

University of Belgrade Technical Faculty in Bor



International Mineral Processing & Recycling Conference



Proceedings

Editors: Jovica Sokolović Milan Trumić

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TABLE OF CONTENTS

PLENARY LECTURES	1
L. Guo, Y. Zhao, Q. Ma, G. Tang, C. Jia, C. Li RESEARCH PROGRESS, TRENDS, AND INNOVATIONS OF DEVELOPMENT ON MINING BACKFILL TECHNOLOGY OF UNDERGROUND METALLIFEROUS MINE	3
V.A. Chanturia, V.V. Morozov, G.P. Dvoichenkova, E.L. Chanturia, Yu. A. Podkamenny INNOVATIVE TECHNOLOGY FOR THE RECOVERY OF ABNORMALLY LUMINESCENT DIAMONDS BASED ON THE USE OF LUMINOPHORE-CONTAINING MODIFIERS	23
G. Vujić N. Maoduš, M. Živančev WTE AS INTEGRATED PART OF CIRCULAR ECONOMY	32
J.C. Gabriel, H. Bo, N. Charpentier, S. Chevrier, Y. Deng, F.Olivier, D. Xia CRITICAL METALS RECOVERY FROM E-WASTE: FROM MICROFLUIDICS HYDROMETALLURGY TO ECONOMICALLY VIABLE PROCESSES	39
SESSION LECTURES	41
F. Nakhaei, I. Jovanović 3D IMAGING AND APPLICATIONS IN MINERAL PROCESSING	43
D. Singh, S. Basu, B. Mishra. R. Bhima Rao NOVEL APPROACHES TO RECOVER TOTAL HEAVY MINERALS FROM DIFFERENT GRADE BEACH SAND DEPOSITS USING GRAVITY CONCENTRATORS	54
M. Trumić, K. Balanović ROLE OF PARTICLE SHAPE IN THE FLOATABILITY OF TONER PARTICLE	64
I. Smičiklas, M. Egerić, M. Jović COPPER SORPTION CAPACITY OF THE SOIL TREATED WITH UNCONVENTIONAL ALKALIZING AGENTS	73
V. Conić, I. Jovanović COPPER ORE BIOLEACHING FROM ECOLOGICAL POINT OF VIEW	79
S. Cvetković, M. Popović, J. Perendija LIFE CYCLE ASSESSMENT AND USE OF NATURAL RESOURCES	89
WORKSHOP PAPERS	95
P. M. Angelopoulos, G. Anastassakis, N. Kountouris, N. Koukoulis, M. Taxiarchou COMBINED USE OF ORGANOSOLV LIGNIN AND XANTHATES ON SPHALERITE FLOTATION FROM MIXED SULPHIDES	97
P. M. Angelopoulos, N. Kountouris, G. Anastassakis, M. Taxiarchou PARTIAL REPLACEMENT OF XANTHATE BY ORGANOSOLV LIGNIN ON PYRITE/ARSENOPYRITE FLOTATION	103
K. Hrůzová, July Ann Bazar, Leonidas Matsakas, Anders Sand, Ulrika Rova, Paul Christakopoulos ORGANOSOLV LIGNIN PARTICLES: A NOVEL GREEN REAGENT THAT INCREASES THE FLOTATION EFFICIENCY OF SULFIDE ORES	109
A. Peppas, D. Skenderas, P.M. Angelopoulos, C. Politi ENVIRONMENTAL BENEFITS OF LIGNIN BASED ECOFRIENDLY SURFACTANTS FOR FLOTATION PROCESSES TOWARDS CURRENT PRACTICES	115

A. Peppas, K. Hurzova, D. Skenderas, C. Politi, L. Matsakas, P.M. Angelopoulos EVALUATION OF BATTERY MINERALS FLOTATION PROCESS ECO FRIENDLINESS UTILISING BIODEGRADABLE LIGNIN REAGENTS	121
A. Peppas, C. Politi, D. Skenderas, P.M. Angelopoulos ENVIRONMENTAL ASSESSMENT OF RARE EARTHS RECOVERY METHOD FROM BALIXITE RESIDUES	126
PAPERS	133
A. Jankovic, M. Sederkennya	
MODIFIED BOND AND RITTINGER ENERGY-SIZE RELATIONSHIPS FOR LABORATORY FINE GRINDING	135
V. Nikolić, M. Trumić, D. Tanikić OPTIMIZATION OF MICRONIZING ZEOLITE GRINDING USING ARTIFICIAL NEURAL NETWORKS	143
E. Petrakis, K. Komnitsas THE EFFECT OF MICROWAVE RADIATION ON DRY GRINDING KINETICS OF BAUXITE ORE	150
M.H. Tyeb, S. Mishra, A.K. Majumder LSTM AND CNN COMBINATION BASED MODELLING APPROACH FOR PARTITION CURVE PREDICTION IN HYDROCYCLONES	157
I. Jovanović, M.Ž. Trumić, J. Sokolović, M.S. Trumić, J. Nešković DETERMINATION OF LIMITING SETTLING VELOCITY IN THE SLURY PIPELINE FROM GRINDING PLANT, USING DIFFERENT APPROACHES – A CASE STUDY	163
N. Omarova, R. Sherembayeva, A.Amirkhan, Zh. Ibraybekov, A. Nesipbay FLOTATION OF POLYMETALLIC LEAD-ZINC ORES OF THE BAKALSKOYE DEPOSIT	168
V.A. Chanturiya, I.Zh. Bunin, M.V. Ryazantseva THE APPLICATION OF THE DIELECTRIC BARRIER DISCHARGE (DBD) FOR THE IMPROVEMENT OF THE SEPARATION OF PYRITE AND ARSENOPYRITE	174
V. Ignatkina, A. Kayumov, N. Yergesheva, P. Chernova BASIC SELECTIVE REAGENT REGIMES FOR COMPLEX SULFIDE ORE FLOTATION	179
S. Chaudhuri, S. Maity, S.C. Maji, D. Roy, U.S. Chattopadhyay STUDIES ON THE FLOATABILITY CHARACTERISTICS OF LOW VOLATILE COKING COAL FINES USING X-RAY DIFFRACTION (XRD) ANALYSIS AS A DIAGNOSTIC TOOL	186
V.I. Ryaboi, V.P. Kretov, E.D. Schepeta, I.V. Ryaboi, S.E. Levkovets APPLICATION OF COLLECTOR BTF-15221 IN FLOTATION OF COPPER- AND GOLD - CONTAINING ORES	193
I. Dervišević, A. Dervišević, M. Tomović, J. Galjak COMPARATIVE ANALYSIS OF REAGENTS FOR GOLD EXTRACTION FROM FLOTATION TAILS	202
E.M.S. Silva, A.C. Silva, J.M.B.S. Cabral, P.S. Oliveira, A.F. Nascimento, A.P. Vieira Filho, S.A. Santos TESTS WITH DIFFERENT FLOCCULANTS FOR CHROMIUM ORE TAILINGS	208
C. Ouyang, B. Lv, K. Jia, Y. Yang STUDY ON THE APPLICATION OF HIGH-EFFICIENCY AND ENVIRONMENT-FRIENDLY COPPER COLLECTOR TO ASSOCIATED COPPER IN AN IRON ORE	214
S. Sredić, Lj.Tankosić KINETIC STUDIES OF THE ADSORPTION POLYACRILAMIDE-BASED FLOCCULANTS ON NATURAL GOETHITE, QUARTZ AND CLAY MINERALS	221

XV International Mineral Processing and Recycling Conference	e, 17-19 May 2023, Belgrade, Serbia
--	-------------------------------------

G. D. Bogdanović, D. Marilović, B. Nikolić, S. J. Petrović COLUMN LEACHING OF LOW-GRADE COPPER SULFIDE ORE WITH SULFURIC ACID	230
K Gáborová M Achimovičová M Hegedüs O Šestinová	
AN INFLUENCE OF MECHANICAL ACTIVATION ON THE COPPER LEACHING KINETICS	236
OF BERZELIANITE	200
D Medić I Đorđević M Nujkić A Papludis V Nedelkovski S Alagić S Milić	
LICE OF CODDED DOWDED AS A DEDUCING AGENT IN THE LEACHING DEOCESS OF	242
	242
LICUU2	
J. Difficingevic, S. Jevic, A. Matrikovic, W. Siffic, W. Rophvica, J. Petrovic	240
REMOVAL OF HEAVY METALIONS FROM MULTIMETALLIC SOLUTION BY MODIFIED	248
UAI SIRAW	
M.R. Rath, A.S. Patra, S. Kiran Kumar, M. Mukherjee, A. Chatterjee, A. Ranjan, A.K.	
Bhatnagar, A.K. Mukherjee	254
A PROCESS TO DECREASE THE CLAY COATING OF IRON ORE LUMPS & FINES BY THE	
APPLICATION OF DISPERSANTS	
H. Kurama, S. Kurama	262
SURFACTANTS AND THEIR FUNCTIONS ON NANO-POWDER SYNTHESIS	202
A. Goryachev, D. Makarov	
METHODS FOR PROCESSING NATURAL AND ANTHROPOGENIC COPPER- NICKEL	275
RAW MATERIALS IN THE ARCTIC	
Y. Yuankun, D. Mirović	
DAM BREACH ANALYSIS USING HEC-RAS: A CASE STUDY OF COPPER AND GOLD	283
"ČUKARU PEKI" MINE DAMS	
A. Milovanović Brkić, Y. Yuankun, N. Buđelan	
MANAGEMENT OF FLOTATION TAILINGS AS MINING WASTE ON THE COPPER AND	289
GOLD MINE "CUKARU PEKI"	
N. Pavlovic, F. Palkovits, A. Hall	
GEO-STABLE DISPOSAL OF COAL COMBUSTION BYPRODUCTS	297
N. Pavlovic, F. Palkovits, A. Hall	
TAIL WAGGING THE DOG-WHY INTEGRATED SOLUTIONS ARE BETTER-TAILINGS	303
	505
V Alivoivodic N Petrovnijevic	
POSITION OF CODDER WITHIN LIBBAN MINING - RECOVERING POTENTIAL FROM	300
	305
Mine Taleinos	
	215
BACTERIOSTATIC ACTIVITY OF GEORGIAN HEULANDITE ENRICHED WITH	315
V. Isitsishvili, M.Panayotova, N.Dolaberidze, N.Mirdzveli, M.Nijaradze, Z.Amiridze,	
B.Khutsishvili, N.Jakipbekova, S.Sakibayeva	321
THERMAL STABILITY OF NATURAL HEULANDITE-CHABAZITE MIXTURES	
V.Tsitsishvili, M.Panayotova, N.Dolaberidze, N.Mirdzveli, M.Nijaradze, Z.Amiridze,	
B.Khutsishvili, N.Klarjeishvili, N.Jakipbekova	327
COMPOSITION OF GEORGIAN AND KAZAKHSTANI NATURAL HEULANDITES	
S. Matijašević, S. Grujić , V. Topalović, J. Stojanović, J. Nikolić , V. Savić, S. Zildžović	222
NANOCRYSTALLIZATION OF POTASSIUM NIOBIUM GERMANATE GLASSES	555

XV International Mineral Processing and Recycling Conference,	, 17-19 May 2023, Belgrade, Serbia
---	------------------------------------

A.C. Silva, E.M.S. Silva, P.S. Oliveira, A.F. Nascimento, A.P. Vieira Filho, D.B. Carvalho Neto ESTIMATING THE ACCURACY, PRECISION, AND RECALL OF THE HAND-SORTING OF A BRAZILIAN CHROMIUM ORE	338
V.V. Morozov, Y.P. Morozov, G. Zorigt, D. Lodoy, E. Jargalsaikhan, I.V. Pestriak SCANNING FLATBED OPTICAL ORE QUALITY ANALYZER	344
B. B. Tchouffa, N. J. Ndemou, M. G. Frida Ntsama CHARACTERIZATION, ENRICHMENT TEST AND VALORIZATION OF IRON ORE FROM NABEBA (NORTH – CONGO)	350
K. Jia, S. Đorđević, C. Ouyang, B. Lv LABORATORY BENEFICIATION TECHNOLOGY AND DEVELOPMENT RESEARCH ON TITANIUM MAGNETITE ORE	355
D. S. Radulović, V. Jovanović, B. Ivošević, D. Todorović, S. Milićević, M. Marković INVESTIGATION OF THE POSSIBILITY OF VALORIZATION OF TWO BORATE SAMPLES FROM THE DEPOSIT "POBRĐE" – BALJEVAC	361
S. Hredzák, M. Matik, O. Šestinová, A. Zubrik, D. Kupka, S. Dolinská, I. Znamenáčková, M. Sisol, M. Marcin, L. Pašek STUDY OF ORE SAMPLES FROM THE ZLATÉ HORY DEPOSIT (HRUBÝ JESENÍK Mts., SILESIA, CZECH REPUBLIC)	367
J. Sokolović, I. Ilić, D. Krstić COMPARISON OF THE RESULTS OF SEPARATION OF DIFFERENT COALS IN THE ANTHRACITE MINE "VRSKA CUKA"	373
B.R. Reddy, K. Abhishek, J.M. Korath, M.R Rath A COMPUTATIONAL TOOL FOR PREDICTION OF JIG CONCENTRATOR OPERATING PARAMETER TO GET IMPROVED YIELD OF CONCENTRATE	379
I. Jovanović, V. Conić, D. Milanović, F. Nakhaei, S. Krstić RELATIVE PREDICTION ERROR OF FLOTATION INDICES BY ANFIS MODELS	387
Z. Štirbanović, R. Stanojlović, J. Sokolović, D. Stanujkić, N. Ćirić, I. Miljanović, G. Popović APPLICATION OF VIKOR METHOD FOR SELECTION OF COLLECTOR IN PORPHYRY COPPER ORE FLOTATION	391
S. Milutinović, Lj. Obradović, S. Petrović S. Magdalinović, I. Svrkota RANKING OF FLOTATION TAILINGS POND IN EASTERN SERBIA USING THE AHP METHOD	398
I. Jovanović, V. Conić, J. Sokolović, D. Kržanović, D. Radulović SIMPLE FUZZY MODELS FOR PREDICTION OF FLOTATION INDICES	404
S. Mishra, M.H. Tyeb, A.K. Majumder DEVELOPMENT OF A VIBRATION SENSOR-BASED ONLINE MONITORING SYSTEM FOR DETECTING ROPING IN HYDROCYCLONES	410
B. Farkaš, A. Hrastov, E. Orbanić THE IMPROVEMENT OF MINERAL PROCESSING – CASE STUDY	416
T. Mohit, P. Patel, P. Kaushal, J. Sahoo, V. Arumuru, B. Deo, M. Jain, R. Manchanda IMPROVED ON-LINE FAILURE PREDICTION METHOD OF COAL INJECTION SYSTEM USED IN A SPONGE IRON ROTARY KILN	423
M. Mikić, R. Rajković, S. Trujić, D. Kržanović, M. Jovanović IMPACT ON THE ENVIRONMENT AND OF THE OPEN MINE AND LANDFILLS IN SOUTH MINING DISTRICT – MAJDANPEK	429

M. Jovanović, D. Kržanović, R. Rajković, M. Mikić, M. Maksimović APPLICATION OF GEOGRIDS IN RECULTIVATION MEASURES AGAINST LAND DEGRADATION	435
V. Gardić, R. Marković, Z. Stevanović, A. Isvoran, T. Marković	
APPLICATION OF SUSTAINABLE CYCLING MANAGEMENT SYSTEM IN	441
PHYTOREMEDIATION TECHNOLOGY OF CONTAMINATED SOILS	
D Đựrđević-Milošević A Petrović I Elez G Gagula V Kalaba	
	445
	775
B. Cakova M. Matliovska M. M. Bunchova V. Volkoski B. Kuzmanovski	
DICITALIZATION OF WASTE WAYS FOR MORE EFFICIENT WASTE MANAGEMENT	451
A Vacilaiaday & Zaras A Dimaydi	
A. Vasiielauou, S. Zoras, A. Dimouui	458
INVESTIGATION OF SLAGGING CHARACTERISTICS OF INDUSTRIAL SOLID WASTES	
A. Vasileiadou, S. Zoras, A. Dimoudi	
MODELLING OF COX AND NOX EMISSIONS FROM INDUSTRIAL SOLID WASTES	464
COMBUSTION USING ANSYS CHEMKIN PRO	
Z. Bayer Ozturk, S. Kurama, A. Eser	
THE USAGE AND EFFECT OF BASALT CUTTING WASTE (BCW) IN CERAMIC GLAZE	470
COMPOSITIONS CONTAINING OPAQUE AND MATT FRIT	
D. Dinić, S. Stupar, N. Jovanović, M. Tanić, S. Jevtić	
SYNTHESIS AND CHARACTERIZATION OF POROUS CERAMICS BASED ON COPPER	480
SLAG	
M. Šišić. Dž. Dautbegović. M. Duraković	
ANALYSIS OF THE CHARACTERISTICS OF SLAG FROM METALLURGICAL PLANTS IN	486
ZENICA DISPOSED OF INDUSTRIAL WASTE LANDEILL "RACA"	
Dz Datubegovic M Hasanbasic M Sisic V Birdabic	
	102
THE WASTE COLLECTION SYSTEM IN THE CITY OF ZENICA	452
	100
CDANULATED PLAST EUDNACE SLAC	498
A. Stojicevic, IVI. Antic, IVI. Puric	
VEGETABLE INDUSTRY BY-PRODUCTS AS RAW MATERIALS IN FUNCTIONAL FOOD	507
PRODUCTION	
A. Petrović, R. Marković, D. Božić	
CARBON NANOTUBES AS POTENTIAL MATERIAL FOR WASTEWATER TREATMENT -	514
A REVIEW	
M. Marić, A. Ivković, B. Ivković, A. Janošević Ležaić, S. Uskoković-Marković, J. Savić,	
M. Milojević-Rakić, D. Bajuk-Bogdanović	519
REMOVAL OF METHYLENE BLUE FROM AQUEOUS SOLUTIONS USING AN IRON-	515
RICH SOIL	
R. Marković, V. Gardić, R. Kovačević, Zoran Stevanović, A. Isvoran, V. Marjanović,	
A. Petrović	524
BOR DISCRICT RIVERS WATERCOURSES CONTAMINATION BY Cu AND NI IONS	
P. Kekarjawlekar, N. Kamal, K. Manivar. B. Deo. P. Nanda. P. Malakar.	
, , ,	
R. Manchanda	
R. Manchanda	530

D. Milošević, M. Radosavljević, S. Polavder, Ž. Praštalo ARRANGEMENT OF FIELDS DEVASTATED BY CONSTRUCTION OF MAIN GAS PIPELINE	536
D. Đurđević-Milošević, A. Petrović, J. Elez, V. Kalaba, G. Gagula ENVIRONMENTAL PROTECTION THROUGH THE RATIONAL USE OF SODIUM HYPOCHLORITE AS A FUNGICIDE	542
G. Kyparissis, A. Goulkoudis, G. Papadimas, E. Tasiopoulos, A. Vasileiadou CASE STUDY OF ENERGY SAVING IN A PUBLIC SCHOOL THROUGH THE INSTALLATION OF A PHOTOVOLTAIC SYSTEM ON THE ROOF	548
D. Topalović, J. Marković, M. Jović, S. Dragović, I. Smičiklas THE ARSENIC SORPTION CAPACITY OF DIFFERENT SERBIAN SOILS	554
F. Popescu, M. Zot, E.A. Laza USING SHERPA TOOL FOR ASSESSMENT OF EUROPEAN WATERBORNE TRANSPORT SECTOR IMPACT ON AIR QUALITY	560
A. Stojić, D. Tanikić, E. Požega THE IMPACT OF EXPLOITATION OF PRIMARY AND ALTERNATIVE ENERGY SOURCES ON THE ENVIRONMENT	566
A. Radojević, S. Šerbula, T. Kalinović, J. Milosavljević, J. Kalinović MOBILE PHONES – A VALUABLE COMPONENT OF E-WASTE STREAM	572
K. Janković, M. Stojanović, D. Bojović, A. Terzić, S. Stanković APPLICATION OF COAL COMBUSTION BYPRODUCTS IN SELF-COMPACTING CONCRETE: INFLUENCE ON FLOWABILITY	579
D. Radosavljević, A. Jelić, M. Stamenović IMPACT OF STUDENT MIGRATIONS ON SUSTAINABLE AND TECHNOLOGICAL DEVELOPMENTS OF THE REPUBLIC OF SERBIA	585
D. Radosavljević, A. Jelić, M. Stamenović DEVELOPMENT OF EDUCATION FOR SUSTAINABLE DEVELOPMENT AND MANAGEMENT OF RECYCLABLE WASTE IN THE REPUBLIC OF SERBIA	592
Deependra Singh SUSTAINABLE RECOVERY OF INDIAN PLACER MINERALS-THEIR DISTRIBUTION AND MINERAL ASSEMBLAGES	598
ABSTRACTS	607
M. Tasić, I. Stojković, V. Pavićević, V. Veljković SIMULATION OF HYDRODYNAMIC CAVITATION-ASSISTED BIODIESEL PRODUCTION FROM WASTE COOKING OIL USING ASPEN PLUS	609
A. Jocić, S. Marić, A. Dimitrijević RECOVERY OF METALS FROM INDUSTRIAL EFFLUENTS USING AN IONIC LIQUID- BASED STRATEGY	610
S. Marić, A. Jocić, A. Dimitrijević IONIC LIQUID-BASED TECHNOLOGY FOR METAL RECOVERY FROM ELECTRONIC WASTE	611
J. Vučićević, S. Čupić, M. Jauković, V. Đurđević, M. Stamenović, A. Božić, A. Janićijević CURRENT STATE OF THE QUALITY OF THE LUG RIVER IN THE MUNICIPALITY OF MLADENOVAC	612

XV International N	Aineral Processing	and Recycling C	Conference, 17-1	.9 May 2023,	Belgrade, Serbia

D. Žnidarič			
THE ENERGY CRISIS AND THE EXPLOITATION OF MINERAL RESOURCES IN THE			
LIGHT OF INCREASING LOADS IN SPACE			
S. Zeković			
A NEW GLOBAL CHALLENGES AND REGULATION FOR SUSTAINABLE SPATIAL			
DEVELOPMENT OF MINING			
P.M. Angelopoulos, P. Oustadakis, G. Anastassakis, M. Georgiou, N. Kountouris			
HYDROTHERMAL TREATMENT OF BAUXITE RESIDUE FOR IRON RECOVERY	615		
ENHANCEMENT BY MAGNETIC SEPARATION			
O. Ayoglu, M. Sinche-Gonzalez, M. Moilanen			
TEXTURAL MINERALOGICAL UNDERSTANDING OF MAGNETITE LIBERATION	616		
CONTAINING COPPER INCLUSIONS			
M. Sinche-Gonzalez			
MASTER IN MINERAL PROCESING (EMJM-PROMISE) IN THE CONTEXT OF DEMAND			
OF CRITICAL MATERIALS AND ENERGY TRANSITION			
ADVERTISING MATERIALS	619		
Department for Mineral and Recycling Technologies	621		
Serbia Zijin Mining	624		
Serbia Zijin Copper	627		
Analysis d.o.o.	629		
tozero	631		
Monicom	632		
EMJM-PROMISE	633		



BOR DISCRICT RIVERS WATERCOURSES CONTAMINATION BY Cu AND Ni IONS

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ABSTRACT – The influence of the acid mine drainage and metallurgical wastewater on Cu and Ni ions concentration on the Bor district rivers watercourses is tested in the period from September 2020 to September 2021. Four sampling campaigns are realized in this period. Sampling points are selected in relation to the impact on Bor River, Krivelj River, Bela River, Timok River and Danube River. The presence of Cu and Ni ions in metallurgical wastewater has the dominant influence on the presence of Cu and Ni ions in the Bor district river watercourses.

Keywords: Wastewater, Acid Mine Drainage, Metallurgical, Cu, Ni.

INTRODUCTION

The need for minerals and metals necessary for global development makes mining one of the most important branches of the economy. The development of mining and related industries of production leads to significant economic growth and the benefit of countries on the one hand and on the other hand to the generation of different type of wastes. Mining operations have a huge local impact on the environment and population and the common challenge of all human society is to reduce the pollution and environmental damages produced by different processes. Even if the mining activities are stopped, the accumulated waste continuously pollutes and conduct to environmental damages and health effects. In the Bor Discrict, copper mineralization is mostly porphyry type of deposits containing mainly sulphur minerals associated with pyrites that are one of the sulphuric acid generators in contact with the atmosphere. Generally, the pH drops to values below 4, which causes dissolving of the metal ions [1,2]. Also, mining wastes generated during the copper ore treatment could be divided in the next types: tailings generated during flotation processes containing a variety of metallic and non-metallic minerals, spent ores consisting of the material remaining in either dump or heap leach piles when leaching ceases, acid rain resulting from the combination of rain and SO₂ causing damage to crops, trees and buildings for many miles downwind. Furthermore, the disposal of an enormous volume of tailings dumps poses a serious risk to the surrounding environment through air pollution due to air-dried out tailings, [#] corresponding author: <u>radmila.markovic@irmbor.co.rs</u>

erosion of the tailings with the potential of valuable land degradation, and leaching of soluble inorganic potentially toxic chemical species (Cu, Ni, Pb, Zn, Cd, and Cr) occurring in a variety of minerals present in the solid wastes [3].

During the metallurgical activities, harmful and dangerous materials also are generated.

In the area of the influence of mining and metallurgy activities the wastewater are discharged into the local watercourses through the Bor and Timok rivers as a tributaries of Danube River [3].

In order to find measures and solutions for the reduction, remediation and elimination of Cu and Ni ions, it is necessary to have a true picture of the consequences of more than a century of continuous mining and metallurgical activities in the Bor District. The influence of the type of wastewater on the Cu and Ni ions concentration in the rivers downstream was analyzing in a period from September 2020 to September 2021 on fifteen sampling points that are selected in relation to the impact on Bor River, Krivelj River, Bela River, Timok River and Danube River as a target river.

EXPERIMENTAL

In this paper, aiming to assess the risk of mining activities in the vicinity of the Bor copper mine from Serbia which pollutes the surface water of Bor and Krivelj rivers with Cu and Ni ions, physico-chemical analysis of the collected samples were performed. Sampling was performed quarterly in the period September 2020 to September 2021, of the Bor River (W5), as well as from locations upstream and downstream of the Bor River (marked W1-W4, W6-W10). The sampling points that are selected for the Cu and Ni ions concentration monitoring are: W1 - Robule accumulation (AMD); W2 - Robule accumulation 1 (AMD); W3 - AMD from flotation tailing dam RTH; W4 - Metallurgical wastewater; W5 - Bor River; W6 - Krivelj River; W7 - Bela River after the confluence of Bor and Krivelj rivers; W8 - Ravna River; W9 - Bela River after flows of Ravna River; W10 - Bela River before of confluence with Timok River; W11 - Timok River before of confluence with Bela River; W12 - Timok River after confluence with Bela River (near the village Rajac); W13 - Timok River (near the village Mokranje); W14 - Timok River (near the village Bukovce); W15 - Danube River (near the village Radujevac). After confluence of Bor and Krivelj rivers downstream from the village of Slatina arises the Bela River. Ravna River which is outline of the copper mining activities inflows in Bela River, and Bela River inflows in Timok River which flows in Danube River. Bor and Krivelj rivers are polluted by the acid mine drainage originating from the active copper mining activities or from delayed mine overburden and flotation tailings. Krivelj River is polluted with the wastewater originating from the active mines (Bor pit, Veliki Krivelj, Cerovo, tailing dam in operation), as well as with the wastewater from the waste dump and flotation tailings which are not in operation during the long period (field 2 of the large flotation tailings Veliki Krivelj) [4]. The pollution of the Bor River is a consequence of the untreated municipal wastewater, metallurgical wastewater from copper metallurgical plant, wastewater from the mine tailings dump of the old Bor mine and Bor flotation tailing, as well as, from the old flotation tailings in Bor.

Sampling is realized by a hand tools, according to the sampling methods: SRPS EN ISO 5667-1; SRPS EN ISO 5667-3; SRPS ISO 5667-4; SRPS ISO 5667-6 [4].

Atomic emission spectrometer with inductively coupled plasma (ICPAES), model Spectro Arcos was used for determination the Cu and Ni ions concertation. The method of calibration curve was used. All reagents used for the Reagents of high purity grade chemicals were used for analyses. The certified reference material (CRM) and blank samples were used for quality control of chemical analysis. Measurement of the sample pH values was conducted in the field by the pH meter, model Dostmann.

RESULTS AND DISCUSSION

Results for pH values as so as the values of Cu and Ni ions concentration obtained during the measurement campaigns are discussed in this paper. Measured pH values for the water sampling points are presented in Figure 1. From Figure 1 it can be seen that the lowest pH value is registered for the sample point W4 (metallurgical wastewater) during each sampling campaign. The pH values that are in the range from 1.87 to 5.61 are lower than the allowable pH values regarding to Serbian legislation (range from 6.5 to 8.5) [5,6,7]. pH values for the sampling points W6 and W11 – W15 are in accordance with Serbian legislation.



Figure 1 pH value

The pH values for the similar sample points, except for W10 - Bela River before of confluence with Timok River, were the similar for realized sampling campaigns.

The values of the Cu and Ni ions concentration in the water samples from the selected sample points are presented in Figure 2.

Cu ions maximal concentration is measured for the sampling point W4 - Metallurgical wastewater for all sampling campaigns. Having in mind that W4 – metallurgical wastewater inflows in Bor River (W5), concentration of Cu ions is also high in those samples. Cu ions are also present in AMD samples (W1, W2 and W3). Bela River (W7), a

river formed by the joining of W5 – Bor River and W6 – Krivelj River has the lower values for the Cu ions concentration. The presence of the Cu ions in the other sampling points is consequence of the inflows of W4 – metallurgical wastewater and AMD from the sampling points W1 - Robule accumulation, W2 Robule accumulation 1 and W3 - AMD from flotation tailing dam RTH. Concentration of Cu ions in metallurgical wastewater is about 300 times higher that maximal allowed concentration (MAC) according to the Serbian legislation for the IV class waters (Cu = 1 mg/l) and concentration of Cu ions in the AMD waters is maximal about 65 times higher than MAC. Similar flow rate of those wastewater confirmed that the Cu ions concentration from the metallurgical wastewater has the significant influence on the rivers downstream of the sampling points. Values for Cu concentration in W6 – Krivelj River, W8 - Ravna River and W11- Timok River upstream of the copper mining activities, are the lower than MAC value. After confluence of Bela River with Timok River, concentration of Cu ions has the lower values than MAC value for III water class of 0.5 mg/l.



Figure 2 Cu ions concentration for different sampling quarters



Figure 3 Ni ions concentration for different sampling quarters

Maximal value of Ni ions concentration is registered in the sample W4 - Metallurgical wastewater and this value is about 470 times higher than MAC value (Ni = $34 \mu g/l$). Regarding the maximal concentration of Ni ions in AMD wastewater (sample W1), obtained value is about 20 times higher than MAC value for IV water class [7]. Based on the data presented in Figure 3, increased Ni ions concentration in W5 - Bor River, W7, W9 and W10 – Bela River on a different sampling points regarding to the confluence with the other rivers downstream of Bor River is consequence of the Ni ions content in metallurgical wastewater and AMD. Also, as in the case of the wastewater type influence on Cu ions concentration in the in the Bor district rivers watercourses, metallurgical wastewater has the significant influence on the value of Ni ions concentration in the rivers. After confluence of Bela River with Timok River the Ni ions concentration is reduced, but only in W15 – Danube River concentration is for realized sampling campaigns was lower than MAC value for II surface water class according to Serbian legislative.

CONCLUSION

Obtained results for Cu and Ni ions concentration in AMD and metallurgical wastewater sampling points are confirmed that values are higher than MAC values according to the Serbian legislation. Concentration of Cu ions in metallurgical wastewater is about 300 times higher than the MAC value and Ni ions concentration is higher about 470 times than the MAC. Value for Cu and Ni ions concentration in the AMD wastewater is higher for about 65 times and 20 times, respectively. Also, pH value of metallurgical wastewater sample is much lower than the pH of AMD samples. Results are confirmed that the high concentration of Cu and Ni ions in metallurgical wastewater has the main impact on Cu and Ni content in the Bor district rivers watercourses.

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