	-175	-174	-173	-171	-170	-169	-168
0.3	0.7	-212	-217	-221	-226	-231	-236	-240	-245	-251
0.2	0.8	-204	-212	-220	-228	-236	-245	-253	-261	-269
0.1	0.9	-139	-146	-153	-160	-167	-174	-181	-189	-196
0	1	0	0	0	0	0	0	0	0	0

Table 2 *Calculated values for , J/mol using the Redlich-Kister parameters [9]*

Alloy		**, , J/mol**								
X_{In}	**X_{Cu}**	**873K**	**973K**	**1073K**	**1173K**	**1273K**	**1373K**	**1473K**	**1573K**	**1673K**
0	1	0	0	0	0	0	0	0	0	0
0.1	0.9	-272	-307	-351	-402	-460	-524	-593	-669	-749
0.2	0.8	-520	-566	-631	-713	-810	-921	-1045	-1182	-1330
0.3	0.7	-929	-950	-1005	-1091	-1205	-1344	-1507	-1693	-1899
0.4	0.6	-1568	-1528	-1542	-1605	-1713	-1861	-2048	-2270	-2525
0.5	0.5	-2397	-2268	-2216	-2233	-2314	-2454	-2648	-2893	-3185
0.6	0.4	-3259	-3032	-2903	-2863	-2904	-3021	-3207	-3458	-3769
0.7	0.3	-3887	-3581	-3386	-3292	-3290	-3374	-3536	-3772	-4077
0.8	0.2	-3901	-3573	-3352	-3228	-3193	-3240	-3364	-3558	-3818
0.9	0.1	-2808	-2562	-2391	-2288	-2247	-2263	-2332	-2451	-2615
1	0	0	0	0	0	0	0	0	0	0

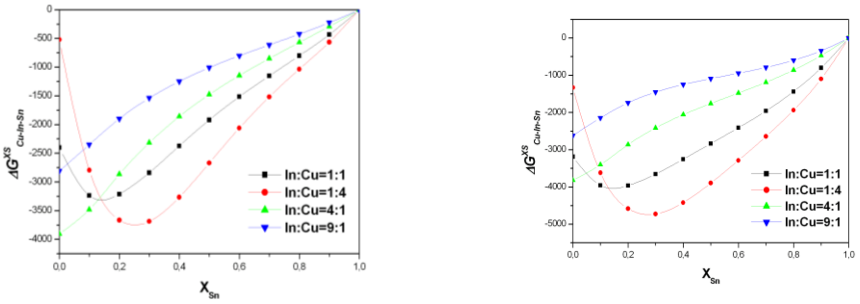
Table 3 *Calculated values for , J/mol using the Redlich-Kister parameters [9]*

Alloy		, J/mol								
X_{Sn}	X_{Cu}	873K	973K	1073K	1173K	1273K	1373K	1473K	1573K	1673K
0	1	0	0	0	0	0	0	0	0	0
0.1	0.9	-657	-735	-846	-893	-972	-1050	-1129	-1208	-1286
0.2	0.8	-1237	-1366	-1552	-1622	-1751	-1879	-2007	-2136	-2264
0.3	0.7	-1893	-2046	-2275	-2352	-2505	-2659	-2812	-2965	-3118
0.4	0.6	-2672	-2830	-3074	-3145	-3303	-3460	-3618	-3775	-3933
0.5	0.5	-3525	-3671	-3907	-3963	-4109	-4255	-4400	-4546	-4692
0.6	0.4	-4297	-4420	-4629	-4665	-4788	-4911	-5033	-5156	-5279
0.7	0.3	-4736	-4828	-4996	-5012	-5105	-5197	-5289	-5381	-5473
0.8	0.2	-4487	-4546	-4662	-4663	-4721	-4780	-4838	-4897	-4955
0.9	0.1	-3094	-3120	-3179	-3173	-3199	-3226	-3252	-3278	-3305
1	0	0	0	0	0	0	0	0	0	0

Kohler method

Figure 1 shows the dependence of integral molar Gibbs energy for Cu-In-Sn system for all sections, and at 873 K as well as 1673 K. It should be noted that the increase of temperature does not significantly affect the excess Gibbs energy dependence of composition.

Tin activities for all examined temperatures and almost all the sections are very close to the Raoult's line. The exceptions are sections with molar ratio of In:Cu = 1:1 and 1:4, where the negative deviation is observed for the compositions to X_{Sn}<0.4 (Figure 3). Alloys with higher content of indium, as in section In:Cu=9:1 showed the less deviation from the ideal solution.



a) 873K *b) 1673K*

Figure 1 *Calculated values for* $\Delta G^{xs}_{Cu-In-Sn}$ *in the Cu-In-Sn system by the Kohler method*

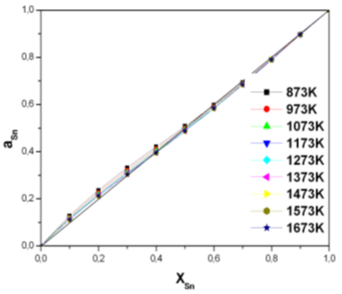
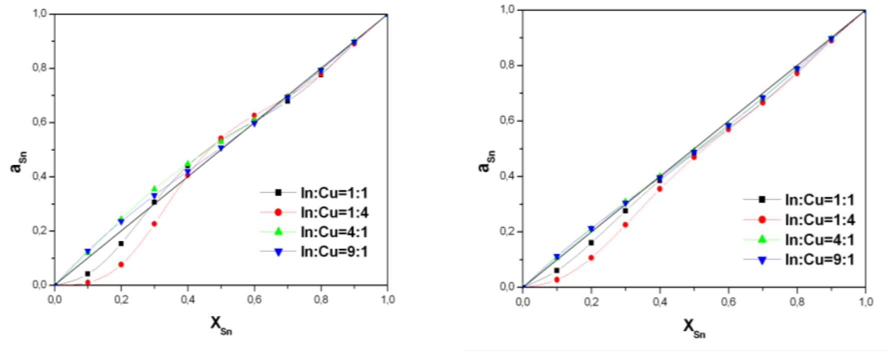


Figure 2 *Tin activity in the Cu-In-Sn system (In:Cu=9:1) at various temperature by the Kohler method*

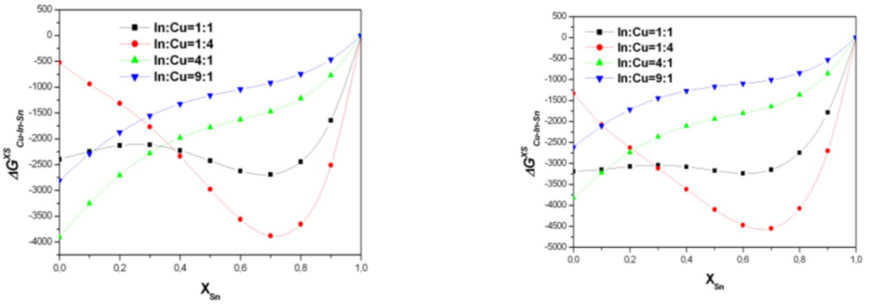


a) 873K *b) 1673K*

Figure 3 *Tin activity in the Cu-In-Sn system for various molar ratio In:Cu by the Kohler method*

Toop method

The results of Toop model application pointed out that the values for tin activity are almost identical in the sections with higher concentrations of indium, depending on temperature. By increase the content of indium, tin activity values are close to the Raoult's line (Figure 5), while the alloys in section In:Cu = 1: 4 have the largest negative deviation at all temperatures (Figure 6).



a) 873K *b) 1673K*

Figure 4 *Calculated values for* $\Delta G^{xs}_{Cu-In-Sn}$ *in the Cu-In-Sn system by the Toop method*

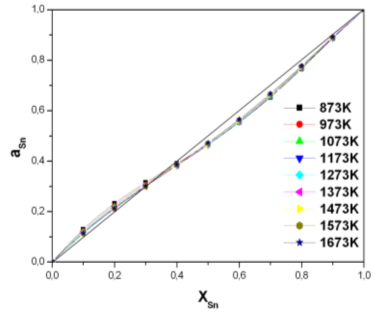
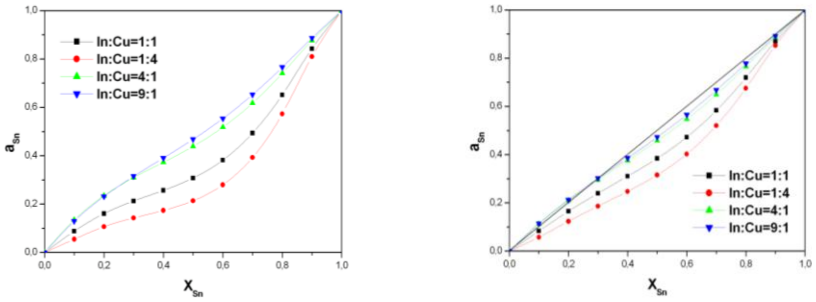


Figure 5 *Tin activity in the Cu-In-Sn system (In:Cu=9:1) at various temperature by the Toop method*



a) 873K *b) 1673K*

Figure 6 *Tin activity in the Cu-In-Sn system for various molar ratio In:Cu by the Toop method*

Both models show good results, so that is a question which one better describe those Cu-In-Sn alloys. Considering the fact that Popović et al. [12] experimentally obtained indium activity in this system at 1173 K, and the calculated values for the same are obtained by Milosavljević [13], it seems to be that the best agreement shows the Kohler method. Calculated values for indium activity by the Toop model [13] showed absolutely disagreement with experimentally obtained activities for the Cu-In-Sn alloys [12]. Therefore, it can be confirmed that the better one is symmetric type of predicted model.

CONCLUSIONS

The results of thermodynamic prediction presented in this paper included values of thermodynamic properties which are calculated using by geometric solution models in wide temperature range from 873 up to 1673 K. Therefore the Kohler and Toop models were used in order to obtained integral and partial molar excess of the Gibbs energies and tin activities for investigated sections in Cu-In-Sn system.

As a potential candidate for ecological solder alloy, the Cu-In-Sn system needs to be well investigated, so these calculated thermodynamic quantities of chosen alloys enabling better understanding and expansion of existing database for this kind of alloys. The application of symmetric models for thermodynamic prediction is confirmed with calculations as well as experimentally.

REFERENCES

[1] Korhonen T.M., Kivilahti J.K., JEM, 27(1998)149

[2] Ohnuma I., Cui Y., Liu X.J., et al., JEM, 29(2000)1113

[3] Liu X. J., Inohana Y., Takaku Y., Ohnuma I., al., JEM, 31(2002)1139

[4] Moser Z., Gasior W., Pstrus J., et al., JEM, 30(2001)1120

[5] S. K. Lin, C. F. Yang, S. H. Wu, S. W. Chen, JEM, 37 (2008) 498

[6] X. J. Liu, H. S. Liu, I. Ohnuma, et. al., JEM, 30 (2001) 1093

[7] Milosavljević A., Živković D., Manasijević D., Talijan N., Ćosović V., Grujić A. International Journal Materials and Product Technology 39 (1-2) (2010) 95.

[8] A.T. Dinsdale, A. Watson, A. Kroupa, J. Vrestal, A. Zemanova, J. Vizdal, Cost Action 531-Atlas of Phase Diagrams for Lead-free Soldering, 2008.

[9] http://resource.npl.co.uk/mtdata/cost531.htm

[10] Kohler F., Monatsh. Chem. 91(1960) 738

[11] Toop G.W., Trans. Met. Soc. AIME 233(1965)850

[12] Popović A., Bencze L., International Journal of Mass Spectrometry 257 (2006) 41

[13] Milosavljević A., Doctoral Dissertation, Bor, 2010

MINING AND METALLURGY INSTITUTE BOR
UDK: 622

ISSN: 2334-8836 (Štampano izdanje)
ISSN: 2406-1395 (Online)

UDK: 622.356:665.12(045)=111

doi:10.5937/MMEB1503129M

Slavica R. Mihajlović[*]*, Živko T. Sekulić*[*]*, Božo M. Kolonja*[**]*, Dragan S. Radulović*[*]

REACTIONS OF CALCITE IN WATER IN THE PRESENCE OF STEARIC ACID[***]

Abstract

In the suspension of water and calcite, with pH 10.14, on the border of calcite / water was formed a double electric layer. Its structure, or hydrophilic properties of minerals, depended on the concentration of potential determination ions, Ca^{2+} *i* CO_3^{2-} *, pH of the environment, and the adsorption of water molecules and ions (and molecules), formed in a suspension of calcite as a result of its solubility in alkaline media. The structure of such a way formed electrical double layer, influenced on interaction of minerals with stearic acid as a surface of active substance. In the presence of stearic acid, the pH value of slurry decreased to 8.72 due to the dissociation of stearic acid in alkaline medium and reaction of neutralization. As the result of dissociation, in the suspension, besides the un-dissociated acid molecules, there were also stearine ions* $CH_3(CH_2)_{16}COO^-$*,* (St^-)*, which have reacted with the surface of minerals, transforming it from hydrophilic to hydrophobic.*

Keywords: *calcite, stearic acid, solubility, electric double leyer*

INTRODUCTION

Name of pure calcite is derived from the Greek word cals, which means slaked lime. By chemical composition, it is $CaCO_3$, hardness per Moss-3 and very brittle. The density of the pure mineral is 2.72 kgm^{-3}, and if it contains impurities, density varies from 2.7 kgm^{-3} to 2.85 kgm^{-3}. Its brightness is glassy, and according to the fissile planes can be noticed the overflow of color. Calcite is transparent to milky. When it is clean and totally colorless, it is called the icelandic calcite. It is usually white, but can be colored differently: bluish, grayish yellow, greenish, reddish, etc. Calcite is relatively easily to soluble during the atmospheric precipitation and surface water when it can be converted to calcium bicarbonate $Ca(HCO_3)_2$, which is significantly more soluble than calcium carbonate [1]. Calcite has rhombohedral crystallisation. In the nature, a large number of crystal forms (300) exist. The crystals were generally prism or rhomboeder or skalenoeder shaped, which one are the most common. In some cases of calcite forming, the skeletal crystals arise. It occurs in the form of stalactites, then like coarse to fine grain and compact calcite [1].

---

[*] *Institute for Technology of Nuclear and Other Mineral Raw Materials, Franse d' Eperea 86, 11000 Belgrade, Serbia, e-mail address: s.mihajlovic@itnms.ac.rs*

[**] *University of Belgrade, Faculty of Mining and Geology, Djusina 7, 11000 Belgrade, Serbia*

[***] *This paper is the result of research on the Project TR34013 titled "Development of Technological Processes for Obtaining of Ecological Materials Based on Nonmetallic Minerals", and the Project TR34006 titled "Mechanochemical Treatment under Insufficient Mineral Resources,", funded by the Ministry of Education, Science and Technological Development of the Republic of Serbia for the period 2011-2015.*

EXPERIMENTAL PART

Material and methods

A sample of limestone is used in the experimental tests from THE deposit "Venčac" -AranDJelovac. The characterization of this sample showed that the dominant mineral is calcite (> 95%), so due to this, in the further discussion of results, instead the term calcite shall be used instead the term limestone. To obtain the acidic medium is used stearic acid, $CH_3(CH_2)_{16}COOH$, by technical grade, produced by the firm "Fluka" - Switzerland. For acid dissolving was used chloroform $CHCl_3$, p.a>99%, produced by „Centrohem“ - Stara Pazova.

Process for preparing the suspension for testing. In 500 ml of distilled water heated to 50°C (temperature measured by thermometer), with vigorous stirring, 50 g of a limestone (calcite) sample was added which resulted obtaining 9.1% suspension. Weight of stearic acid in 6 samples, calculated on 100 g of calcite was: 0.5 g; 1 g; 1.5 g; 2 g; 3 g and 4 g. Apropos stearic acid was added into 100 g of calcite, its concentration is expressed in the phr units (phr- parts per hundred parts of resin). Mixing time of suspension was 15 minutes at a given rpm of mixer which is 1500 r/min.

Procedure of determination Ca^{2+} ions in the aqueous suspension of calcite. In 50 ml of water heated at 50°C, 5 g of calcite was added and mixed with stirring machine 1min, and then, the suspension was centrifuged. Ca^{2+} ions are determined in resulting filtrate.

For mixing the suspension was used a laboratory mixer model "RE 166", manufacturer "Janke & Kunkel" - Germany, which has a range from 50 to 6000 r/min. The chemical composition of limestone and content of Ca^{2+} ions in filtrate from suspension is determined on the atomic absorption spectrophotometer, type "Perkin Elmer 703 Analyst 300".

RESULTS AND DISCUSSION

Chemical composition of the starting sample of limestone

Based on the CaO content, obtained by chemical analysis of a limestone sample (54.77%), and assuming that all the present MgO (0.79%)is related to dolomite, it was found by computation that a sample has 95.84% $CaCO_3$. According to the division of limestones, the starting pattern belongs to a class of pure limestone, because it contains more than 95% $CaCO_3$, and less than 1.2% MgO, [2].

Reactions of the calcite in aqueous solutions

To define the composition of saturated aqueous solution of calcite, it is necessary to take into account three groups of equilibrium chemical reactions [3]. These reactions are:

1. Equilibrium chemical reactions of carbonate species in the suspension of calcite and water

$$(g) + \quad \rightleftarrows \tag{1}$$

$$\rightleftarrows \quad + \tag{2}$$

$$\rightleftarrows \quad + \tag{3}$$

$$+ \tag{4}$$

2. The balance of ion pairs

$$+ \quad \rightleftarrows \tag{5}$$

(6)

$$\rightleftarrows \tag{7}$$

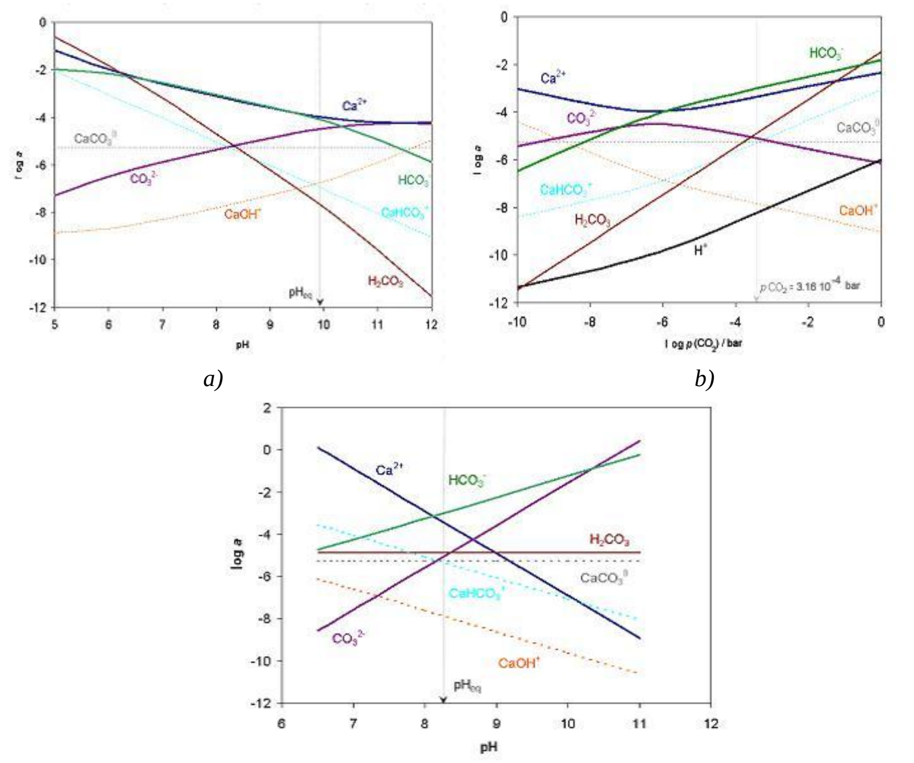
3. The balance of solid-liquid

(8)

The composition of saturated solution of calcite can be opened or closed related to the atmosphere. In the open system, solution is balanced with partial pressure of CO_2, $p(CO_2)$, equation 1, while in the closed system there is no exchange CO_2 with the atmosphere. The pH of solution can vary by addition the acids or bases as well as changing $p(CO_2)$.

Distribution of ions and molecules in the closed and open system calcite / water

Distribution of ions and molecules that occurs in indoor and outdoor system calcite/water and distribution the chemical species of saturated aqueous solution of calcite in equilibrium with the atmospheric CO_2, ($p(CO_2) = 1.36\text{x}10^{-4}$ bar) at 25°C are shown in Figures 1a, 1b and 1c [4]. It is observed that on distribution of chemical species it has a significant influence of pH and $p(CO_2)$ as well as the mutual reactions of chemical species. Dependence of share the chemical species of saturated aqueous solution of calcite from $p(CO_2)$ in the closed and open system according to the atmosphere is shown in Figures 1a and 1b. Figure 1c shows a diagram of chemical species of saturated aqueous composition of calcite for composition balanced with atmospheric $p(CO_2)$.



a)

b)

c)

Figure 1 *Distribution of ions and molecules in the closed (a); in open (b) system calcite/water and species distribution diagram for saturated calcite/water system in equilibrium with atmospheric* CO_2 *(*$p(CO_2)=1{,}36\cdot10^{-4}$ *bar), at 25°C (c)*

It can be seen on diagrams shown in Figure 1a that increasing pH of solution reduces the share of and ions, and increases the proportion of ions. During the equilibrium of pH (pH = 9.9), in the suspension dominate and ions while are present to a lesser extent. It can be seen on diagrams shown in

Figure 1b that reducing $p(CO_2)$ increases the pH of solution as a result of reduction the concentration of carbonic acid. Decreasing p (CO_2) from 1.0 to $1.58\text{x}10^{-7}$ bar, the equilibrium pH increased from 6.0 to 11.3. At the pH <10.5, in solution are dominated and ions, whereas ion is presented in the lesser extent. When the pH increases from 6 to 10.5, the equilibrium concentration from increases, and at the same time reduces the concentration and but they are still dominant in the suspension. At the pH> 10.5 starts dominance ions with increasing ions in order to keep the charge balance. From diagrams shown in Figure 1c, it can be seen that the activity of is not pH dependent and it is defined according to the reaction (1). In the open system during the constant pCO_2 $(p(CO_2)=1.36\text{x}10^{-4}$ bar) by addition of acid/base (HCl/NaOH), the pH of solution does not change. Adding the base takes to the higher concentration of negatively charged ions, mainly i , while adding the acid increases the concentration of positively charged ions, mainly .

Interphase calcite-water

Many researchers dealt by the interphase calcite-water. So, Hansen and his associates [5] concluded that the presence of water on the calcite surface reaction takes place according to the following equation:

$$CaCO_3 + H_2O \rightleftarrows Ca^{2+} + HCO_3^- + OH^- \qquad (9)$$

As a result of this process, the calcite suspension becomes alkaline. Using the results of Foxall and associates [6], these authors have pointed out that in calcite, ions that determine the electrokinetics properties are calcium ions and carbonate ions, rather than H^+ and OH^- ions. These ions, apropos pH of the environment, only determine which chemical species dominates in solution: CO_3^{2-}, HCO_3^- or H_2CO_3. Determining the presence of Ca^{2+} ions in the aqueous suspension of calcite, which was used in the assays presented in this paper, 12 mg of Ca^{2+}/liter is obtained. According to some literature data about the contact calcite and water, a double electric layer is formed that is shown in Figure 2 [7].

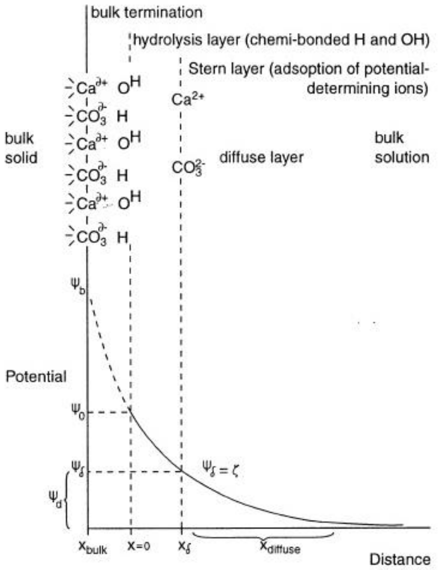


Figure 2 *Model of double electrical layer of calcite on the interface mineral/water [7]*

According to this model, where electrical double layer is in contact calcite with water, directly along the boundary surface of mineral, which consists of Ca^{2+} and CO_3^{2-} ions, there are located, due to the hydrolysis reaction, the chemisorbed H^+ and OH^- ions. These ions compensate the excess positive or negative charge on the surface of calcite. With formed chemisorbed layer, calcium ions and CO_3^{2-} ions are absorbed in the Stern layer. These ions are responsible for electrokinetics properties of calcite minerals. When the chemisorbed layer of H^+ and OH^- ions is removed then Ca^{2+} and CO_3^{2-} ions from the Stern layers again become an integral part of the three-dimensional crystal lattice of calcite. The tests presented in this paper showed that calcite is mineral which belongs to the type of salt and is water soluble. In the resulting aqueous suspension may take place and the specific reactions and form the different ions and molecules of carbonic acid, which the concentration depends on concentration of dissolved CO_2, and , also, pH of the solution (Figure 1a, 1b, 1c). From the results which are presented in this paper, 9.1% suspension of the starting calcite sample by specific surface area of 4.8 m^2/g had a pH of 10.14 (Figure 3). Based on values of the alkaline pH suspension, it was concluded that dominated are the reactions which leads to increasing the concentration of hydroxyl ions in solution, reaction 10:

$$CaCO_3 + H_2O \rightleftarrows Ca^{2+} + HCO_3^- + OH^- \quad (10).$$

On the border of calcite/water is forming a double electric layer, whose structure apropos hydrophilic properties of minerals, depends on concentration of potential determination of ions, Ca^{2+} and CO, dissolved CO_2 and pH of solution (concentration of H^+ and OH^- ions) and adsorption of formed ions (and molecules) in solution, that are towards the distribution diagram (Figures 1a, 1b, 1c) dominant in the alkaline medium. The structure of such a formed electrical double layer still affects the interaction of minerals with surfactant (stearate ions and molecules of stearic acid), which should lead to hydrophobization of mineral surfaces.

Reactions of calcite in the presence of stearic acid

According to the literature, adsorption of stearic acid on natural calcite usually takes place in a nonpolar solvent, because the calcite dissolves in water and pH of aqueous medium influence to its solubility, and also to the degree of dissociation of stearic acid. However, Hansen et al. showed that the treatment of calcite with water before addition stearic acid into the n-decane improves the adsorption of stearic acid on the calcite surface [5]. In order to monitor the behavior of calcite in the presence of stearic acid with different concentrations of stearic acid, the pH of each solution was measured after separation the solid phase. The results were compared with the pH value of 9.1% suspension of calcite, which amounts to 10.14. Curve of depending pH value of solution from the concentration of stearic acid is shown in Figure 3.

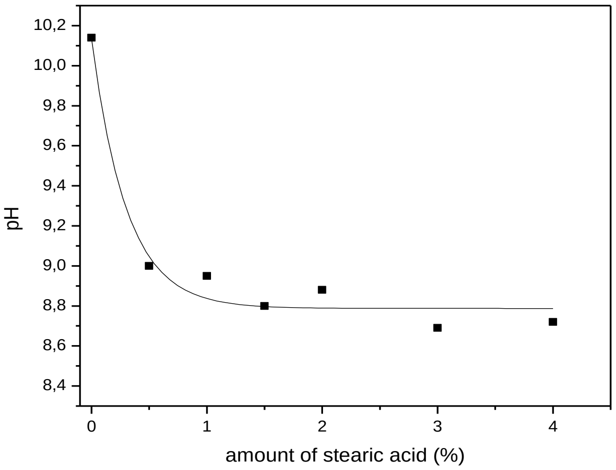


Figure 3 *The pH value of the solution in function of concentration of stearic acid*

It can be seen that the pH 9.1% of aqueous suspension of calcite is 10.14 and in the presence of low concentration of stearic acid (0.5 phr ≈ 0.5%) leads to decrease the pH value of solution at pH = 9.00. With further increase of concentration of stearic acid, further weakly decrease of the pH value can be noticed (during the concentration of stearic acid 1 phr, the pH is 8.95, and at concentration of 4 phr ≈ 3.9%, pH is 8.72). Characteristics of calcium carbonate in an aqueous solution have been studied by many researchers [8]. The dissociation constant of calcite at 25°C is in the order of 10^{-9} and it is separated according to the reaction 11.

$$CaCO_3 \rightleftarrows Ca^{2+} + CO_3^{2-} \quad K = \frac{\left[Ca^{2+}\right]\left[CO_3^{2-}\right]}{\left[CaCO_3\right]} = 3.7x10^{-9}\ to\ 8.7x10^{-9}\ \text{at } 25^{o}C \qquad (11)$$

A suspension of calcite/H_2O has, according to some published data the pH about 9 [9], depending on partial pressure of CO_2. In the aqueous suspension of calcite may occur according to the reactions 1-8 different ions and molecules of carbonic acid, whose concentration depends on the concentration of dissolved CO_2, and pH of solution. Based on the literature data, it can be assumed that even at the border calcite/water in 9.1% suspension, used in these studies, also forms an electric double layer, but in it dominate ions by distribution diagram at pH = 10.14 which are present in a given system. So, 9.1% suspension of calcite has pH = 10.14 (Figure 3), which is higher than pKa of stearic acid (pKa = 5.7), after addition into this suspension of stearic acid solution in non-polar solvent where its dissociation acts:

$$CH_3(CH_2)_{16}COOH \rightleftarrows CH_3(CH_2)_{16}COO^- + H^+ \qquad (12)$$

As a result of stearic acid dissociation, the concentration of H^+ ions grows, also the concentration of $CH_3(CH_2)_{16}COO^-$, stearate ion (St^-). The results in this paper fortified that, by the fact that there is decrease of the pH value of solution after addition, even low concentration of stearic acid from 0.5% (pH = 9.00), apropos until the neutralization reaction.

Isoelectric point (pH at which the zeta potential is 0) in some samples of calcite is pH = 11.4. Anionic surfactants (surface active agents) can be adsorbed from solution with lower pH values, however, in an acidic medium, $CaCO_3$ decompose with formation of CO_2, water, and Ca^{2+} ions. According to Martinez-Luevanos and coworkers [10], the reaction between protons and $CaCO_3$ occurs at pH 8.3, so at pH 8 is achieved the best balance between these two reactions. The results obtained in this study showed that in the presence of stearic acid, pH of the suspension decreases (Figure 3). At concentration of 0.5 phr $\approx$ 0.5% the pH value of the suspension was 9.00, whereas at concentration of 4 was 8.72 phr. Since the pKa of stearic acid (pKa = 5.7) is less than the pH of 9.1% suspension of calcite (pH = 10.14), the decrease in pH value can be explained, as already mentioned, by dissociation of stearic acid in an alkaline medium by reacting neutralization.

CONCLUSION

For observing the reactions of calcite in water,9.1% suspension was used whose pH was 10.14. For testing the reaction in an acidic medium is used a precisely ordered mass of stearic acid, 0.5 g; 1 g; 1.5 g; 2 g; 3 g and 4 g of added per 100 g of the calcite. Solubility of calcite in water depends by dissolved CO_2 and pH of the environment. Suspension of calcite, used for the tests, had pH = 10.14. Based on the alkaline pH value of suspension, it can be concluded that in the suspension are dominated reactions which leads to increasing the concentration of hydroxyl ions, like the reaction, for example: $CaCO_3 + H_2O \rightleftarrows Ca^{2+} + HCO_3^- + OH^-$. On the border of calcite/water, a double electric layer is formed. Its structure, apropos, hydrophilic properties, are dependent from the concentration of potential determination ions, Ca^{2+} and CO, pH value of the environment, and adsorption of molecules of water and ions (and molecules) formed in this suspension due to its solubility. The structure of such formed electrical double layer, further influenced on the minerals interaction with surface-active substance (a stearate ion and molecule of stearic acid). In the presence of stearic acid, the pH value of slurry decreased. At concentration of 0.5 phr, the pH value was 9.00 and at 4 phr it was 8.72. Bearing in the mind that the pKa of stearic acid (pKa = 5.7) is lower than pH of calcite suspension of calcite (pH = 10.14), the decrease of pH value can be explained by dissociation of stearic acid in an alkaline medium and neutralization reaction. As a result of this, dissociation of stearic acid occurs in alkaline environment, and neutralization reaction. Like consequence of stearic acid dissociation and neutralization reaction, in suspension, besides non dissolved molecules, ions of stearate $CH_3(CH_2)_{16}COO^-$, (St^-) were in certain concentration which reacted with the surface of minerals transformed it from hydrophilic to hydrophobic form.

REFERENCES

[1] S. Janjić, P. Ristić, Mineralogy, Naučna knjiga, Belgrade, 1989 (in Serbian)

[2] S. R. Mihajlović, Physico-chemical Modification of Calcite with Stearic Acid, Doctoral Dissertation, Faculty of Mining and Geology, University of Belgrade, 2011 (in Serbian)

[3] H. N. S. Wiechers, P. Sturrock, G. V. R. Marais, Calcium Carbonate Crystallization Kinetics, Water Res. 9 (1975) 835-845.

[4] P. Somasundaran, J.O. Amankonah, K.P. Ananthapadmanabhan, Mineral–solution Equilibria in Sparingly Soluble Mineral Systems, Colloids Surf. 15 (1985) 309-333.

[5] G. Hansen, A. A. Hamouda, R. Denoyel, The Effect of Pressure on Contact Angles and Wettability in the Mica/Water/n-decane System and the Calcit+stearic acid/water/n-decane System. Colloids Surf. A: Physicochem. Eng. Aspects. 172 (2000) 7-16.

[6] T. Foxsall, G. C. Peterson, H. M. Rendall, A. L. Smith, Charge Determination at Calcium salt/aqueous Solution Interface, J. Chem. Soc. Faraday Trans. 75 (1979) 1034-1039.

[7] S. L. S. Stipp, Toward a Conceptual Model of the Calcite Surface: Hydration, Hydrolysis, and Surface Potential, Geochim. Cosmochim. Ac. 63 (1999) 3121-3131.

[8] J. O. Amankonah, P. Somasundaran, Effects of Dissolved Mineral Species on the Electrokinetic Behavior of Calcite and Apatite, Colloids Surf. 15 (1985) 335-353.

[9] P. Q. Yuan, Z. M. Cheng, Z. M. Zhou, W. K. Yuan, R. Semiat, Zeta Potential on the Anti-scalant Modified Submicro Calcite Surface, Colloids Surf. A: Physicochem. Eng. Aspects 328 (2008) 60-66.

[10] Martinez-Luevanos, A. Uribe-Salas, A. Lopez-Valdivieso, Mechanism of Adsorption of Sodium Dodecyl-sulfonate on Celestite and Calcite, Miner. Eng. 12 (1999) 919-936.

INSTITUT ZA RUDARSTVO I METALURGIJU BOR ISSN: 2334-8836 (Štampano izdanje)
UDK: 622 ISSN: 2406-1395 (Online)

UDK: 622.356:665.12(045)=163.41 doi:10.5937/MMEB1503129M

Slavica R. Mihajlović[*], *Živko T. Sekulić*[*], *Božo M. Kolonja*[**], *Dragan S. Radulović*[*]

REAKCIJE KALCITA U VODI I U PRISUSTVU STEARINSKE KISELINE[***]

Izvod

U suspenziji kalcita i vode, čiji je pH 10,14, na granici kalcit/voda formirao se dvojni električni sloj. Njegova struktura, odnosno hidrofilne osobine minerala, su zavisile od koncentracije potencijal određujućih jona, Ca^{2+} *i* CO_3^{2-} *, pH sredine i adsorpcije molekula vode i jona (i molekula) formiranih u suspenziji kalcita usled njegove rastvorljivosti u alkalnoj sredini. Struktura tako formiranog dvojnog električnog sloja je uticala na interakciju minerala sa stearinskom kiselinom kao površinski aktivnom materijom. U prisustvu stearinske kiseline pH vrednost suspenzije je opadala do 8,72 zbog disocijacije stearinske kiseline u alkalnoj sredini i reakcije neutralizacije. Kao posledica disocijacije u suspenziji su se pored nedisosovanih molekula kiseline nalazili u određenoj koncentraciji i stearatni joni* $CH_3(CH_2)_{16}COO^-$*, (*St^-*) koji su reagovali sa površinom minerala prevodeći je iz hidrofilne u hidrofobnu.*

***Ključne reči**: kalcit, stearinska kiselina, rastvorljivost, dvojni električni sloj*

UVOD

Naziv minerala kalcita potiče od grčke reči *cals* koja označava gašeni kreč. Po hemijskom sastavu je $CaCO_3$, tvrdine po Mos-u 3 i vrlo je krt. Gustina čistog minerala je 2,72 kgm^{-3}, a ako sadrži primese gustina varira od 2,7 kgm^{-3} do 2,85 kgm^{-3}. Sjajnost mu je staklasta, a po ravnima cepljivosti može da se zapazi prelivanje boja. Kalcit je providan do mutan. Kada je čist i potpuno bezbojan naziva se islandski kalcit. Obično je beo, ali može biti i različito obojen: plavičast, sivkast, žut, zelenkast, crvenkast itd. Kalcit je relativno lako rastvoran pri delovanju atmosferskih padavina i površinskih voda pri čemu se prevodi u kalcijum - bikarbonat $Ca(HCO_3)_2$, koji je znatno rastvorljiviji od samog kalcijum karbonata [1].

Kalcit kristališe romboedarski. U prirodi se sreće veliki broj kristalnih formi (oko 300). Kristali su obično oblika prizme, romboedra ili skalenoedra, koji su najčešći. U nekim slučajevima nastajanja kalcita obrazuju se skeletni kristali. Javlja se u obliku stalaktita, zatim kao krupno do sitnozrnasti i kompaktni kalcit [1].

---

[*] *Institut za tehnologiju nuklearnih i drugih mineralnih sirovina, Franše d'Eperea 86, 11000 Beograd, Srbija, e-mail: s.mihajlovic@itnms.ac.rs*

[**] *Univerzitet u Beogradu, Rudarsko-geološki fakultet, Đušina 7, 11000 Beograd, Srbija*

[***] *Ovaj rad je nastao kao rezultat istraživanja na Projektu TR 34013: „Osvajanje tehnoloških postupaka dobijanja ekoloških materijala na bazi nemetaličnih mineralnih sirovina“ i Projektu TR 34006: „Mehanohemijski tretman nedovoljno kvalitetnih mineralnih sirovina“, koje finansira Ministarstvo prosvete, nauke i tehnološkog razvoja Republike Srbije za period 2011-2015.*

EKSPERIMENTALNI DEO

Materijal i metode

Uzorak krečnjaka korišćen u eksperimentalnim ispitivanjima je iz ležišta „Venčac“ - Aranđelovac. Karakterizacijom ovog uzorka utvrđeno da je dominantni mineral kalcit (> 95 %), pa će se u diskusiji rezultata umesto termina krečnjak koristiti termin kalcit. Za dobijanje kisele sredine korišćena je stearinska kiselina, $CH_3(CH_2)_{16}COOH$, tehničke čistoće, koju proizvodi firma „Fluka“- Švajcarska. Za rastvaranje kiseline upotrebljen je hloroform $CHCl_3$, p.a>99%, proizvođač „Centrohem“ - Stara Pazova.

Postupak pripreme suspenzije za ispitivanje. U 500 ml destilovane vode zagrejane do 50^oC (temperatura merena termometrom), uz intenzivno mešanje, dodato je 50 g uzorka krečnjaka (kalcita) pri čemu je dobijena 9,1% suspenzija. Masa stearinske kiseline u 6 ovakvih proba obračunata na 100 g kalcita bila je: 0,5 g; 1 g; 1,5 g; 2 g; 3 g i 4 g. Pošto je stearinska kiselina dodavana u 100 g kalcita njena koncentracija je izražena u phr jedinicama (phr - Abbreviation for parts per hundred parts of resin). Vreme mešanja suspenzije je bilo 15 minuta, pri broju obrtaja na mešalici od 1500 ^{o}/min.

Postupak određivanje Ca^{2+} jona u vodenoj suspenziji kalcita. U 50 ml vode zagrejane na 50^oC dodato je 5 g kalcita i mešano na mešalici 1 min, a zatim je suspenzija centrifugirana. U dobijenom filtratu su određeni Ca^{2+} joni.

Za mešanje suspenzije je korišćena laboratorijska mešalica model „RE 166“ proizvođača „Janke & Kunkel“ - Nemačka, koja ima opseg 50 do 6000 ^{o}/min. Hemijski sastav krečnjaka i sadržaj Ca^{2+} jona u filtratu iz suspenzije je određen na atomskom apsorpcionom spektrofotometru tipa „Perkin Elmer 703 Analyst 300“.

REZULTATI I DISKUSIJA

Hemijski sastav polaznog uzorka krečnjaka

Na osnovu sadržaja CaO koji je dobijen hemijskom analizom uzorka krečnjaka (54,77 %) i uz pretpostavku da je sav prisutan MgO (0,79 %) vezan za dolomit, računskim putem je dobijeno da u uzorku ima 95,84 % $CaCO_3$. Prema podeli krečnjaka, polazni uzorak spada u čist krečnjak, jer sadrži više od 95 % $CaCO_3$, a manje od 1,2 % MgO, [2].

Reakcije kalcita u vodenim rastvorima

Za definisanje sastava zasićenog vodenog rastvora kalcita neophodno je uzeti u obzir tri grupe ravnotežnih hemijskih reakcija [3]. Te reakcije su:

1. Ravnotežne hemijske reakcije karbonatnih vrsta u suspenziji kalcita i vode

$$(g) + \quad \rightleftarrows \qquad (1)$$

$$\rightleftarrows \quad + \qquad (2)$$

$$\rightleftarrows \quad + \qquad (3)$$

$$+ \qquad (4)$$

2. Ravnoteža jonskih parova

$$+ \quad \rightleftarrows \qquad (5)$$

$$(6)$$

$$\rightleftarrows \qquad (7)$$

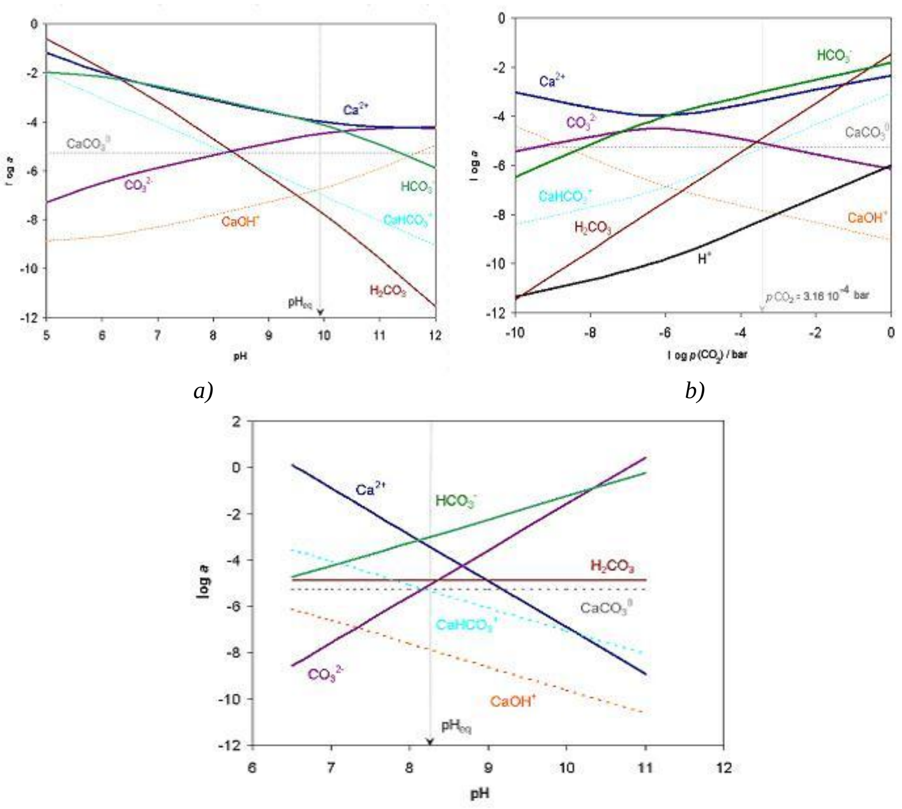
3. Ravnoteža čvrsto-tečno

$$(8)$$

Sastav zasićenog rastvora kalcita može biti otvoren ili zatvoren prema atmosferi. U otvorenom sistemu rastvor je uravnotežen sa parcijalnim pritiskom CO_2, $p(CO_2)$, jednačina 1, dok u zatvorenom sistemu nema razmene CO_2 sa atmosferom. pH rastvora može da se menja dodatkom kiselina ili baza kao i promenom $p(CO_2)$.

Distribucija jona i molekula u zatvorenom i otvorenom sistemu kalcit/voda

Distribucije jona i molekula koji se javljaju u zatvorenom i otvorenom sistemu kalcit/voda kao i distribucija hemijskih vrsta zasićenog vodenog rastvora kalcita u ravnoteži sa atmosferskim CO_2 ($p(CO_2)$ = 1,36x10^{-4} bar), na 25°C prikazani su na slikama 1a, 1b i 1c [4]. Uočava se da na distribuciju hemijskih vrsta veliki uticaj ima pH i $p(CO_2)$ kao i međusobne reakcije hemijskih vrsta. Zavisnost udela hemijskih vrsta zasićenog vodenog rastvora kalcita od $p(CO_2)$ u zatvorenom i otvorenom sistemu prema atmosferi prikazana je na slikam 1a i 1b. Na slici 1b je prikazana distribucija hemijskih vrsta zasićenog vodenog rastvora kalcita u ravnoteži sa atmosferskim $p(CO_2)$.



a) *b)*

c)

Sl. 1. *Distribucija jona i molekula zasićenog vodenog rastvora kalcita u zatvorenom (a) i otvorenom (b) sistemu kalcit/voda i distribucija hemijskih vrsta zasićenog vodenog rastvora kalcita u ravnoteži sa atmosferskim* CO_2 *(*$p(CO_2)=1{,}36\cdot10^{-4}$ *bar), na 25°C*

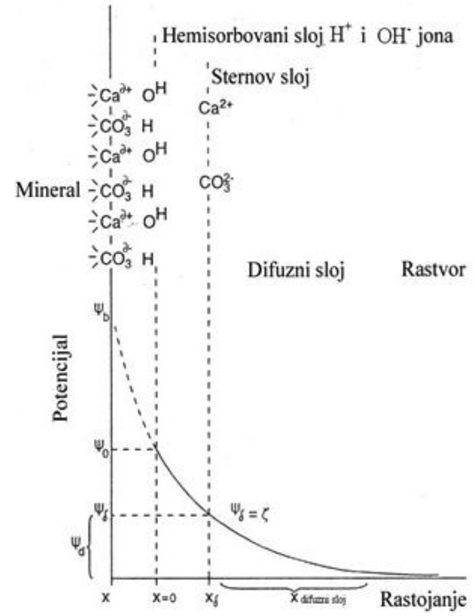
Na dijagramima prikazanim na slici 1a uočava se da sa povećanjem pH rastvora smanjuje udeo i jona, a povećava udeo jona. Pri ravnotežnom pH (pH=9,9) u suspenziji dominiraju i dok su joni prisutni u manjoj meri. Na dijagramima prikazanim na slici 1b uočava se da smanjenjem $p(CO_2)$ povećava se pH rastvora kao posledica smanjenja koncentracije karbonatne kiseline. Pri smanjenju $p(CO_2)$ od 1,0 na $1{,}58 \cdot 10^{-7}$ bar, ravnotežni pH se poveća od 6,0 do 11,3. Pri pH<10,5 u rastvoru dominiraju i joni, dok je jon prisutan u manjoj meri. Kada pH poraste sa 6 na 10,5 ravnotežna koncentracija se se povećava uz istovremeno smanjenje koncentracije i ali koji su i dalje dominantni u suspenziji. Pri pH>10,5 počinje dominacija jona uz povećanje jona kako bi se zadržala ravnoteža naelektrisanja. Sa dijagrama prikazanog na slici 1c vidi se da aktivnost ne zavisi od pH i definisan je prema reakciji (1). U otvorenom sistemu pri konstantnom pCO_2 ($p(CO_2)$=$1{,}36 \times 10^{-4}$ bar) dodavanjem kiseline/baze (npr. HCl/NaOH) dolazi do promene pH rastvora. Dodatkom baze dolazi do povećanja koncentracije negativno naelektrisanih jona, uglavnom i , dok dodatak kiseline povećava koncentraciju pozitivno naelektrisanih jona, uglavnom .

Međupovršina kalcit-voda

Mnogi istraživači si se bavili međupovršinom kalcit-voda. Tako je Hansen sa saradnicima [5] zaključio da se u prisustvu vode na površini kalcita odigrava reakcija prema sledećoj jednačini:

$$CaCO_3 + H_2O \rightleftarrows Ca^{2+} + HCO_3^- + OH^- \tag{9}$$

Kao rezultat ovog procesa suspenzija kalcita postaje alkalna. Koristeći rezultate Foxall-a i saradnika [6] ovi autori su istakli da kod kalcita, joni koji određuju elektrokinetičke osobine su joni kalcijuma i karbonatni joni, a ne H^+ i OH^- joni. Ovi joni, odnosno pH sredine, određuju samo koja hemijska vrsta dominira u rastvoru: CO_3^{2-}, ili H_2CO_3. Određivanjem prisustva Ca^{2+} jona u vodenoj suspenziji kalcita koji je korišćen u ispitivanjima prikazanim u ovom radu dobijeno je 12 mg Ca^{2+}/litru. Prema nekim literaturnim podacima u kontaktu kalcita sa vodom formira se dvojni električni sloj prikazan na slici 2 [7].



Sl. 2. *Model dvojnog električnog sloja kalcita na granici mineral/voda [7]*

Po ovom modelu dvojnog električnog sloja u kontaktu kalcita sa vodom neposredno uz graničnu površinu minerala, koju čine Ca^{2+} i CO_3^{2-} joni, nalaze se usled reakcije hidrolize hemisorbovani H$^+$ i OH$^-$ joni. Ovi joni kompenzuju višak pozitivnog, odnosno negativnog naelektrisanja na površini kalcita. Uz nastali hemisorbovan sloj se u Šternovom sloju nalaze i adsorbovani joni kalcijuma i CO_3^{2-} joni. Upravo ovi joni su odgovorni za elektrokinetičke osobine minerala kalcita. Kada se hemisorbovan sloj H$^+$ i OH$^-$ jona ukloni tada Ca^{2+} i CO_3^{2-} joni iz Šternovog sloja postaju ponovo sastavni deo trodimenzione kristalne rešetke kalcita.

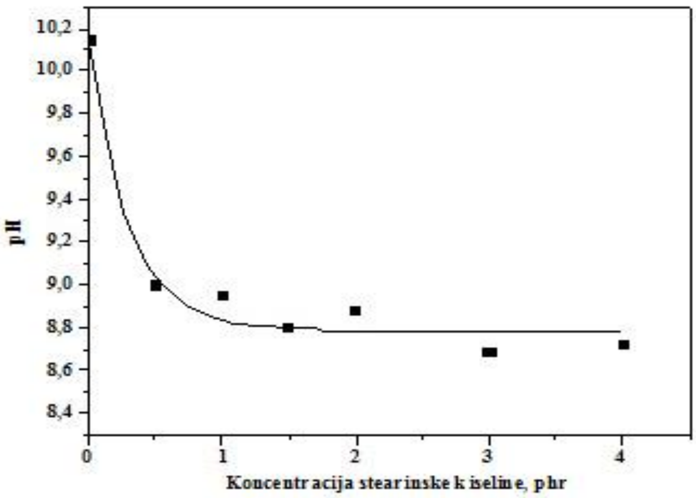
Ispitivanja prikazana u ovom radu su pokazala da je kalcit mineral tipa soli i rastvorljiv u vodi. U nastaloj vodenoj suspenziji mogu se odigrati određene reakcije i formirati različiti joni i molekuli ugljene kiseline čija koncentracija zavisi od koncentracije rastvorenog CO$_2$ i pH rastvora (slike 1a, 1b, 1c). Iz rezultata koji si prikazani u ovom radu 9,1 % suspenzija polaznog uzorka kalcita specifične površine 4,8 m^2/g imala je pH=10,14 (slika 3.). Na osnovu alkalne vrednosti pH suspenzije zaključeno je da dominiraju reakcije koje su dovele do povećanja koncentracije hidroksilnih jona u rastvoru, kao npr. reakcija 10:

$$CaCO_3 + H_2O \rightleftarrows Ca^{2+} + HCO_3^- + OH^- \quad (10).$$

Na granici kalcit/voda formira se dvojni električni sloj, čija struktura, odnosno hidrofilne osobine minerala, zavise od koncentracije potencijalodređujućih jona, Ca^{2+} i CO_3^{2-}, rastvorenog CO$_2$ i pH rastvora (koncentracije jona H$^+$ i OH$^-$) i adsorpcije formiranih jona (i molekula) u rastvoru, koji su prema distribucionom dijagramu (slika 1a, 1b, 1c) dominantni u alkalnoj sredini. Struktura tako formiranog dvojnog električnog sloja dalje utiče i na interakciju minerala sa površinski aktivnom materijom (stearatnim jonom i molekulom stearinske kiseline), koja treba da dovede do hidrofobizacije mineralne površine.

Reakcije kalcita u kiselom rastvoru

Prema literaturi adsorpcija stearinske kiseline na prirodnom kalcitu se obično odigrava u nepolarnom rastvaraču, jer se kalcit rastvara u vodi, a pH vodene sredine utiče kako na njegovu rastvorljivost tako i na stepen disocijacije stearinske kiseline. Međutim, Hansen i saradnici su ukazali da tretman kalcita sa vodom pre dodavanja rastvora stearinske kiseline u n-dekanu poboljšava adsorpciju stearinske kiseline na površini kalcita [5]. Kako bi se pratilo ponašanje kalcita u prisustvu stearinske kiseline dodavane su različite koncentracije stearinske kiseline i meren je pH svakog rastvora posle odvajanja čvrste faze. Dobijeni rezultati su upoređeni sa pH vrednosti 9,1 % suspenzije kalcita koja iznosi 10,14. Kriva zavisnosti pH rastvora od koncentracije dodate stearinske kiseline prikazana je na slici 3.



Sl. 3. *pH rastvora u zavisnosti od koncentracije stearinske kiseline*

Može se videti da pH 9,1 % vodene suspenzije kalcita iznosi 10,14 i da u prisustvu male koncentracije stearinske kiseline (0,5 phr ≈ 0,5 %) dolazi do opadanja pH vrednosti rastvora na pH = 9,00. Sa daljim povećanjem koncentracije stearinske kiseline zapaža se dodatno slabo opadanje pH vrednosti (pri koncentraciji stearinske kiseline od 1 phr pH iznosi 8,95, a pri koncentraciji od 4 phr ≈ 3,9 %, pH je 8,72). Osobine kalcijum karbonata u vodenom rastvoru su ispitivali mnogi istraživači [8]. Konstanta disocijacije kalcita na 25°C je reda veličine 10^{-9} i odvoja se prema reakciji 11.

$$\mathrm{CaCO_3} \rightleftarrows \mathrm{Ca^{2+}} + \mathrm{CO_3^{2-}} \qquad K = \frac{[Ca^{2+}][CO_3^{2-}]}{[CaCO_3]} = 3.7x10^{-9}\ do\ 8.7x10^{-9}\ \text{na } 25^{\circ}\mathrm{C} \qquad (11)$$

Suspenzija kalcit/H_2O ima prema nekim publikovanim podacima pH oko 9 [9], zavisno od parcijalnog pritiska CO_2. U vodenoj suspenziji kalcita se mogu prema reakcijama 1-8 javiti različiti joni i molekuli ugljene kiseline, čija koncentracija zavisi od koncentracije rastvorenog CO_2 i pH rastvora. Na osnovu prikazanih literaturnih podataka može se pretpostaviti da se i na granici kalcit/voda u 9,1 % suspenziji koja je korišćena u ovim ispitivanjima takođe formira dvojni električni sloj, ali u kome dominiraju joni koji su prema distribucionom dijagramu na pH=10,14 prisutni u datom sistemu.

Kako 9,1% suspenzije kalcita ima pH=10,14 (slika 3.), dakle veći od pKa stearinske kiseline (pKa = 5,7), nakon dodatka u ovu suspenziju rastvora stearinske kiseline u nepolarnom rastvaraču odigrava se i njena disocijacija:

$$\mathrm{CH_3(CH_2)_{16}COOH} \rightleftarrows \mathrm{CH_3(CH_2)_{16}COO^-} + \mathrm{H^+} \qquad (12)$$

Kao posledica disocijacije stearinske kiseline raste koncentracija kako H^+ jona, tako i koncentracija $CH_3(CH_2)_{16}COO^-$, stearatnog jona (St^-). Rezultati u ovom radu to i potvrđuju s obzirom da dolazi do opadanja pH vrednosti rastvora nakon dodavanja i male koncentracije stearinske kiseline od 0,5 % (pH=9,00), odnosno do odigravanja reakcije neutralizacije.

Izoelektrična tačka (pH pri kome je zeta potencijal 0) se kod nekih uzoraka kalcita nalazi na pH= 11,4. Anjonski surfaktanti (površinski aktivne materije) se mogu više adsorbovati iz rastvora sa nižim pH vrednostima, međutim u kiseloj sredini $CaCO_3$ se raspada uz stvaranje CO_2, vode i jona Ca^{2+}. Prema Martinez-Luevanos-u i saradnicima [10], reakcija između $CaCO_3$ i protona se odigrava pri pH 8,3, tako da se do pH 8 ostvaruje najbolji balans između ove dve reakcije. Rezultati dobijeni u ovom radu su pokazali da u prisustvu stearinske kiseline pH suspenzije opada (slika 3). Pri koncentraciji 0,5 phr ≈ 0,5 % vrednost pH suspenzije je bila 9,00, dok je pri koncentraciji 4 phr iznosila 8,72. S obzirom da je pKa stearinske kiseline (pKa = 5,7) manji od pH 9,1 % suspenzije kalcita (pH=10,14), opadanje pH vrednosti se može objasniti, kako je već rečeno, disocijacijom stearinske kiseline u alkalnoj sredini reakcijom neutralizacije.

ZAKLJUČAK

Za ispitivanje reakcija kalcita u vodi korišćena je 9,1% suspenzija čiji je pH bio 10,14. Za ispitivanje reakcija u kiseloj sredini korišćena je tačno odmerena masa stearinske kiseline 0,5 g; 1 g; 1,5 g; 2 g; 3 g i 4 g dodate na 100 g kalcita. Rastvorljivost kalcita u vodi zavisi od rastvorenog CO_2 i pH sredine. Suspenzija kalcita koja je korišćena u ovim ispitivanjima imala je pH=10,14. Na osnovu alkalne pH vrednosti suspenzije moglo se zaključiti da u suspenziji dominiraju reakcije koje dovode do povećanja koncentracije hidroksilnih jona, kao npr. reakcija: $CaCO_3 + H_2O \rightleftarrows Ca^{2+} + HCO_3^- + OH^-$. Na granici kalcit/voda formirao se dvojni električni sloj. Njegova struktura, odnosno hidrofilne osobine, su zavisile od koncentracije potencijal određujućih jona, Ca^{2+} i CO_3^{2-}, pH sredine i adsorpcije molekula vode i jona (i molekula) formiranih u ovoj suspenziji usled njegove rastvorljivosti. Struktura tako formiranog dvojnog električnog sloja dalje je uticala na interakciju minerala sa površinski aktivnom materijom (stearatnim jonom i molekulom stearinske kiseline). U prisustvu stearinske kiseline pH vrednost suspenzije je opadala. Pri koncentraciji 0,5 phr vrednost pH je bila 9,00, a pri 4 phr 8,72. Imajući u vidu da je pKa stearinske kiseline (pKa = 5,7) manji od pH suspenzije kalcita (pH=10,14), opadanje pH vrednosti se objašnjava disocijacijom stearinske kiseline u alkalnoj sredini i reakcijom neutralizacije. Kao posledica disocijacije stearinske kiseline i reakcije neutralizacije u suspenziji su se pored nedisosovanih molekula kiseline nalazili u određenoj koncentraciji i stearatni joni $CH_3(CH_2)_{16}COO^-$, (St^-) koji su reagovali sa površinom minerala prevodeći je iz hidrofilne u hidrofobnu.

LITERATURA

[1] S. Janjić, P. Ristić, Mineralogija, Naučna knjiga, Beograd, 1989.

[2] S. R. Mihajlović, ″Fizičko-hemijsko modifikovanje kalcita stearinskom kiselinom″, doktorska disertacija, Rudarsko-geološki fakultet Univerziteta u Beogradu, 2011.

[3] H. N. S. Wiechers, P. Sturrock, G. V. R. Marais, Calcium carbonate crystallization kinetics, Water Res. 9 (1975) 835-845.

[4] P. Somasundaran, J.O. Amankonah, K.P. Ananthapadmanabhan, Mineral-solution equilibria in sparingly soluble mineral systems, Colloids Surf. 15 (1985) 309-333.

[5] G. Hansen, A. A. Hamouda, R. Denoyel, The Effect of Pressure on Contact Angles and Wettability in the Mica/Water/n-decane System and the Calcit+stearic acid/water/n-decane System. Colloids Surf. A: Physicochem. Eng. Aspects. 172 (2000) 7-16.

[6] T. Foxsall, G. C. Peterson, H. M. Rendall, A. L. Smith, Charge determination at calcium salt/aqueous solution interface, J. Chem. Soc. Faraday Trans. 75 (1979) 1034-1039.

[7] S. L. S. Stipp, Toward a conceptual model of the calcite surface: Hydration, hydrolysis, and surface potential, Geochim. Cosmochim. Ac. 63 (1999) 3121-3131.

[8] J.O. Amankonah, P. Somasundaran, Effects of dissolved mineral species on the electrokinetic behavior of calcite and apatite, Colloids Surf. 15 (1985) 335-353.

[9] P. Q. Yuan, Z. M. Cheng, Z. M. Zhou, W. K. Yuan, R. Semiat, Zeta potential on the anti-scalant modified sub-micro calcite surface, Colloids Surf. A: Physicochem. Eng. Aspects 328 (2008) 60-66.

[10] Martinez-Luevanos, A. Uribe-Salas, A. Lopez-Valdivieso, Mechanism of adsorption of sodium dodecylsulfonate on celestite and calcite, Miner. Eng. 12 (1999) 919-936.

MINING AND METALLURGY INSTITUTE BOR
UDK: 622

ISSN: 2334-8836 (Štampano izdanje)
ISSN: 2406-1395 (Online)

UDK: 620.193:546.76/.11(045)=111
doi:10.5937/MMEB1503145J

Bore Jegdić[*], *Biljana Bobić*[*], *Aleksandar Jegdić*[*], *Maja Stevanović*[*]

MECHANISMS OF HYDROGEN EVOLUTION ON CHROMIUM[**]

Abstract

In this work, the mechanisms of hydrogen evolution on the metal chromium in a solution of 0.1 M $Na_2SO_4 + H_2SO_4$*, pH 1 to pH 7 were analysed. In the pH < 3 range, hydrogen is evolved according to three different mechanisms, depending on the experimental conditions: electrochemical evolution of* H_2 *by reaction of* H^+ *ions according to the Volmer-Heyrovsky mechanism, on the bare chromium surface, during chemical dissolution of chromium by the Kolotyrkin mechanism, which does not depend on the electrode potential, and electrochemical hydrogen evolution by the Volmer-Heyrovsky mechanism, but on the passive chromium. At pH values greater than 3, the fourth mechanism of hydrogen evolution is observed, that is electrochemical reaction of water molecules on the surface of oxide covered chromium surface.*

Keywords: *chromium, corrosion, chemical dissolution, hydrogen evolution*

INTRODUCTION

In parallel with the electrochemical dissolution of chromium, its chemical dissolution takes place, which does not depend on potential, and is a dominant process of dissolution in some circumstances [1-8]. During chemical dissolution of chromium, the hydrogen evolution occurs, which does not obey the laws of electrochemical kinetics. The chemical evolution of hydrogen can explain the observed processes of corrosion fatigue and stress corrosion of stainless steels in conditions where its electrochemical evolution is impossible. The low current efficiency in galvanic deposition of chromium coatings may be the result of parallel chemical dissolution of chromium during electrodeposition of chromium.

Chromium is in the passive state after immersion in a test solution, with the characteristic corrosion potential $E_{cor.1}$. During cathodic polarization at -0.900 V in a few tens of seconds, the passive film dissolves, whereas the chromium electrode is activated. The corrosion potential $E_{cor.2}$ is then formed, which corresponds to the active chromium.

EXPERIMENTAL PART

Samples of metallic chromium were sealed in methacrylate mass, and the sample surface was mechanically polished with abrasive paper, gradually to the fineness 1000. The samples were then rinsed with distilled water and placed in an electrochemical cell. The test solutions (0.1 M $Na_2SO_4 + H_2SO_4$, pH 1 to pH 7) were dearated with the use of purified nitrogen.

To perform electrochemical tests, the three-part glass electrochemical cell was

---

[*] *Institute for Chemistry, Technology and Metallurgy, University of Belgrade, Njegoševa 12, Belgrade, Serbia, e-mail: borejegdic@yahoo.com*

[**] *This work was supported by the Ministry of Education, Science and Technological Development of the Republic of Serbia, trough the Projects No. 34 028 and No. 34016.*

used, with water jacket, and with Pt foil as a counter electrode and a saturated calomel electrode (SCE) as a reference electrode. All measured potentials are shown in relation to the SCE.

In some cases, before the measurement, the electrode of chromium was activated by cathodic polarization at -0.900 V for 120 s, to remove any surface oxide which can be spontaneously formed on chromium in contact with the air. After ~ 15 min of corrosion potential stabilization, polarization curves were recorded potentiodynamically, at sweep rate of 2 mV s^{-1}. Electrochemical measurements were performed using the potentiostate-galvano-state PAR 273.

The preferential orientation of individual grains on the surface of the chromium sample (sample texture) was determined by the electron backscatter diffraction, EBSD.

RESULTS AND DISCUSSION

Figure 1 shows the inverse polar image of chromium texture obtained by the EBSD method. As can be seen on the coloured scale, the relative frequency of the crystal planes with orientation (111) on the surface of sample is 4.851 times higher than the frequency of sample without texture.

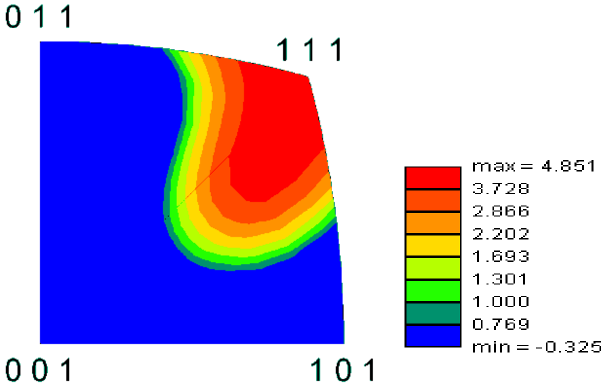


Figure 1 *Inverse polar image of chromium texture obtained by the EBSD method. The colored scale indicates the relative frequency of particular crystallographic orientations*

Figure 2 shows the cyclic voltammogram of chromium electrode in 0.1 M Na_2SO_4 + H_2SO_4, pH 1. The voltammogram shows the unusual behaviour at reverse change of potential. The recorded current, instead of being always anodic in the potential region between the corrosion potential $E_{cor.2}$ and positive limits of the potential (Inset in Figure 2), changes its character twice in this potential region, forming another corrosion potential $E_{cor.1}$ and a cathodic peak. This is a cathodic peak of hydrogen evolution on the passive film, but not a peak of oxide reduction. During potential hold in the mentioned potential region, the cathodic current has a stable value, which does not change over time. This indicates that this peak is not a peak of oxide reduction.

The corrosion potential $E_{cor.1}$ is formed on the electrode of chromium which is directly immersed in solution. The oxide layer on chromium electrode has been spontaneously formed. $E_{cor.2}$ refers to the corrosion potential that was formed on the surface of chromium after cathodic treatment at -0.900 V, for the purpose of oxide film reduction.

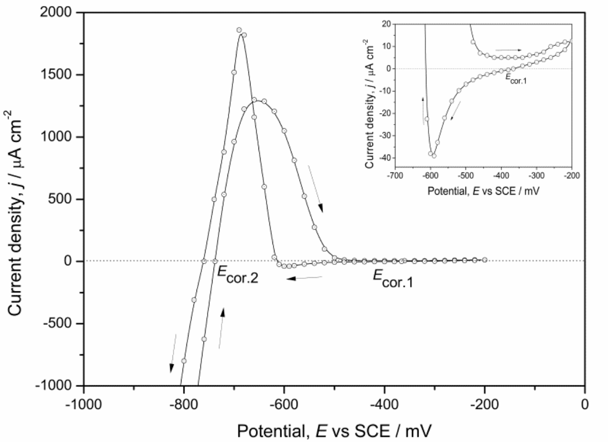


Figure 2 *Cyclic voltammogram for chromium electrode after cathodic activation. Inset shows enlarged cathodic peak at reverse potential change. This peak refers to cathodic hydrogen evolution on passivated chromium surface.*

A voltammogram example, similar to that in the inset in Figure 2, is shown in Figure 3. Reverse parts of cyclic voltammograms, recorded at different temperatures, express the cathodic hydrogen evolution on the pasivated chromium surface. As it can be seen, cathodic current increases with increasing temperature. However, the position of corrosion potential $E_{cor.1}$ and cathodic peak is not changed.

Accordingly, the cathodic current is a result of cathodic hydrogen evolution on the oxide covered chromium surface. The corrosion potential $E_{cor.1}$ is controlled by the reaction of cathodic hydrogen evolution and anodic dissolution of chromium through passive film. Hydrogen is evolved on the passivated chromium surface until the potential is reached that corresponds to the potential of oxide dissolution (~ -0.580 V). Sample of chromium is then activated, and current rapidly passes from cathodic to anodic region.

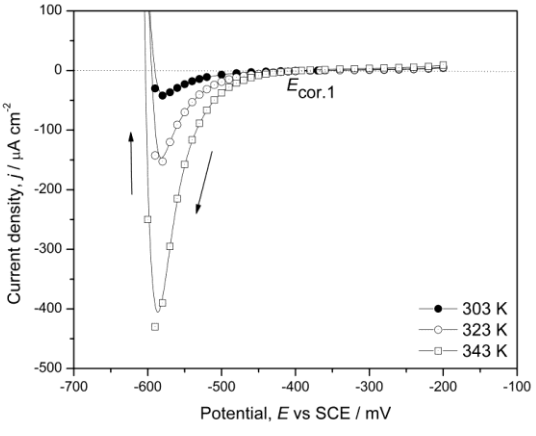


Figure 3 *A reverse part of cyclic voltammogram of chromium electrode in solution of 0.1 M Na_2SO_4 + H_2SO_4, pH 1, at various temperatures*

At room temperature, the Tafel slopes on the oxide covered chromium electrode, change gradually from the value approximately equal to 0.12 V dec^{-1} at pH 3 to the value of 0.06 V dec^{-1} to pH 1 [3].

Cathodic and anodic Tafel lines with approximately equal Tafel slopes of about 0.12 V dec^{-1} were obtained for chromium electrode, previously cathodically activated in the solutions with a pH below 3. Typical diagrams for a Cr in the solutions with a pH 1 and pH 2 are shown in Figure 4. The intersection of Tafel lines at the corrosion potential $E_{cor.2}$ shows that the corrosion potential is determined in terms of the Wagner-Traud model of electrochemical processes for anodic dissolution of chromium and cathodic hydrogen evolution. In parallel with the electrochemical dissolution of chromium the chemical dissolution of chromium occurs according to the Kolotyrkin mechanism [2].

The cathodic hydrogen evolution on the active surface of chromium with a slope of 0.12 V dec^{-1} indicates the following reaction:

$$Cr + 2H^+ + 2e^- \rightarrow Cr + H_2 \qquad (1)$$

This reaction probably occurs by the Volmer-Heyrovsky mechanism.

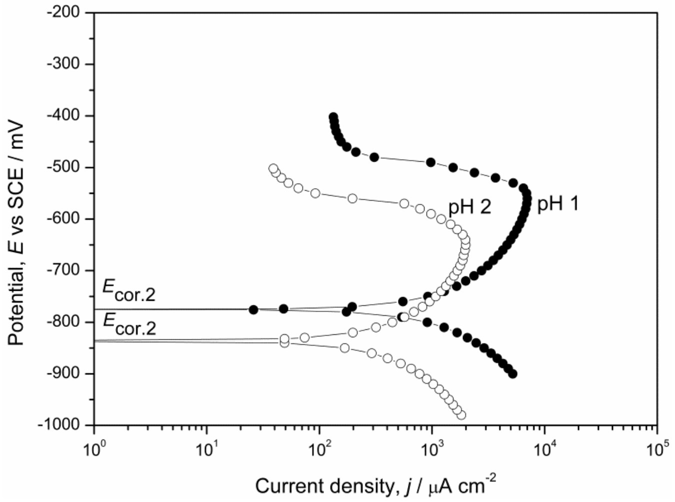


Figure 4 *Anodic and cathodic polarization curves for chromium electrode previously cathodically activated, in dependence on the pH value of solution*

Corrosion potential $E_{cor.2}$ in a solution of 0.1 M Na_2SO_4 + H_2SO_4, pH 2 is shifted by approximately 0.06 V in the direction of negative potential, in relation to the corrosion potential, in a solution with a pH of 1. This might be expected taking into account the influence of pH on position of the cathodic Tafel lines. Position of the anodic Tafel line does not depend on the pH value of the solution. Also, for the same reason, the corrosion current in the solution with pH 2 has a lower value than in a solution with pH 1.

On the oxide surface of passive chromium (Figure 5) hydrogen also evolves by the Volmer-Heyrovsky mechanism [3]:

$$Cr_{ox} + 2H^+ + 2e^- \rightarrow Cr_{ox} + H_2 \qquad (2)$$

At higher cathodic polarization of the passive chromium, at a pH > 3, the limiting diffusion current of H^+ ions can be seen, while at still higher polarizations Tafel lines independent on the pH value appear, that are characteristic for discharging of H_2O molecules [3]:

$$Cr_{ox} + 2H_2O + 2e^- \rightarrow Cr_{ox} + H_2 + 2OH^- \qquad (3)$$

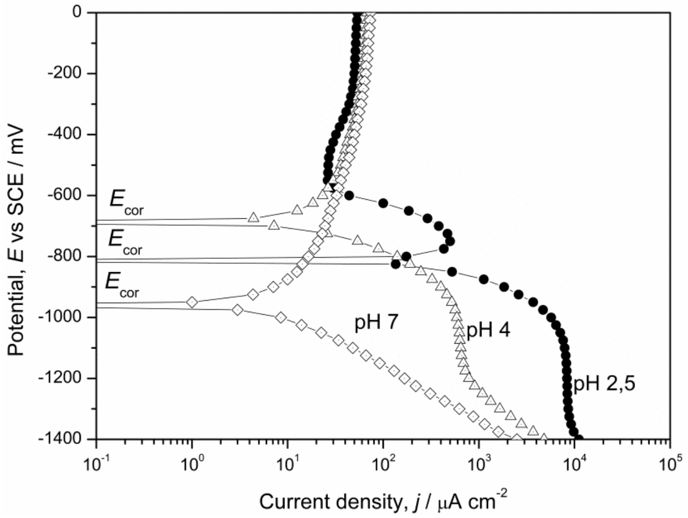


Figure 5 *Anodic and cathodic polarization curves for the electrode of chromium, depending on the pH value of the solution.*

In solutions of 0.1 M Na_2SO_4 + H_2SO_4, pH < 3 hydrogen evolves depending on experimental conditions, according to the following three different mechanisms:

1. Electrochemical evolution of H_2 by reaction of H^+ ions according to the Volmer-Heyrovsky mechanism, on the bare chromium surface,
2. During chemical dissolution of chromium by the Kolotyrkin mechanism [2], which does not depend on the electrode potential, and
3. Electrochemical hydrogen evolution as under (1) but on the oxide covered chromium surface (ie, on the passive chromium).

At pH > 3 the fourth mechanism of electrochemical hydrogen evolution is observed, that is reaction of water molecules on the oxide covered chromium surface.

CONCLUSION

Corrosion potential which is formed on the surface of passivated chromium ($E_{cor.1}$) is due to the cathodic reaction of hydrogen evolution on the oxide covered chromium surface, and the anodic reaction of chromium dissolution through the passive film. Corrosion potential which is formed on the surface of bare chromium is the result of cathodic hydrogen evolution and anodic dissolution of chromium from the bare surface. In this case, the established corro-sion potential is $E_{cor.2}$.

In sulfate solutions in the pH < 3 range, hydrogen is evolved according to three different mechanisms, depending on the experimental conditions: (1) the electrochemical evolution of H_2 by reaction of H^+ ions according to the Volmer-Heyrovsky mechanism on the bare chromium surface, (2) during chemical dissolution of chromium by the Kolotyrkin mechanism, which does not depend on electrode potential, and (3) electrochemical hydrogen evolution by the Volmer-Heyrovsky mechanism on the oxide covered chromium surface. At pH > 3, the fourth mechanism of hydrogen evolution is observed (4), that is electrochemical reaction of water molecules on the oxide covered chromium surface.

REFERENCES

[1] Wilde B. E., Hodge F. G., The Cathodic Discharge of Hydrogen on Active and Passive Chromium Surfaces in Dilute Sulphuric Acid Solutions, Electrochim. Acta 14 (7) (1969) pp. 619-627;

[2] Kolotyrkin Ya. M., Florianovich G.M., Anomalnoe rastvorenie metallov. Eksperimentalnie fakti i ih teoreticheskoe tolkovanie, Zashch. Metal. 20 (1) (1984) pp. 14-24;

[3] Dražić D.M., Popić J.P., Anomalous Dissolution of Metals and Chemical Corrosion (Review), J. Serb. Chem. Soc. 70 (3) (2005) pp. 489-513;

[4] Sukhotin A. M., Khoreva N. K., Passivnost khroma. Osobenosti katodnogo aktivirovaniya khroma, Electrokhimiya 18 (1) (1982) pp. 132-134;

[5] Jegdić B., Dražić D. M., Popić J. P., Structural Effects of Metallic Chromium on its Electrochemical Behavior, J. Serb. Chem. Soc. 72 (6) (2007) pp. 563-578;

[6] Jegdić B., Dražić D. M., Popić J. P., Influence of Chloride Ions on the Open Circuit Potentials of Chromium in Deaerated Sulfuric Acid Solutions, J. Serb. Chem. Soc. 71 (11) (2006) pp. 1187-1194.

[7] Jegdić B., Dražić D. M., Popić J. P., Open Circuit Potentials of Metallic Chromium and Austenitic 304 Stainless Steel in Aqueous Sulphuric Acid Solution and the Influence of Chloride Ions on them, Corr. Sci. 50 (2008) pp. 1235-1244;

[8] Jegdić B., Stevanović M., Jegdić A., Chemical and Electrochemical Dissolution of Chromium at Room and Elevated Temperatures, Mining and Metallurgy Engineering Bor (accepted paper).

INSTITUT ZA RUDARSTVO I METALURGIJU BOR ISSN: 2334-8836 (Štampano izdanje)
UDK: 622 ISSN: 2406-1395 (Online)

UDK: 620.193:546.76/.11(045)=163.41 doi:10.5937/MMEB1503145J

Bore Jegdić[*], *Biljana Bobić*[*], *Aleksandar Jegdić*[*], *Maja Stevanović*[*]

MEHANIZMI IZDVAJANJA VODONIKA NA HROMU[**]

Izvod

U ovom radu analizirani su mehanizmi izdvajanja vodonika na metalnom hromu u rastvoru 0,1 M $Na_2SO_4 + H_2SO_4$, *pH 1 do pH 7. U oblasti* $pH < 3$ *vodonik se izdvaja u zavisnosti od eksperimentalnih uslova po tri različita mehanizma: elektrohemijskim izdvajanjem* H_2 *reagovanjem* H^+ *jona po mehanizmu Folmer-Hejrovski na čistoj površini hroma, pri hemijskom rastvaranju hroma po mehanizmu Kolotirkina, a koje ne zavisi od elektrodnog potencijala i elektrohemijskim izdvajanjem vodonika po mehanizmu Folmer-Hejrovski, ali na pasivnom hromu. Pri pH vrednostima većim od 3 uočava se i četvrti mehanizam izdvajanja vodonika elektrohemijskim reagovanjem molekula vode na oksidom presvučenoj površini hroma.*

Ključne reči: *hrom, korozija, hemijsko rastvaranje, izdvajanje vodonika*

UVOD

Paralelno sa elektrohemijskim rastvaranjem hroma odvija i njegovo hemijsko rastvaranje, koje ne zavisi od potencijala i koje je u nekim uslovima dominantan proces rastvaranja [1-8]. Hemijsko rastvaranje hroma je uzrok pojavi izdvajanja vodonika, koja ne podleže zakonitostima elektrohemijske kinetike. Pojava hemijskog izdvajanja vodonika može biti objašnjenje za uočeno odvijanje procesa korozionog zamora i naponske korozije nerđajućih čelika u uslovima kada je nemoguće njegovo elektrohemijsko izdvajanje. Nisko iskorišćenje struje pri nanošenju prevlake hroma, može biti posledica paralelnog hemijskog rastvaranja hroma tokom galvanskog taloženja hroma.

Hrom se nalazi u pasivnom stanju posle uranjanja u rastvor za ispitivanje, sa karakterističnim korozionim potencijalom $E_{kor,1}$.

Katodnom polarizacijom na -0,900 V u toku nekoliko desetina sekundi, pasivni film se rastvara, pri čemu se elektroda aktivira. Tada se formira korozioni potencijal $E_{kor,2}$ koji odgovara aktivnom hromu.

EKSPERIMENTALNI DEO

Uzorci metalnog hroma su zatopljeni u metakrilatnu masu, površina uzoraka je mehanički polirana brusnim papirom do finoće 1000. Uzorci su zatim ispirani destilovanom vodom i stavljeni u elektrolitičku ćeliju radi ispitivanja. Rastvori za ispitivanje bili su 0,1 M $Na_2SO_4 + H_2SO_4$, pH 1 do pH 7, koji su deaerisani provođenjem prečišćenog azota.

Za izvođenje elektrohemijskih ispitivanja korišćena je trodelna staklena elektrohemijska ćelija sa vodenim plaštom za

---

[*] *NU Institut za hemiju, tehnologiju i metalurgiju, Univerziteta u Beogradu, Njegoševa 12, Beograd, Srbija, e-mail: borejegdic@yahoo.com*

[**] *Ovaj red je finansiran od strane Ministarstva prosvete, nauke i tehnološkog razvoja Republike Srbije, Projekti No. 34 028 i No. 34016.*

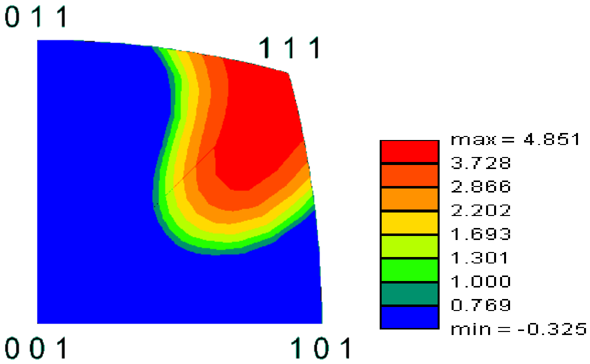
termostatiranje, sa Pt pomoćnom elektrodom i zasićenom kalomelovom elektrodom (ZKE) kao referentnom elektrodom. Svi izmereni potencijali prikazani su u odnosu na ZKE.

U nekim slučajevima, pre merenja, elektroda hroma je aktivirana katodnom polarizacijom na –0,900 V u toku 120 s, radi uklanjanja površinskog oksida, koji se na hromu spontano stvara u dodiru sa vazduhom. Posle ~15 min stabilizacije korozionog potencijala polarizacione krive su snimane potenciodinamički, pri linearnoj brzini promene potencijala od 2 mV s^{-1}. Elektrohemijska merenja su izvedena primenom potenciostata-galvanostata PAR 273.

Preferencijalna orijentacija pojedinih zrna na površini uzorka hroma (tekstura uzoraka) je određena metodom difrakcije odbijenih elektrona (electron backscatter diffraction, EBSD).

REZULTATI I DISKUSIJA

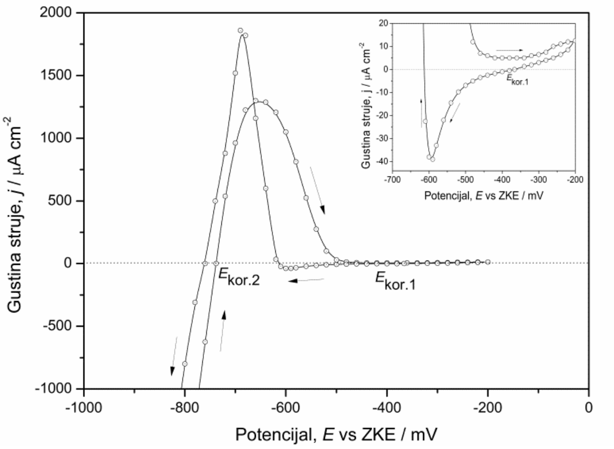
Na slici 1 je prikazana inverzna polarna slika teksture uzorka hroma dobijena EBSD metodom. Kao što se vidi sa obojene skale, relativna učestalost kristalnih ravni sa orijentacijom (111) na površini uzorka je 4,851 puta veća u odnosu na učestalost te orijentacije na uzorku bez teksture.



Sl. 1. *Inverzna polarna slika teksture uzorka hroma dobijena EBSD metodom. Obojena skala označava relativnu učestalost pojedinih kristalografskih orijentacija*

Na slici 2 je prikazan ciklični voltamogram za elektrodu hroma u rastvoru 0,1 M Na_2SO_4 + H_2SO_4, pH 1. Ciklični voltamogram pokazuje neobično ponašanje pri reversnoj promeni potencijala. Naime, registrovana struja umesto da bude uvek anodna u oblasti potencijala između korozionog potencijala $E_{kor,2}$ i pozitivne granice promene potencijala (isečak na slici 2), menja svoj znak dva puta u toj oblasti potencijala, formirajući još jedan korozioni potencijal $E_{kor,1}$ i katodni pik, koji nije pik redukcije oksida. Da se radi o katodnom piku izdvajanja vodonika na pasivnom filmu, a ne o redukciji oksida, utvrđeno je potenciostatskim ispitivanjem u toj oblasti potencijala. Tokom potenciostatskog zadržavanja potencijala u navedenoj oblasti, katodna struja je imala stabilnu vrednost, koja se nije menjala tokom vremena, što ukazuje da se ne radi o redukciji oksida.

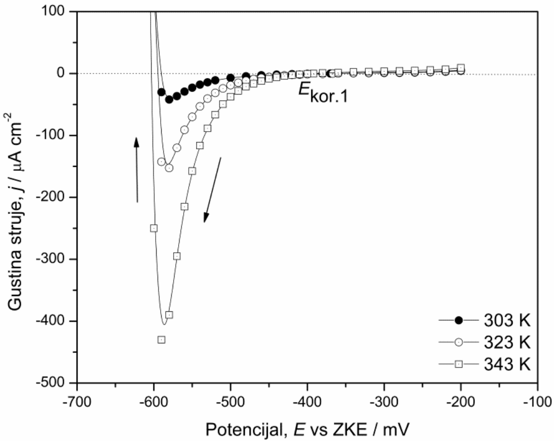
Korozioni potencijal $E_{kor.1}$, se obrazuje na elektrodi hroma neposredno uronjenoj u rastvor (koja ima spontano formiran oksidni sloj na svojoj površini), a $E_{kor.2}$ se odnosi na korozioni potencijal koji se obrazuje na površini hroma posle katodnog tretmana na potencijalu -0,900 V u cilju redukcije prisutnog oksidnog filma.



Sl. 2. *Ciklični voltamogram za elektrodu hroma posle katodne aktivacije. Isečak prikazuje uvećano katodni pik pri povratnoj promeni potencijala koji predstavlja katodno izdvajanje vodonika na pasiviranoj površini.*

Primer voltamograma, sličnog onom na isečku na slici 2, je prikazan na slici 3. Reversni delovi cikličnih voltamograma, snimljeni na različitim temperaturama, predstavljaju katodno izdvajanje vodonika na pasiviranoj površini hroma. Kao što se može videti, katodna struja se povećava sa povećanjem temperature, međutim položaj korozionog potencijala $E_{kor,1}$ i katodnog pika se ne menja.

Prema tome, katodne struje su posledica katodnog izdvajanja vodonika na hromu prekrivenom oksidom, a korozioni potencijal $E_{kor,1}$ je kontrolisan tom reakcijom katodnog izdvajanja vodonika i reakcijom anodnog rastvaranja hroma kroz pasivni film. Vodonik se izdvaja na pasiviranom hromu sve do dostizanja potencijala koji odgovara potencijalu rastvaranja oksida (~-0,580 V). Uzorak hroma se zatim aktivira, a struja naglo prelazi iz katodne u anodnu oblast.



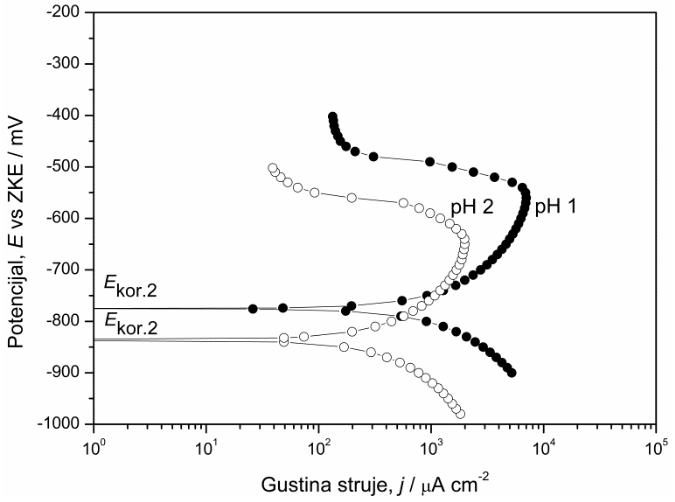
Sl. 3. *Reversni delovi voltamograma za elektrodu hroma u rastvoru 0,1 M Na_2SO_4 + H_2SO_4, pH 1 na različitim temperaturama.*

Na sobnoj temperaturi se Tafelovi nagibi, za elektrodu hroma prekrivenu oksidnim slojem, postepeno menjaju od vrednosti približno jednake -0,12 V dek^{-1} za pH 3 do vrednosti -0,06 V dek^{-1} za pH 1 [3].

Polarizacijom hroma prethodno katodno aktiviranog u rastvorima sa pH < 3 dobijene su katodne i anodne Tafelove linije sa približno jednakim Tafelovim nagibima od oko 0,12 V dek^{-1} (tipični dijagrami za prevlaku Cr u rastvorima sa pH 1 i pH 2 su prikazani na slici 4). Presek Tafelovih linija na korozionom potencijalu $E_{kor.2}$ pokazuje da je korozioni potencijal određen u smislu Vagner-Traudovog modela elektrohemijskim procesima anodnog rastvaranja hroma i katodnog izdvajanja vodonika. Paralelno sa elektrohemijskim rastvaranjem odvija se i hemijsko rastvaranje hroma po mehanizmu Kolotirkina [2]. Katodno izdvajanje vodonika na aktivnoj površini hroma sa nagibom od 0,12 V dek^{-1} ukazuje na reakciju:

$$Cr + 2H^+ + 2e^- \rightarrow Cr + H_2 \qquad (1)$$

koja se najverovatnije odvija po mehanizmu Folmer-Hejrovski.



Sl. 4. *Anodne i katodne polarizacione krive za elektrodu hroma prethodno katodno aktiviranu, u zavisnosti od pH vrednosti rastvora*

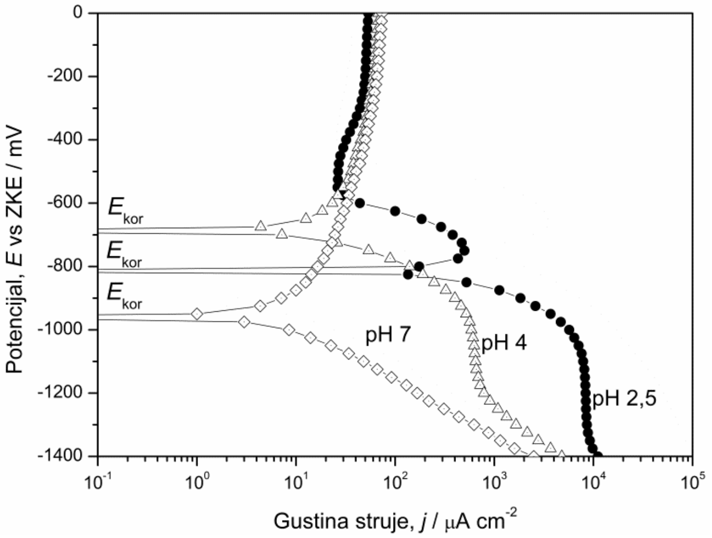
Korozioni potencijal $E_{kor.2}$ u rastvoru 0,1 M Na_2SO_4 + H_2SO_4, pH 2 je pomeren za približno 0,06 V u smeru negativnijih potencijala u odnosu na korozioni potencijal u rastvoru sa pH 1, što se moglo i očekivati na osnovu razmatranja uticaja pH vrednosti na položaj katodnih Tafelovih pravih. Položaj anodne Tafelove prave ne zavisi od pH vrednosti rastvora. Takođe iz istih razloga struja korozije u rastvoru sa pH 2 ima nižu vrednost nego u rastvoru sa pH 1.

Na pasivnom hromu (Slika 5) vodonik se takođe izdvaja mehanizmom Folmer-Hejrovski, ali na površini hroma prekrivenoj oksidnim slojem [3]:

$$Cr_{ox} + 2H^+ + 2e^- \rightarrow Cr_{ox} + H_2 \qquad (2)$$

Pri većim katodnim polarizacijama pasivnog hroma, pri pH > 3 uočava se granična difuziona struja H^+ jona, a pri još većim polarizacijama pojava Tafelovih pravih nezavisnih od pH, karakterističnih za razelektrisanje molekula H_2O [3]:

$$Cr_{ox} + 2H_2O + 2e^- \rightarrow Cr_{ox} + H_2 + 2OH^- \qquad (3)$$



Sl. 5. *Anodne i katodne polarizacione krive za elektrodu hroma u zavisnosti od pH vrednosti rastvora*

U rastvorima 0,1 M Na_2SO_4 + H_2SO_4, pH < 3 vodonik se izdvaja u zavisnosti od eksperimentalnih uslova po tri različita mehanizma:

1. elektrohemijskim izdvajanjem H_2 reagovanjem H^+ jona po mehanizmu Folmer-Hejrovski na čistoj površini hroma,
2. pri hemijskom rastvaranju hroma po mehanizmu Kolotirkina [2], a koje ne zavisi od elektrodnog potencijala, i
3. elektrohemijskim izdvajanjem vodonika kao pod (1) ali na površini hroma prekrivenoj oksidnim slojem.

Pri pH vrednostima većim od 3 uočava se i četvrti mehanizam izdvajanja vodonika, elektrohemijskim reagovanjem molekula vode na oksidom prevučenj površini hroma.

ZAKLJUČAK

Korozioni potencijal koji se obrazuje na pasiviranoj površini hroma ($E_{kor.1}$) je posledica odvijanja katodna reakcije izdvajanja vodonika i reakcije anodnog rastvaranja hroma kroz pasivni film. Korozioni potencijal koji se obrazuje na čistoj površini hroma je posledica katodnog izdvajanja vodonika i anodnog rastvaranja hroma sa te površine. U tom slučaju uspostavlja se korozioni potencijal $E_{kor.2}$.

U sulfatnim rastvorima, u oblasti pH < 3 vodonik se izdvaja u zavisnosti od eksperimentalnih uslova po tri različita mehanizma: (1) elektrohemijskim izdvajanjem H_2, reagovanjem H^+ jona po mehanizmu Folmer-Hejrovski na čistoj površini hroma, (2) pri hemijskom rastvaranju hroma po mehanizmu Kolotirkina, a koje ne zavisi od elektrodnog potencijala, i (3) elektrohemijskim izdvajanjem vodonika po mehanizmu Folmer-Hejrovski, ali na površini hroma prekrivenoj oksidnim slojem. Pri pH vrednostima većim od 3 uočava se i četvrti mehanizam izdvajanja vodonika (4) elektrohemijskim reagovanjem molekula vode na površini hroma prekrivenoj oksidnim slojem.

LITERATURA

[1] Wilde B. E., Hodge F. G., The cathodic discharge of hydrogen on active and passive chromium surfaces in dilute sulphuric acid solutions, Electrochim. Acta 14 (7) (1969), str. 619-627.

[2] Kolotyrkin Ya. M., Florianovich G. M., Anomalnoe rastvorenie metallov. Eksperimentalnie fakti i ih teoreticheskoe tolkovanie, Zashch. Metal. 20 (1) (1984), str. 14-24.

[3] Dražić D. M., Popić J. P., Anomalous dissolution of metals and chemical corrosion (Review), J. Serb. Chem. Soc. 70 (3) (2005), str. 489-513.

[4] Sukhotin A. M., Khoreva N. K., Passivnost khroma. Osobenosti katodnogo aktivirovaniya khroma, Electrokhimiya 18 (1) (1982), str. 132-134.

[5] Jegdić B., Dražić D. M., Popić J. P., Structural effects of metallic chromium on its electrochemical behavior, J. Serb. Chem. Soc. 72 (6) (2007), str. 563-578.

[6] Jegdić B., Dražić D. M., Popić J. P., Influence of chloride ions on the open circuit potentials of chromium in deaerated sulfuric acid solutions, J. Serb. Chem. Soc. 71 (11) (2006), str. 1187-1194.

[7] Jegdić B., Dražić D.M., Popić J.P., Open circuit potentials of metallic chromium and austenitic 304 stainless steel in aqueous sulphuric acid solution and the influence of chloride ions on them, Corr. Sci. 50 (2008), str. 1235-1244.

[8] Jegdić B., Stevanović M., Jegdić A., Chemical and Electrochemical Dissolution of Chromium at Room and Elevates Temperatures, Mining and Metallurgy Engineering Bor (accepted paper).

MINING AND METALLURGY INSTITUTE BOR
UDK: 622

ISSN: 2334-8836 (Štampano izdanje)
ISSN: 2406-1395 (Online)

UDK: 547.914:622.01:624(045)=111

doi:10.5937/MMEB1503157T

Prvoslav Trifunović[*], *Rade Tokalić*[*], *Nebojša Vidanović*[*], *Draško Marković*[**]

POLYMER RESINS WITH FOAM EFFECT AND THEIR APPLICATION IN MINING[***]

Abstract

For stabilization of degraded rock massif around the built underground mining premises, the procedures of injecting of polymer synthetic resins with foam effect are in use today more and more. By injecting of polymer resins in drill holes or cracks and their hardening, the spreading of deformity by depth is stopped, and therefore the stability of degraded rock material and built premises is provided.

For increasing the stability of mining premises, the fast reacting phenolic resins are used, filling up the cracks in the cracked rock mass and preventing their expansion. In that way they contribute improving the operative safety and efficiency in building the mining premises.

Few years ago, two-component poliurethan foamy resins appeared that have found an application for strengthening, insulation and rehabilitation of mining premises demanding a medium or longer period of usage.

Urea of silicate non-flammable resin is approved for usage in the coal mines and in building the underground premises in heavy work conditions. Stabilization and strengthening of weaked zones in these cases is done by combining the drainage and injecting the fast reacting foamy resins.

New materials and technologies have enabled very significant improvements in many areas of mining and constructions, both in domain of faster, safer and more efficient building, and in domain of maintenance and rehabilitation the mining and construction facilities.

Keywords: *foamy polymer resins, strengthening and stabilization, degraded rock massif, mining, construction, geotechnics*

1 INTRODUCTION

Polymer resins with foam effect have found a wide application in strengthening, stabilization and insulation of degraded materials in mining, geotechnics, hydratechnics, construction and other related activities.

In mining, they have application for stabilization and strengthening of degraded rocks around underground facilities, stopping of water inflow, etc. In geotechnics and hydrotechnics, they are used in strengthening of sandy and gravelish soil of constructions with the aim of increasing the bearing capacity; filling of cavities and injecting of cracks of concrete and wall constructions; anchoring of different elements into the built facilities, rocks and groundwork; strengthening of damaged docks and

---

[*] *Univerzity of Belgrade, Faculty of Geology and Mining, Djusina 7, 11000 Belgrade, Serbia, e-mail: prvoslav.trifunovic@rgf.bg.ac.rs*

[**] *Administration for Inspection Affairs, Department of Mining, Geological and Inspection for Hydrocarbons, Rimski trg no. 46, 81000 Podgorica, Montenegro*

[***] *This work is the result of the Project No. TR 33029, funded by the Ministry of Education, Science and Technological Development of the Republic of Serbia*

pillars of bridges, even bellow water level; preventing of leaking barriers and walls of hydrotechnical dams, insulation of mineral water streaming, etc.

2 BASIC CHARACTERISTICS OF POLYMER RESINS WITH FOAM EFFECT

Foam is a gas emulsion of bubbles in injecting mass, arising from ordinary injection mixture by action of reagents for creating of bubbles. Gas bubbles have mostly spherical shape, of uniform diameter, where 80% of them has diameter (0.9-1.1)*d*, where *d* is an average diameter depending from type of reagent [1].

Foam is characteristic by two coefficients: expansion coefficient *e* and overgrowth coefficient *f*.

Expansion coefficient *e* is a relation between gas volume and suspension volume, and an equivalent to a porosity coefficient with incoherent soil.

Overgrowth coefficient *f* is a relation between the final and starting foam volume.

If expansion coefficient *e* is <0.2 there is no foam effect, and when *e* is > 0.8 foam is getting stiffen. Cement suspension foams can reach a coefficient up to e=3, and polymer resins foams can reach coefficient up to e=50.

Foam can be produced in suspensions and solutions in two ways:

- By adding of reagent which increases surface tension of water, and mixing creates foam;
- By adding of reagent which in chemical reaction releases gas emulsifies in a bubble shape.

In the first way, foam is created by physical reaction almost in the moment of mixing. Diameter of bubbles is uniform and under one millimeter.

In the second way, foam is created by chemical reaction that needs time from 10 to 20 minutes depending on temperature. That increases the expansion coefficient and improves foam properties, especially its stability.

Due to described characteristics, foams are especially used for closing and filling the large cavities (caverns, systems of large cracks and similar), and mass consumption is small. They are especially suitable for closing of cracks through which water flows, because of sudden stiffening after exit from the injecting pipe, for both, foams and in combination with the cement suspensions.

3 APPLICATION OF TWO-COMPONENT FAST REACTING POLYMER RESINS IN MINING

For stabilization, strengthening and insulation of degraded rock massif around built underground premises and objects today are used: two-component fast reacting phenolic resins, two-component polyurethane foamy resins and urea of silicate inflammable resin.

Two-component fast reacting phenolic resins start to foam immediately on mixing, gaining excellent physico-chemical properties. Injecting resin prevents expanding of deformities in cracked rock massif, fills gaps and increases stability of support the mining premises. In that way it contributes to improvement the operative safety and efficiency during performing the mining operations. Increasing of support stability using the fast reacting phenolic resins [5], is schematically shown in Figure 1.

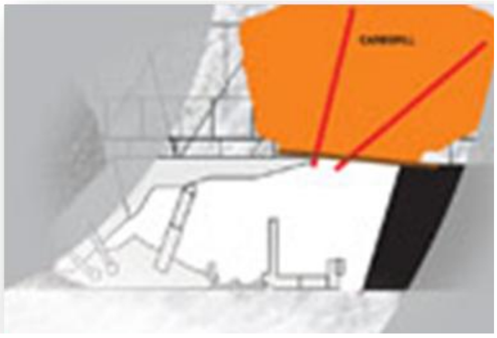


Figure 1 *Increasing the support stability using the fast reacting phenolic resins*

The base component (A) is made of material based on synthetic resin, and the other component (B) is made of catalyzer-hardener, placed in a small cartridge inside the first one. Mixture is made on the spot in ratio 4:1 using a two-component pump and hose (see Figure 2).

Figure 2 *Two-component injecting pump WIVA 2K-Inject*

During mixing it comes to polymerization caused by catalyzer, wherein resin foams, increases volume by several times and gets hard. Injecting mixture can be pumped through hoses, pipes or anchors filled by phenolic resin with catalyzer.

Technical data for components and foamy mass are presented in Tables 1 and 2.

Table 1 *Technical data for components*

Components technical data	Unit	Resin		Catalyzer
Density at 25^{0}C	kg/cm^3	1290 ± 30		1540 ± 30
pH-value		~ 8		1 - 0
Expiration date	months	3	12	6
Storage temperature	^{0}C	max. 20^0	max. 5^0	-5^0 – 30^0

Table 2 *Technical data for resin-foamy mixture*

Technical data for resin-mixture(on 20^{0}C)	Unit	Mixture
Starting time of binding	s	immediately
Reacting time	s	180 ± 60
Expansion coefficient (e)		32 - 38
Consumption	kg/m^3	~ 36 - 42

Two-component polyurethane foamy resins are used for strengthening and insulation the rocks, soil, or constructions in the mines, geotechnical underground and construction engineering. Polyurethane resins are suitable for repair, reinforcement and insulation the cracks in concrete constructions and walls, achieving the high level of adhesion. Some types can be used for insulating of cracked constructions against penetration of water and gas. Foamy types have thermal and soundproof insulation properties.

Application of polyurethane foamy resins injecting technology in mining and tunnel construction is reflectedin the following [8]:

- Strengthening of rock massif with improving the mechanical properties of rock environment,
- Improving of mechanical properties of exploited materials before exploitation,
- Decreasing and preventing the water flow in mines,
- Anchoring and rock stabilization,
- Decreasing of gas penetration in the mine area,
- Preventing of unwanted gas leaking from mine into the environment,
- Preventing of waste water flowing from the abandoned mine areas,
- Preventing of flowing the unwanted air currents in the mine,
- Filling of cracks of multiple broken rocks,
- Injecting of dams and their environment with the aim to prevent water infiltration,
- Anchoring and injecting of coal surface during exploitation,
- Injecting of rocks of small stability in building the tunnels and excavation the horizontal pit premises, and
- Securing the mine operation movement over the techtonic damages.

Some examples of using the polyurethane resins in mining [2] are shown in Figures 3 and 4.

Figure 3 *Injecting of water barrier in the coal mines with the aim to prevent flowing of water through a barrier; the used material - Geopur*

Figure 4 *Sealing of cracks in a coal mine*

Two-component resin consists of component A and B. Component A is a liquid of honey color (all types), consisting of mixture of: polyalcohol, accelerators, compounds reducing flammability, foam stabilizers and water. Component B is a dark brown - yellow liquid (all types), made of: polymethilene, polyphenylisocyants, diphenylmethane, disocyanate (MDI) and mixture of polycyclic oligomers depending on a function.

After mixing the two basic components in a given proportion, through exothermic reaction, apolyurethane resin is formed. Degree of resin foam determines its physical and chemical characteristics. Start foaming and hardening reaction can be delayed for all systems up to 360 seconds. Standard compositions of these resins start to foam in 2 minutes. Delaying of reaction can be achieved only while components are still not mixed adding the special additives [8].

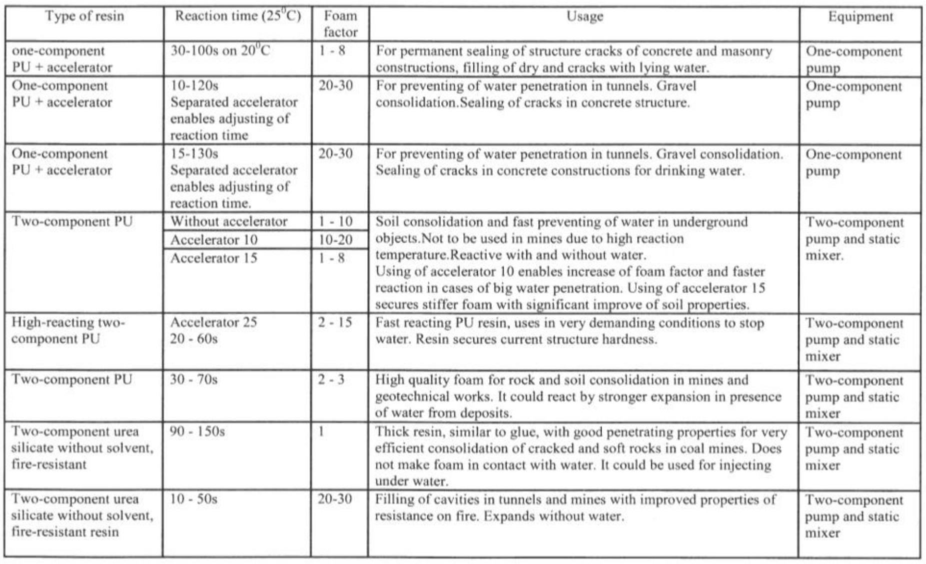
Urea of silicate inflammable resin is approved for use in the coal mines and in building the underground premises in heavy work conditions. Stabilization and strengthening of weaked zones around underground premises are performed by combination of drainage and injecting of fast reacting foamy resins [4].

Urea of silicate resin fulfills the modern requests of tunnel construction and building the underground premises in mining. Large number of these resins is produced from one-component resins for small works in preventing the water flow, to special robust two-component systems for efficient solving the problems of massif water penetration.

Properties and advantages of urea silicate injecting resins: besides they are “designed specifically“ for tunnel construction and mining, these resins are without solvents and form a cell structure from foam. For many urea silicate resins using in preventing of water in tunnel construction, the usage of various accelerators on the spot can adjust properties to match the concrete work conditions. Large number of urea silicate resins is on the market whose usage improves the fire protection and increases the safety in tunnel construction and mining.

Comparative review of polyurethane resins and urea silicate resins [8, 4] is given in Table 3.

Table 3 *Polyurethane (PU) and urea silicate resins*



Type of resin	Reaction time (25^{0}C)	Foam factor	Usage	Equipment
one-component PU + accelerator	30-100s on 20^{0}C	1 - 8	For permanent sealing of structure cracks of concrete and masonry constructions, filling of dry and cracks with lying water.	One-component pump
One-component PU + accelerator	10-120s Separated accelerator enables adjusting of reaction time	20-30	For preventing of water penetration in tunnels. Gravel consolidation.Sealing of cracks in concrete structure.	One-component pump
One-component PU + accelerator	15-130s Separated accelerator enables adjusting of reaction time.	20-30	For preventing of water penetration in tunnels. Gravel consolidation. Sealing of cracks in concrete constructions for drinking water.	One-component pump
Two-component PU	Without accelerator	1 - 10	Soil consolidation and fast preventing of water in underground objects.Not to be used in mines due to high reaction temperature.Reactive with and without water. Using of accelerator 10 enables increase of foam factor and faster reaction in cases of big water penetration. Using of accelerator 15 secures stiffer foam with significant improve of soil properties.	Two-component pump and static mixer.
	Accelerator 10	10-20		
	Accelerator 15	1 - 8		
High-reacting two-component PU	Accelerator 25 20 - 60s	2 - 15	Fast reacting PU resin, uses in very demanding conditions to stop water. Resin secures current structure hardness.	Two-component pump and static mixer
Two-component PU	30 - 70s	2 - 3	High quality foam for rock and soil consolidation in mines and geotechnical works. It could react by stronger expansion in presence of water from deposits.	Two-component pump and static mixer
Two-component urea silicate without solvent, fire-resistant	90 - 150s	1	Thick resin, similar to glue, with good penetrating properties for very efficient consolidation of cracked and soft rocks in coal mines. Does not make foam in contact with water. It could be used for injecting under water.	Two-component pump and static mixer
Two-component urea silicate without solvent, fire-resistant resin	10 - 50s	20-30	Filling of cavities in tunnels and mines with improved properties of resistance on fire. Expands without water.	Two-component pump and static mixer

The large world producers produce the polyurethane resins with foam effect under different commercial names: Carbofill, Carbopur, Geopur, WilkitFoamT, MEYCO, etc.

4 CONCLUSION

Modern materials based on polymer mixtures have increasing application for stabilization, strengthening and insulation the degraded rock massif in mining and construction area.

Polymer resins are widely used for strengthening the contours of mining premises and construction objects, if they are making in degraded environment, cracked and splitted rock massif or in case of unbidden sediments. The main advantages are: simple application, fast reaction and capability to stabilize whole formations of surrounding rocks exposed to the high pressures and movements.

Application of technology of injecting polyurethane resins in mining reflects in the next: strengthening of surrounding rock mass with achieving a high hardness under tightening and under pressure; decrease and stopping of water flow in the mines; anchoring and stabilization of rocks; decrease of gas penetration in the mine area; preventing of unwanted gas leakage from mine in the environment; preventing the waste water run out from the abandoned areas of mine; preventing of running out of unwanted air currents in mine; filling of cracks of multiple broken rocks; anchoring and injecting of coal surface during exploitation; providing of work moving in mine over tectonic damages and other.

Choice of polymer material is made individually for all specific cases under construction and recovery of underground mining and construction facilities, depending on requested stability and functionality of facilities in a specific time period.

REFERENCES

[1] Culibrk R. (2001), Geotechnical Works in Solid Rocks, Faculty of construction, Subotica, pp. 120-126, 169-178, 246-250;

[2] Bolesta M., Eichstaedt F., Hoffmann P. (1997), Recommendations for the Selection and Application of Injection Products for Ground Consolidation, Glückauf Int. Ed. 133 pp.550-559;

[3] Code SIA 267/1 (2003), Geotehnical Design - Supplementary Specifications, Swiss Society of Engineers and Architects, Zurich;

[4] Cornely W.(2003), Elastifield Silicate Resins and Polyuretane Foam Resins for the Stabilisation of Strata - a Comparison.

[5] V. V. Vasilev, (1986): Polymernye Kompozicii v gornom dele, Moscow, p.57ff.;

[6] Cokorilo V. et al., (2002), Rationalization and Modernization of Building and Supporting of Mining Premises in Mines with Underground Exploitation, Study, Codel Engineering, Belgrade, pp. 211-233;

[7] Nonveiller E. (1989): Injection of Soil, Theory and Practice, Zagreb, School book, pp. 47-50, 74-82.

[8] Polyurethane Resins: Geopure, *www.geopurewt.com*

INSTITUT ZA RUDARSTVO I METALURGIJU BOR
UDK: 622

ISSN: 2334-8836 (Štampano izdanje)
ISSN: 2406-1395 (Online)

UDK: 547.914:622.01:624(045)=163.41

doi:10.5937/MMEB1503157T

Prvoslav Trifunović[*], *Rade Tokalić*[*], *Nebojša Vidanović*[*], *Draško Marković*[**]

POLIMERNE SMOLE SA EFEKTOM PENE I NJIHOVA PRIMENA U RUDARSTVU[***]

Izvod

Za stabilizaciju degradiranog stenskog masiva oko izrađenih podzemnih rudarskih prostorija danas se sve više koriste postupci injektiranja polimernih sintetičkih smola sa efektom pene. Injektiranjem polimernih smeša u bušotine ili pukotine i njihovim očvršćavanjem sprečava se širenje deformacija po dubini, a samim tim obezbeđuje stabilnost degradiranog stenskog materijala i izrađenih objekta.

Za povećanje stabilnosti rudničkih prostorija najčešće se koriste brzo reagujuće fenolne smole koje popunjavaju pukotine u raspucaloj stenskoj masi i sprečavaju njihovo širenje. Na taj način doprinose poboljšanju operativne sigurnosti i efikasnosti pri izradi rudničkih prostorija.

Pre nekoliko godina u upotrebu su ušle dvokomponentne poliuretanske penušave smole, koje su našle primenu za ojačanje, izolaciji i sanaciju rudarskih prostorija koje zahtevaju srednji ili duži rok korišćenja.

Urea silikatne nezapaljive smole odobrene su za korišćenje u rudnicima uglja i kod izrade podzemnih objekata u teškim radnim uslovima. Stabilizacija i ojačanje oslabljenih zona u ovim slučajevima vrši se kombinacijom dreniranja i injektiranja brzo reaktivnih penušavih smola.

Novi materijali i tehnologije omogućili su da se u mnogim oblastima rudarstva i građevinarstva postižu veoma značajna poboljšanja kako u domenu brže, sigurnije i efikasnije gradnje, tako i u domenu održavanja i sanacije radarskih i građevinskih objekata.

***Ključne reči**: penušave polimerne smeše, ojačanje i stabilizacija, degradirani stenski masiv, rudarstvo, građevinarstvo, geotehnika*

1. UVOD

Polimerne smole sa efektom pene našle su široku primenu za ojačanje, stabilizaciju i izolaciju degradiranih materijala u rudarstvu, geotehnici, hidrotehnici, građevinarstvu i drugim srodnim delatnostima.

U rudarstvu se koriste za stabilizaciju i ojačanje degradiranih stena oko podzemnih prostorija, stabilizaciju ispucalih slojeva uglja, popunjavanje pukotina i velikih šupljina oko podzemnih objekata, zaustavljanje dotoka voda itd. U geotehnici i hidrotehnici se koriste za ojačavanje peskovitog i šljunkovitog tla konstrukcija u cilju povećanja nosivosti; ispunjavanje šupljina i injektiranje prslina betonskih i zidanih konstrukcija; ankerisanje različitih elemenata u izrađene objekte, stene i podlogu; ojačavanje oštećenih dokova i stubova mostova čak i

---

[*] *Univerzitet u Beogradu, Rudarsko-geološki fakultet, Đušina 7, 11000 Beograd, Srbija, e-mail: prvoslav.trifunovic@rgf.bg.ac.rs*

[**] *Uprava za inspekcijske poslove, Odsjek za rudarsku, geološku i inspekciju za ugljovodonike, Rimski trg br. 46, 81000 Podgorica*

[***] *Ovaj rad je proistekao iz Projekta br. TR 33029 koji je finansiran sredstvima Ministarstva prosvete, nauke i tehnološkog razvoja Republike Srbije.*

ispod nivoa vode; sprečavanje procurivanja barijera i zidova hidrotehničkih brana, izolaciju dotoka mineralnih voda i dr.

2. OSNOVNE KARAKTERISTIKE POLIMERNIH SMOLA SA EFEKTOM PENE

Pena je gasna emulzija mehurića u injekcionoj smesi, koja nastaje iz obične injekcione smeše delovanjem reagenasa za stvaranje mehurića. Gasni mehurići su pretežno sferičnog oblika, jednoličanog prečnika, pri čemu 80 % njih ima prečnik (0,9-1,1)*d*, gde je *d* prosečni prečnik koji zavisi od vrste reagensa [1].

Penu karakterišu dva koeficijenta: *koeficijent ekspanzije e* i *koeficijent bujanja f.*

Koeficijent ekspanzije e je odnos između zapremine gasa i zapremine suspenzije, a ekvivalentan je koeficijentu poroznosti kod nekoherentnog tla.

Koeficijent bujanja f je odnos između konačne i početne zapremine pene.

Ako je koeficijent ekspanzije $e < 0,2$ nema efekta pene, a kad je $e > 0,8$ pena se ukrućuje. Pene od cementnih suspenzija postižu koeficijent do $e = 3$, a pene od polimernih smola mogu postići koeficijent i do $e = 50$.

Pena se može proizvesti u suspenzijama i rastvorima na dva načina:

- dodavanjem reagensa koji povećava površinski napon vode, pa mešanjem nastaje pena;
- dodavanjem reagensa koji hemijskom reakcijom oslobađa gas koji se emulgira u obliku mehurića.

Prvim načinom, pena nastaje fizičkom reakcijom gotovo u trenutku mešanja. Prečnik mehurića je jednoličan i manji je od jednog milimetra. Drugim načinom, pena nastaje hemijskom reakcijom, što zahteva vreme od 10 do 20 minuta u zavisnosti od temperature. Prečnik mehurića nije jednoličan, a najveći je do nekoliko milimetara.

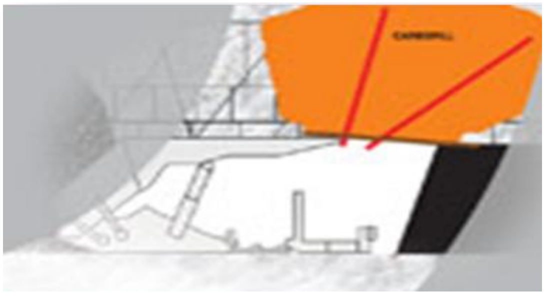
Kombinacijom oba postupka može se proširiti raspon između najmanjih i najvećih mehurića. To povećava koeficijent ekspanzije i poboljšava svojstva pene, naročito njenu stabilnost.

Zbog opisanih svojstava, pene se naročito koriste za zatvaranje i ispunjavanje velikih šupljina (kaverne, sistemi velikih pukotina i sl.), a utrošak mase je mali. Posebno su pogodne za zatvaranje pukotina kroz koje teče voda, zbog naglog ukrućenja nakon izlaska iz injekcione cevi, kako samih pena tako i u kombinaciji sa cementnim suspenzijama.

3. PRIMENA DVOKOMPONENTNIH BRZO REAGUJUĆIH POLIMERNIH SMOLA U RUDARSTVU

Za stabilizaciju, ojačanje i izolaciju degradiranog stenskog masiva oko izrađenih podzemnih prostorija i objekata u rudarstvu danas se koriste: dvokomponentne brzo reagujuće fenolne smole, dvokomponente poliuretanske penušave smole i urea silikatne nezapaljive smole.

Dvokomponentne brzo reagujuće fenolne smole počinju da pene odmah pri mešanju, pri čemu dobijaju odlične fizičko-mehaničke osobine. Injektirana smola sprečava širenje deformacija u ispucaloj stenskoj masi, popunjava pukotine, povećava stabilnost podgrade rudničkih prostorija. Na taj način doprinosi poboljšanju operativne sigurnosti i efikasnosti pri izvođenju rudarskih radova. Povećavanje stabilnosti podgrade korišćenjem brzo reagujućih fenolnih smola [5], šematski je prikazano na sl. 1.



Sl. 1. *Povećavanje stabilnosti podgrade korišćenjem brzo reagujućih fenolnih smola*

Osnovu komponentu (A) čini material na bazi sintetičke smole, a drugu komponentu (B) katalizator-učvršćivač, koji se nalazi u manjoj patroni unutar prve. Smeša se spravlja na licu mesta u razmeri 4:1, korišćenjem dvokomponente pumpe i creva (v. sl. 2.).

Sl. 2. *Dvokomponentna pumpa za injektiranje WIWA 2K-Inject*

Prilikom mešanja dolazi do polimerizacije koju izaziva katalizator, pri čemu smola penuša, uvećava zapreminu nekoliko puta i očvršćava. Injekciona smeša može da se umumpava kroz creva, cevi ili ankere koji su ispunjeni fenolnom smolom sa katalizatorom.

Tehnički podaci za komponente i penastu mešavinu dati su u tabeli 1 i 2.

Tabela 1. *Tehnički podaci za komponente*

Tehnički podaci za komponente	Jedinica	Smola		Katalizator
Gustina na 25^0C	kg/cm^3	1290 ± 30		1540 ± 30
pH-vrednost		~ 8		1 - 0
Rok trajanja	meseci	3	12	6
Temperatura skladištenja	^{0}C	max. 20^0	max. 5^0	$-5^0 – 30^0$

Tabela 2. *Tehnički podaci za smolu-penastu mešavinu*

Tehnički podaci smola-mešavine (na 20^{0}C)	**Jedinica**	**Mešavina**
Vreme početka vezivanja	s	odmah
Reagujuće vreme	s	180 ± 60
Koeficijent ekspanzije (e)		32 - 38
Potrošnja	kg/m^3	~ 36 - 42

Dvokomponente poliuretanske penušave smole se koriste za ojačanje i izolaciju stena, zemljišta ili konstrukcija u rudnicima, geotehničkom podzemnom i građevinskom inženjeringu. Poliuretanske smole su prikladne za popravku, armiranje i izolaciju pukotina u betonskim konstrukcijama i zidovima, pri čemu postižu veliki stepen adhezije. Neki tipovi mogu da se koriste za izolaciju ispucalih konstrukcija protiv prodora vode i gasa. Penušavi tipovi imaju svojstva termičke i zvučne izolacije.

Primena tehnologije injektiranja poliuretanskih penušavih smola u rudarstvu i tunelogradnji ogleda se u sledećem [8]:

- Ojačavanje stenske mase uz poboljšavanje mehaničkih svojstava stenske okoline.
- Poboljšanje mehaničkih svojstava eksploatisanih materijala pre eksploatacije.
- Smanjivanje i sprečavanje doticanja vode u rudnike.
- Ankerisanje i stabilizacija stena.
- Smanjenje prodiranja gasa u oblast rudnika.
- Sprečavanje neželjenog isticanja gasa iz rudnika u okolinu.
- Sprečavanje isticanja otpadnih voda iz napuštenih oblasti rudnika.
- Sprečavanje proticanja neželjenih vazdušnih struja u rudniku.
- Ispunjavanje pukotina višestruko izlomljenih stena.
- Injektiranje brana i njihove okoline radi sprečavanja infiltracije vode.
- Ankerisanje i injektiranje površine uglja za vreme eksploatacije.
- Injektiranje stena male stabilnosti pri izradi tunela i iskopavanju horizontalnih jamskih prostorija.
- Obezbeđivanje prelaza radova u rudniku preko tektonskih oštećenja.

Neki primeri upotrebe poliuretanskih smola u rudarstvu [2] dati su na sl. 3 i 4.

Sl. 3. *Injektiranje vodene barijere u rudnicima uglja u cilju sprečavanja proticanja vode kroz barijeru; upotrebljeni materijal Geopur*

Sl. 4. *Zaptivanje pukotina u rudniku uglja*

Dvokomponentna smeša sastoji se od komponente A i B. Komponenta A je tečnost boje meda (svi tipovi), sastoji se od mešavine: polialkohola, akceleratora, jedinjenja koja redukuju zapaljivost, stabilizatora pene i vode. Komponenta B je tamno braon – žuta tečnost (svi tipovi), sastavljena od: polimetilena, polifenilizocijanata, difenilmetana, dizocijanata (MDI) i mešavine policikličnih oligomera zavisno od funkcije.

Nakon mešanja dve osnovne komponente u datoj razmeri, egzotermnom reakcijom, nastaje poliuretanska smola. Stepen penušavosti smole determiniše njena fizičko-mehanička svojstva. Početak reakcije penušanja i očvršćavanja može se odložiti za sve sisteme do 360 sekundi. Standardni sastavi ovih smola počinju da pene kroz 2 minuta. Odlaganje početka reakcije može se ostvariti samo dok komponente nisu još pomešane, dodatkom specijalnih aditiva [8].

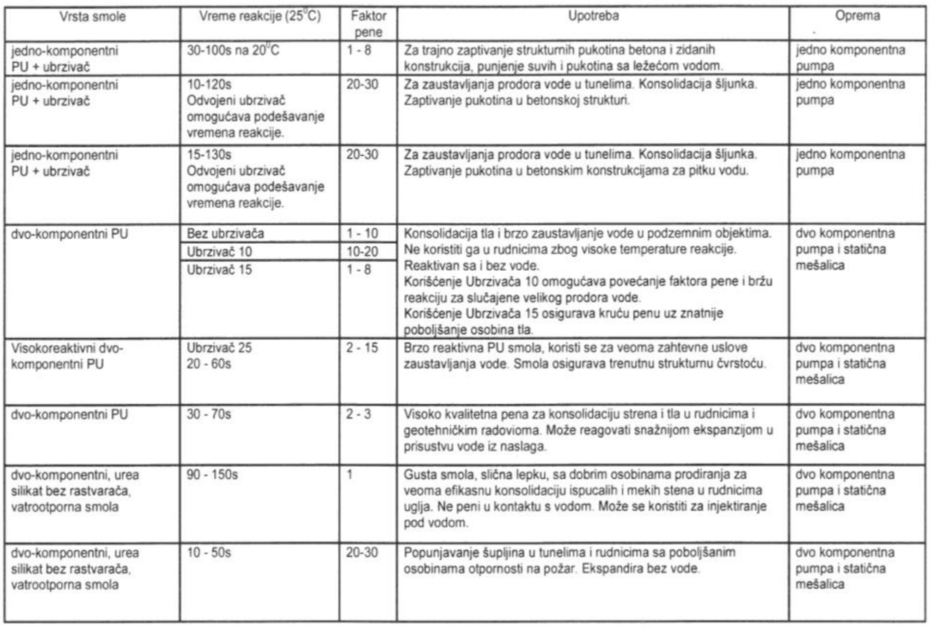
Urea silikatne nezapaljive smole odobrene su za korišćenje u rudnicima uglja i kod izrade podzemnih objekata u teškim radnim uslovima. Stabilizacija i ojačanje oslabljenih zona oko podzemnih prostorija vrši se kombinacijom dreniranja i injektiranja brzo reaktivnih penušavih smola [4].

Urea silikatne smole zadovoljavaju savremene zahteve tunelogradnje i izrade podzemnih prostorija u rudarstvu. Proizvodi se veliki broj ovih smola od jednokomponentnih smola za male poslove na zaustavljanju dotoka voda, do specijalnih robusnih dvokomponentnih sistema za efikasno rešavanje problema sa masivnim prodorom vode.

Osobine i prednosti urea silikatnih injekcionih smola, osim što su "namenski projektovane" za tunelogradnju i rudarstvo, ove smole su bez rastvarača i formiraju ćelijastu strukturu od pene. Mnogim urea silikatnim smolama koje se koriste za zaustavljanje vode u tunelogradnji, mogu se korišćenjem različitih ubrzivača, na licu mesta, podesiti osobine da odgovaraju konkretnim radnim uslovima. Na tršištu postoji veliki broj urea silikatnih smola, čijim korišćenjem se poboljšava protivpožarna zaštita i povećava sigurnost u tunelogradnji i rudarstvu.

Uporedni pregled poliutretanskih penušavih smola i urea silikatnih smola [8, 4] dat je u tabeli 3.

Tabela 3. *Poliuretanske (PU) i urea silikatne smole*



Vrsta smole	Vreme reakcije (25^{0}C)	Faktor pene	Upotreba	Oprema
jedno-komponentni PU + ubrzivač	30-100s na 20^{0}C	1 - 8	Za trajno zaptivanje strukturnih pukotina betona i zidanih konstrukcija, punjenje suvih i pukotina sa ležećom vodom.	jedno komponentna pumpa
jedno-komponentni PU + ubrzivač	10-120s Odvojeni ubrzivač omogućava podešavanje vremena reakcije.	20-30	Za zaustavljanja prodora vode u tunelima. Konsolidacija šljunka. Zaptivanje pukotina u betonskoj strukturi.	jedno komponentna pumpa
jedno-komponentni PU + ubrzivač	15-130s Odvojeni ubrzivač omogućava podešavanje vremena reakcije.	20-30	Za zaustavljanja prodora vode u tunelima. Konsolidacija šljunka. Zaptivanje pukotina u betonskim konstrukcijama za pitku vodu.	jedno komponentna pumpa
dvo-komponentni PU	Bez ubrzivača	1 - 10	Konsolidacija tla i brzo zaustavljanje vode u podzemnim objektima. Ne koristiti ga u rudnicima zbog visoke temperature reakcije. Reaktivan sa i bez vode. Korišćenje Ubrzivača 10 omogućava povećanje faktora pene i bržu reakciju za slučajene velikog prodora vode. Korišćenje Ubrzivača 15 osigurava kruću penu uz znatnije poboljšanje osobina tla.	dvo komponentna pumpa i statična mešalica
	Ubrzivač 10	10-20		
	Ubrzivač 15	1 - 8		
Visokoreaktivni dvo-komponentni PU	Ubrzivač 25 20 - 60s	2 - 15	Brzo reaktivna PU smola, koristi se za veoma zahtevne uslove zaustavljanja vode. Smola osigurava trenutnu strukturnu čvrstoću.	dvo komponentna pumpa i statična mešalica
dvo-komponentni PU	30 - 70s	2 - 3	Visoko kvalitetna pena za konsolidaciju strena i tla u rudnicima i geotehničkim radovioma. Može reagovati snažnijom ekspanzijom u prisustvu vode iz naslaga.	dvo komponentna pumpa i statična mešalica
dvo-komponentni, urea silikat bez rastvarača, vatrootporna smola	90 - 150s	1	Gusta smola, slična lepku, sa dobrim osobinama prodiranja za veoma efikasnu konsolidaciju ispucalih i mekih stena u rudnicima uglja. Ne peni u kontaktu s vodom. Može se koristiti za injektiranje pod vodom.	dvo komponentna pumpa i statična mešalica
dvo-komponentni, urea silikat bez rastvarača, vatrootporna smola	10 - 50s	20-30	Popunjavanje šupljina u tunelima i rudnicima sa poboljšanim osobinama otpornosti na požar. Ekspandira bez vode.	dvo komponentna pumpa i statična mešalica

Veliki svetski proizvođači proizvode poliuretanske smole sa efektom pene pod različitim komercilanim imenima: Carbofill, Carbopur, Geopur, WilkitFoam T, MEYCO itd.

4. ZAKLJUČAK

Savremeni materijali na bazi polimernih smeša imaju sve veću primenu za stabilizaciju, ojačanje i izolaciju degradiranog stenskog masiva u oblasti rudarstva i građevinarstva.

Polimerne smeše široko se koriste za ojačanje kontura rudarskih prosotrija i građevinskih objekata, ukoliko se one izvode u degradiranoj sredini, ispucalom i pukotinski izdeljenom stenskom masivu ili u slučaju nevezanih sedimenata. Glavne prednosti su im: jednostavna primena, brza reakcija i sposobnost da stabilizuje čitave formacije okolnih stena izložene visokim pritiscima i pokretima.

Primena tehnologije injektiranja poliuretanskih smola u rudarstvu se ogleda u sledećem: ojačavanje okolne stenske mase uz postizanje velike čvrstoće pri zatezanju i pri pritisku; smanjivanje i sprečavanje doticanja vode u rudnike; ankerisanje i stabilizacija stena; smanjenje prodiranja gasa u oblast rudnika; sprečavanje neželjenog isticanja gasa iz rudnika u okolinu; sprečavanje isticanja otpadnih voda iz napuštenih oblasti rudnika, sprečavanje proticanja neželjenih vazdušnih struja u rudniku; ispunjavanje pukotina višestruko izlomljenih stena; ankerisanje i injektiranje površine uglja za vreme eksploatacije; obezbeđivanje prelaza radova u rudniku preko tektonskih oštećenja i dr.

Izbor polimernog materijala vrši se pojedinačno za svaki konkretni slučaj pri gradnji i sanaciji podzemnih rudarskih i građevinskih objekata, zavisno od tražene stabilnosti i funkcionalnosti objekata u određenom vremenskom periodu.

LITERATURA

[1] Ćulibrk R. (2001), Geotehnički radovi u čvrstim stenama, Građevinski fakultet, Subotica, str. 120-126, 169-178, 246-250.

[2] Bolesta M., Eichstaedt F., Hoffmann P. (1997), Recommendations for the Selection and Application of Injection Products for Ground Consolidation, Glückauf Int. Ed. 133 pp.550-559.

[3] Code SIA 267/1 (2003), Geotehnical design – supplementary specifications, Swiss Society of Engineers and Architects, Zurich.

[4] Cornely W.(2003), Elastifield silicate resins and polyuretane foam resins for the stabilisation of strata – a comparison.

[5] V. V. Vasilev, (1986): Polymernye Kompozicii v gornom dele, Moscow, p.57ff.

[6] Čokorilo V. i dr., (2002), Racionalizacija i modernizacija izrade i podgrađivanja rudarskih prostorija u rudnicima sa podzemnom eksploatacijom, studija, Codel inženjering, Beograd, str. 211-233.

[7] Nonveiller E. (1989): Injiciranje tla, teorija i praksa, Zagreb, Školska knjiga, str. 47-50, 74-82.

[8] Poliuretanske smole: Geopure, *www.geopurewt.com*

INSTRUCTIONS FOR THE AUTHORS

Journal **MINING AND METALLURGY ENGINEERING BOR** is published four times per a year and publishes the scientific, technical and review paper works. Only original works, not previously published and not simultaneously submitted for publication elsewhere, are accepted for publication in the journal. The papers should be submitted in both, Serbian and English language. The papers are anonymously reviewed by the reviewers after that the editors decided to publish. The submitted work for publication should be prepared according to the instructions below as to be included in the procedure of reviewing. Inadequate prepared manuscripts will be returned to the author for finishing.

Volume and Font size. The work needs to be written on A4 paper (210x297 mm), margins (left, right, upper and bottom) with each 25 mm, in the Microsoft Word later version, font Times New Roman, size 12, with 1.5 line spacing, justified to the left and right margins. It is recommended that the entire manuscript cannot be less than 5 pages and not exceed 10 pages.

Title of Work should be written in capital letters, bold, in Serbian and English. Under the title, the names of authors and institutions where they work are written under the title. The author of work, responsible for correspondence with the editorial staff, must provide his/her e-mail address for contact in a footnote.

Abstract is at the beginning of work and should be up to 200 words, include the aim of the work, the applied methods, the main results and conclusions. The font size is 10, italic.

Key words are listed below abstract. They should be minimum 3 and maximum of 6. The font size is 10, italic.

Basic text. The papers should be written concisely, in understandable style and logical order that, as a rule, including the introductory section with a definition of the aim or problem, a description of the methodology, presentation of the results as well as a discussion of the results with conclusions and implications.

Main titles should be done with the font size 12, bold, all capital letters and aligned with the left margin.

Subtitles are written with the font size 12, bold, aligned to the left margin, large and small letters.

Figure and Tables. Each figure and table must be understandable without reading the text, i.e., must have a serial number, title and legend (explanation of marks, codes, abbreviations, etc.). The text is stated below the figure and above the table. Serial numbers of figures and tables are given in Arabic numbers.

References in the text are referred to in angle brackets, exp. [1, 3]. References are enclosed at the end in the following way:

[1] Willis B. A., Mineral Procesing Technology, Oxford, Pergamon Press, 1979, pg. 35. (for the chapter in a book)

[2] Ernst H., Research Policy, 30 (2001) 143–157. (for the article in a journal)

[3] www: http://www.vanguard.edu/psychology/apa.pdf (for web document)

Specifying the unpublished works is not desirable and, if it is necessary, as much as possible data on the source should be listed.

Acknowledgement is given where appropriate, at the end of the work and should include the name of institution that funded the given results in the work, with the name and number of project, or if the work is derived from the master theses or doctoral dissertation, it should give the name of thesis / dissertation, place, year and faculty where it was defended. Font size is 10, italic.

The paper works are primarily sent by e-mail or in other electronic form.

Editorial address : Journal MINING AND METALLURGY ENGINEERING BOR
Mining and Metallurgy Institute
35 Zeleni bulevar, 19210 Bor
E-mail: nti@irmbor.co.rs; milenko.ljubojev@irmbor.co.rs
Telephone: +381 (0) 30/435-164; +381 (0) 30/454-110

We are thankful for all authors on cooperation

UPUTSTVO AUTORIMA

Časopis MINING AND METALLURGY ENGINEERING BOR izlazi četiri puta godišnje i objavljuje naučne, stručne i pregledne radove. Za objavljivanje u časopisu prihvataju se isključivo originalni radovi koji nisu prethodno objavljivani i nisu istovremeno podneti za objavljivanje negde drugde. Radovi se dostavljaju i na srpskom i na engleskom jeziku. Radovi se anonimno recenziraju od strane recenzenta posle čega uredništvo donosi odluku o objavljivanju. Rad priložen za objavljivanje treba da bude pripremljen prema dole navedenom uputstvu da bi bio uključen u proceduru recenziranja. Neodgovarajuće pripremljeni rukopisi biće vraćeni autoru na doradu.

Obim i font. Rad treba da je napisan na papiru A4 formata (210x297 mm), margine (leva, desna, gornja i donja) sa po 25 mm, u Microsoft Wordu novije verzije, fontom Times New Roman, veličine 12, sa razmakom 1,5 reda, obostrano poravnat prema levoj i desnoj margini. Preporučuje se da celokupni rukopis ne bude manji od 5 strana i ne veći od 10 strana.

Naslov rada treba da je ispisan velikim slovima, bold. Ispod naslova rada pišu se imena autora i institucija u kojoj rade. Autor rada zadužen za korespodenciju sa uredništvom mora da navede svoju e-mail adresu za kontakt u fusnoti.

Izvod se nalazi na početku rada i treba biti dužine do 200 reči, da sadrži cilj rada, primenjene metode, glavne rezultate i zaključke. Veličina fonta je 10, italic.

Ključne reči se navode ispod izvoda. Treba da ih bude minimalno 3, a maksimalno 6. Veličina fonta je 10, italic.

Osnovni tekst. Radove treba pisati jezgrovito, razumljivim stilom i logičkim redom koji, po pravilu, uključuje uvodni deo s određenjem cilja ili problema rada, opis metodologije, prikaz dobijenih rezultata, kao i diskusiju rezultata sa zaključcima i implikacijama.

Glavni naslovi trebaju biti urađeni sa veličinom fonta 12, bold, sve velika slova i poravnati sa levom marginom.

Podnaslovi se pišu sa veličinom fonta 12, bold, poravnato prema levoj margini, velikim i malim slovima.

Slike i tabele. Svaka ilustracija i tabela moraju biti razumljive i bez čitanja teksta, odnosno, moraju imati redni broj, naslov i legendu (objašnjenje oznaka, šifara, skraćenica i sl.). Tekst se navodi ispod slike, a iznad tabele. Redni brojevi slika i tabela se daju arapskim brojevima.

Reference u tekstu se navode u ugličastim zagradama, na pr. [1,3]. Reference se prilažu na kraju rada na sledeći način:

[1] B.A. Willis, Mineral Procesing Technology, Oxford, Perganom Press, 1979, str. 35. *(za poglavlje u knjizi)*

[2] H. Ernst, *Research Policy*, 30 (2001) 143–157. *(za članak u časopisu)*

[3] www: http://www.vanguard.edu/psychology/apa.pdf *(za web dokument)*

Navođenje neobjavljenih radova nije poželjno, a ukoliko je neophodno treba navesti što potpunije podatke o izvoru.

Zahvalnost se daje po potrebi, na kraju rada, a treba da sadrži ime institucije koja je finansirala rezultate koji se daju u radu, sa nazivom i brojem projekta; ili ukoliko rad potiče iz magistarske teze ili doktorske disertacije, treba dati naziv teze/disertacije, mesto, godinu i fakultet na kojem je odbranjena. Veličina fonta 10, italic.

Radovi se šalju prevashodno elektronskom poštom ili u drugom elektronskom obliku.

Adresa uredništva je: Časopis MINING AND METALLURGY ENGINEERING BOR
Institut za rudarstvo i metalurgiju
Zeleni bulevar 35, 19210 Bor
E-mail: nti@irmbor.co.rs ; milenko.ljubojev@irmbor.co.rs
Telefon: 030/435-164; 030/454-110

Svim autorima se zahvaljujemo na saradnji.

CIP - Каталогизација у публикацији
Народна библиотека Србије, Београд

622

MINING and Metallurgy Engineering Bor / editor-in-chief Milenko Ljubojev. - 2013, no. 2- . - Bor : Mining and Metallurgy Institute Bor, 2013- (Bor : Grafomedtrade). - 24 cm

Tromesečno. - Je nastavak: Rudarski radovi = ISSN 1451-0162
ISSN 2334-8836 = Mining and Metallurgy Engineering Bor
COBISS.SR-ID 201387788