

University of Belgrade
Technical Faculty in Bor,
Mining and Metallurgy
Institute Bor

54th International
October Conference
on Mining and Metallurgy

PROCEEDINGS

Editors: Ljubiša Balanović Dejan Tanikić



18-21 October 2023, Bor Lake, Serbia

PROCEEDINGS, 54th INTERNATIONAL OCTOBER CONFERNCE on Mining and Metallurgy

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Technical Editor:

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University of Belgrade, Technical Faculty in Bor

Publisher: University of Belgrade, Technical Faculty in Bor

For the publisher: Dean Prof. dr Dejan Tanikić

Circulation: 200 copies

СІР - Каталогизација у публикацији Народна библиотека Србије, Београд

622(082)(0.034.2) 669(082)(0.034.2)

INTERNATIONAL October Conference on Mining and Metallurgy (54; 2023; Borsko jezero)

Proceedings [Elektronski izvor] / 54th International October Conference on Mining and Metallurgy - IOC 2023, 18-21 October 2023, Bor Lake, Serbia; [organized by] University of Belgrade, Technical Faculty in Bor and Mining and Metallurgy Institute Bor; editors Ljubiša Balanović, Dejan Tanikić. - Bor: University of Belgrade, Technical Faculty, 2023 (Niš: Grafika Galeb). - 1 USB fleš memorija; 1 x 1 x 5 cm

Sistemski zahtevi: Nisu navedeni. - Nasl. sa naslovne strane dokumenta. - Tiraž 200. - Preface / Ljubiša Balanović. - Bibliografija uz svaki rad.

ISBN 978-86-6305-140-9

а) Рударство -- Зборници b) Металургија -- Зборници

COBISS.SR-ID 126659849

Bor Lake, Serbia, October 18-21, 2023



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Conference is financially supported by
The Ministry of Science, Technological
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PREFACE

On behalf of the Organizing Committee, it is a great honor and pleasure to welcome all esteemed participants of the 54th International October Conference on Mining and Metallurgy (IOC 2023), scheduled to take place at the picturesque Bor Lake, Serbia, from October18th to 21st 2023.

The collaborative efforts of the University of Belgrade, the Technical Faculty in Bor, and the Mining and Metallurgy Institute Bor have meticulously organized this year's IOC. Our focus remains unwavering on showcasing the latest research findings and advancements in geology, mining, metallurgy, materials science, technology, environmental protection, and other engineering disciplines. Our primary objective is to foster a dynamic environment where academics, researchers, and industry professionals can come together to share their knowledge, experiences, and innovative ideas while exploring opportunities for collaborative research endeavors.

Our conference agenda is rich and diverse, encompassing plenary sessions, engaging invited lectures, technical presentations, enlightening oral and poster sessions, informative technical tours, a diverse exhibition, and memorable social gatherings. At the heart of this event lies our strong commitment to sustainable development within the mining and metallurgy sector. We are dedicated to exploring ecologically conscious methodologies, responsible resource extraction practices, and cutting-edge technologies that reduce the industry's environmental impact and enhance the well-being of local communities.

The conference proceedings comprise 129 papers authored by individuals from universities, research institutes, and industries in 22 countries. We are proud to welcome participants from Bosnia and Herzegovina, Bulgaria, Canada, China, Croatia, Germany, Greece, India, Iran, Kazakhstan, Libya, North Macedonia, Montenegro, Morocco, Romania, Russia, Slovakia, South Africa, Spain, Turkey, United States, and, of course, Serbia.

We are excited to host the 8th International Student Conference on Technical Sciences (ISC 2023) as part of IOC 2023. This event offers students from Serbia and the wider region a unique chance to showcase their research and discuss the future of their fields with experts.

We sincerely thank the Ministry of Science, Technological Development, and Innovation of the Republic of Serbia for their generous financial support. In addition, we express our profound gratitude to all our sponsors, exhibitors, and friends of the Conference for their contributions and unwavering support for playing a pivotal role in ensuring the success of IOC 2023.

We would like to express our heartfelt thanks to all authors, committees, reviewers, speakers, and chairpersons for their invaluable contributions in shaping IOC 2023.

We look forward to welcoming you to the 55th International October Conference on Mining and Metallurgy (IOC 2024), which will be held in October 2024.

On behalf of the 54th IOC Organizing Committee,

Prof. dr Ljubiša Balanović

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COMBINING NEUTRALIZATION AND ADSORPTION METHODS FOR METALS REMOVAL FROM SARAKA STREAM

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Abstract

The possibility of metals removal from real acid mine drainage from the Saraka stream, that flow near the plant for copper ore mine treatment in Serbia, was investigated by combination of neutralization and adsorption methods. A new approach of metals removal from acid mine drainage is in a two-step neutralization method by controlling the pH value aiming to obtain a different type of sludge during each step of neutralization process. The results are confirmed that the concentration of Cu and Fe is maximally reduced during the first neutralization step on pH 7. Values for the concentration of the other elements on pH 7 is as followining: Mg>Mn>Ni>Cd>Co. On pH 10 (second neutralization step) removal mass percentage is the same for all elements (more than 99 mass%). As an alternative to metal removal at pH values above 7, a method of adsorption with the crosslinked hydrogel obtained by crosslinking the Type B gelatin and chitosan with glutaraldehyde is used. Studies have shown that the highest adsorption removal rate of 81.43% is achieved for Co.

Keywords: real acid mine drainage, metal, removal, neutralization, adsorption

1. INTRODUCTION

Active and passive treatment methods are the common methods for purification of acid mine drainage (AMD) that causes water and soil systems pollution around the mine. Mine waters originating from active or closed copper mines contain copper ions sometimes in a considerable concentration usually associated with an equivalent or even a two times higher concentration of Fe²⁺/Fe³⁺ ions. The presence of the other heavy metal ions such as Mn, Cd, Zn, Pb, Ni, etc. in mine water depends on the mineralization of an ore body but their concentration is much lower than the concentration of copper or iron. Mine waters are acidic with pH value mostly between 2.5 and 4. The most environmentally effective techniques available for AMD are internal neutralization methods, water-covers and biological/natural degradation processes [1].

The aim of this paper is to investigate the multistep neutralization process of acid mine drainage from Saraka stream aim to precipitate the present metal ions in a different sludge type. First neutralization step was realized on pH 7 and second neutralization step was realized on pH 11. According to the literature data [2,3], the pH value for Mn recovery is greater than 7, and for the above reason, the second step of neutralization process (pH 10) is applied. Crosslinked hydrogels were used aim to investigate the possibility of removal the metal ions after the first neutralization step [4].

2. EXPERIMENTAL

2.1. Neutralization process procedure

Laboratory tests

Neutralization process is curried out with 1000 ml of real Saraka samples to reached pH 7; 7.5 and 8. As a neutralizing agent is used lime milk, concentration 25 g/L. After reached the pH 7, 7.5 and 8, solution is filtered by vacuum filtration with aim to separate solid from liquid phase. Dewatered sludge was dried on 40°C to constant mass. AMD neutralized on pH 7; 7.5 and 8 was used as start samples for neutralization on pH 9 and 10. As in the first neutralization stage, liquid and solid phase are separated by vacuum filtration. Liquid phase is used for the chemical analyses and solid phase is dried on 40°C and measured after reaching the constant mass value.

- Two-stage pH control on pilot plant

Approximately 1800 l of AMD was feed to the pilot plant and pH was set: for a first step on pH 7 and for a second step on pH 10. Waste water pump with constant flow rate of 5 l/min is used for waste water transport to pH control tank A. In the same time, in pH control tank A is continually added 2.5 mass% lime milk from lime slurry tank by lime slurry pump. In pH control tank A is immersed pH meter aim to control first neutralization step pH value. Suspension from pH control tank A overflows in flocculation tank A. Flocculant, type Accoflock A-95 (0.05 mass %) is pumped by flocculant pump A with constant flow rate of 0.025 l min⁻¹ to flocculation tank A. The solid-liquid separation is followed in thickener A. Supernatant that overflows from thickener A is going to pH control tank B for second neutralization step pH control (according to the second set pH value of 10). Flocculation is followed in flocculation tank B thereafter, and then solid-liquid separation is occurrence in thickener B. Supernatant that overflows from thickener B is taken for the chemical analysis and discharged continuously by gravity as treated water. Thickener A/B are discharged one by one aim to dewater the sludge on a filter press.

2.2. Adsorption tests with cross-linked hydrogels

Adsorption tests for a metal removal using crosslinked hydrogels prepared from gelatin Type B and chitosan, which are crosslinked with glutaraldehyde, were performed with next type of real waste water: 1. original AMD sample (saraka stream sample), 2. AMD sample after first neutralization step and 3. AMD sample after second neutralization step. Cross-linked hydrogel sheets (8 cm-square shape) were used as adsorbent. Incubation time of each adsorption test was (h): 0.5; 1; 2; 4; 6; 24; 48. Mass of the gelatin hydrogel sample was measured on the start and on the end of each test.

3. RESULTS AND DISCUSION

3.1. Neutralization process

- <u>Laboratory experiments</u>

Saraka stream is the branch of the Krivelj River located down-stream of over burden damp site. The over burden contains oxidized copper minerals as well as pyrite. It suggests that the seepage water from the dump contains copper. It is confirmed by chemical composition of the sample from Saraka stream: Al - 71.005 mg/l; Ca - 529.715 mg/l; Fe - 46.169; Mg - 250.295 mg/l; Mn - 16.145 mg/l; Zn - 1.782 mg/l; Cu - 88.237 mg/l; Co - 1.178 mg/l; Ni - 248.3 µg/l; As - 4.1 µg/l; Se - 29.1 µg/l; Sr - 591.8 µg/l and Cd - 17.9 µg/l. Concentration of Pb, Cr and Cs was below the sensitivity limit of used analytical method. In the Table 1 are presented the results of the first and second neutralization steps.

Table 1 - Concentration of the elements in the AMD after first and second neutralization step

From pH start	Concentration of elements, mg/l						
value: 3.8	Ca	Cd	Co	Cu	Fe	Mn	Ni
to pH 7	626.2	0.0123	0.471	0.842	< 0.1	12.500	0.075
to pH 7.5	638.3	0.0071	0.215	0.521	< 0.1	11.300	< 0.01
to pH 8	646.6	0.0030	0.03	0.1	< 0.1	7.600	< 0.01
Neutralization		Concentration of elements, mg/l					
from pH 7 to	Ca	Cd	Co	Cu	Fe	Mn	Ni
pH 9	638.2	0.004	0.138	0.28	< 0.1	5.8	< 0.01
pH 10	845.2	0.0038	0.007	< 0.1	< 0.1	0.193	< 0.01

Neutralization		Concentration of elements, mg/l					
from pH 7.5 to:	Ca	Cd	Co	Cu	Fe	Mn	Ni
pH 9	701.6	0.007	0.0025	< 0.1	< 0.1	5.8	< 0.01
pH 10	782.1	< 0.0001	0.0001	< 0.1	< 0.1	0.006	< 0.01
Neutralization		Concentration of elements, mg/l					
from pH 8 to:	Ca	Cd	Co	Cu	Fe	Mn	Ni
pH 9	653.9	< 0.0001	0.0015	< 0.1	< 0.1	0.9	< 0.01
pH 10	800.7	< 0.0001	< 0.0001	< 0.1	< 0.1	0.006	< 0.01

- Two-stage pH control on pilot plant

According to the obtained laboratory data for chemical composition and lime milk consumption, test on pilot plant is curried out as following: first neutralization step: on pH 7 and second neutralization step: on pH 10 (Table 2).

Table 2 - Content of the elements after two neutralization steps

From pH start	Concentration of elements, mg/l						
value of 4.3 to:	Ca	Cd	Co	Cu	Fe	Mn	Ni
pH 7	626.2	0.0123	0.471	0.842	< 0.1	12.500	0.075
pH 10	701.7	0.00014	0.0052	0.036	< 0.007	0.18	0.018

2.2. Adsorption tests with cross-linked hydrogels

In the Table 3 are presented the results of metals adsorption degree from different AMD samples.

Table 3 - Adsorption degree of Cu, Co, Cd and Mn

	Tuble 5 Trusbiption degree of Cu, Co, Cu and IVII							
Adsorption time, h	0.5	1	2	4	6	24	48	
Cu, mass %								
Real Saraka water	-	5.53	8.6	15.89	17.11	31.26	30.06	
Co, mass %								
Neutralized on pH 7	7.78		13.2	14.64	16.89	21.56	27.9	
Neutralized on pH 10	51.43	57.14	58.57	62.86	67.14	68.57	81.43	
Cd, mass %								
Real Saraka water			4.81	7.21	11.54			
Neutralized on pH 7	13.56		30.51	33.9	47.46	64.41	71.19	
Mn, mass %								
Real Saraka water	7.81	6.52	15.69	10.18	12.23	12.95	15.07	
Neutralized on pH 7		5.89	7.12	11.64	15.26	21.88	21.39	
Neutralized on pH 10	10.17	9.75	16.1	15.68	18.22	13.98	17.8	

4. CONCLUSION

A new approach of metals recovery from acid mine drainage in combination with adsorption method gives the satisfactory results regarding to reduce the metals concentration. Using two-step neutralization method is obtained a different type of sludge during each step of neutralization process. Concentration of the elements on pH 7 is as follows: Mg> Mn> Ni> Cd> Co>Cu>Fe. On pH 10 (second neutralization step) recovery mass percentage is the same for all elements (more than 99 mass %). Based on data for lime consumption at pH values above 7, method of adsorption with the crosslinked hydrogel obtained by crosslinking the Type B gelatin and chitosan with glutaraldehyde is used. Studies have shown that the highest recovery rate of 81.43% is achieved for Co.

ACKNOWLEDGEMENTS

The authors are grateful for funding by the Minister of Science, Technological Development and Innovation of the Republic Serbia, the Grant No. 451-03-47/2023-01/200052. Also, this work is financially supported by the EU under Program 2nd EIT-HEI call: Building Ecosystem Integration Labs at HEI to foster Smart Specialization and Innovation on Sustainable Raw Materials - HEI4S3-RM.

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ISBN-978-86-6305-140-9







