



University of Belgrade  
Technical Faculty in Bor



Chamber of Commerce  
and Industry of Serbia

# XV International Mineral Processing & Recycling Conference



INTERNATIONAL MINERAL PROCESSING & RECYCLING CONFERENCE

# Proceedings

Editors:  
Jovica Sokolović  
Milan Trumić

17-19 May  
2023

Belgrade  
SERBIA





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## TABLE OF CONTENTS

<b>PLENARY LECTURES</b>	<b>1</b>
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
<b>SESSION LECTURES</b>	<b>41</b>
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
<b>WORKSHOP PAPERS</b>	<b>95</b>
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 BAUXITE RESIDUES	126
<b>PAPERS</b>	<b>133</b>
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 SLURRY 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

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 OF BERZELIANITE	236
D. Medić, I. Đorđević, M. Nujkić, A. Papludis, V. Nedelkovski, S. Alagić, S. Milić USE OF COPPER POWDER AS A REDUCING AGENT IN THE LEACHING PROCESS OF $\text{LiCoO}_2$	242
J. Dimitrijević, S. Jevtić, A. Marinković, M. Simić, M. Koprivica, J. Petrović REMOVAL OF HEAVY METAL IONS FROM MULTIMETALLIC SOLUTION BY MODIFIED OAT STRAW	248
M.R. Rath, A.S. Patra, S. Kiran Kumar, M. Mukherjee, A. Chatterjee, A. Ranjan, A.K. Bhatnagar, A.K. Mukherjee A PROCESS TO DECREASE THE CLAY COATING OF IRON ORE LUMPS & FINES BY THE APPLICATION OF DISPERSANTS	254
H. Kurama, S. Kurama SURFACTANTS AND THEIR FUNCTIONS ON NANO-POWDER SYNTHESIS	262
A. Goryachev, D. Makarov METHODS FOR PROCESSING NATURAL AND ANTHROPOGENIC COPPER- NICKEL RAW MATERIALS IN THE ARCTIC	275
Y. Yuankun, D. Mirović DAM BREACH ANALYSIS USING HEC-RAS: A CASE STUDY OF COPPER AND GOLD "ČUKARU PEKI" MINE DAMS	283
A. Milovanović Brkić, Y. Yuankun, N. Buđelan MANAGEMENT OF FLOTATION TAILINGS AS MINING WASTE ON THE COPPER AND GOLD MINE "CUKARU PEKI"	289
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 AND BACKFILL DISPOSAL	303
V. Alivojvodic, N. Petrovnijevic POSITION OF COPPER WITHIN URBAN MINING - RECOVERING POTENTIAL FROM MINE TAILINGS	309
V.Tsitsishvili, N.Dolaberidze, N.Mirdzveli, M.Nijaradze, Z.Amiridze, B.Khutsishvili BACTERIOSTATIC ACTIVITY OF GEORGIAN HEULANDITE ENRICHED WITH BIOLOGICALLY ACTIVE METALS	315
V.Tsitsishvili, M.Panayotova, N.Dolaberidze, N.Mirdzveli, M.Nijaradze, Z.Amiridze, B.Khutsishvili, N.Jakipbekova, S.Sakibayeva THERMAL STABILITY OF NATURAL HEULANDITE-CHABAZITE MIXTURES	321
V.Tsitsishvili, M.Panayotova, N.Dolaberidze, N.Mirdzveli, M.Nijaradze, Z.Amiridze, B.Khutsishvili, N.Klarjeishvili, N.Jakipbekova COMPOSITION OF GEORGIAN AND KAZAKHSTANI NATURAL HEULANDITES	327
S. Matijašević, S. Grujić, V. Topalović, J. Stojanović, J. Nikolić, V. Savić, S. Zildžović NANOCRYSTALLIZATION OF POTASSIUM NIOBIUM GERMANATE GLASSES	333

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. Orbanic 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 PHYTOREMEDIATION TECHNOLOGY OF CONTAMINATED SOILS	441
D. Đurđević-Milošević, A. Petrović, J. Elez, G. Gagula, V. Kalaba SUSTAINABLE APPROACH TO THE LACTIC ACID PRODUCTION AND ANTIBACTERIAL USE	445
B. Cekova, M. Matlievska, M. M. Puncheva, V. Velkoski, B. Kuzmanovski DIGITALIZATION OF WASTE, WAYS FOR MORE EFFICIENT WASTE MANAGEMENT	451
A. Vasileiadou, S. Zoras, A. Dimoudi INVESTIGATION OF SLAGGING CHARACTERISTICS OF INDUSTRIAL SOLID WASTES	458
A. Vasileiadou, S. Zoras, A. Dimoudi MODELLING OF CO <sub>x</sub> AND NO <sub>x</sub> EMISSIONS FROM INDUSTRIAL SOLID WASTES COMBUSTION USING ANSYS CHEMKIN PRO	464
Z. Bayer Ozturk, S. Kurama, A. Eser THE USAGE AND EFFECT OF BASALT CUTTING WASTE (BCW) IN CERAMIC GLAZE COMPOSITIONS CONTAINING OPAQUE AND MATT FRIT	470
D. Dinić, S. Stupar, N. Jovanović, M. Tanić, S. Jevtić SYNTHESIS AND CHARACTERIZATION OF POROUS CERAMICS BASED ON COPPER SLAG	480
M. Šišić, Dž. Dautbegović, M. Duraković ANALYSIS OF THE CHARACTERISTICS OF SLAG FROM METALLURGICAL PLANTS IN ZENICA DISPOSED OF INDUSTRIAL WASTE LANDFILL "RACA"	486
Dz. Datubegovic, M. Hasanbasic, M. Sisic, V. Birdahic ANALYSIS OF THE IMPACT OF THE INTRODUCTION OF LARGER CONTAINERS INTO THE WASTE COLLECTION SYSTEM IN THE CITY OF ZENICA	492
N. Bušatlić, I. Bušatlić, A. Halilović, N. Merdić, L. Kovač ENVIRONMENTALLY ACCEPTABLE CEMENTS WITH THE ADDITION OF GRANULATED BLAST FURNACE SLAG	498
A. Stojićević, M. Antić, M. Purić VEGETABLE INDUSTRY BY-PRODUCTS AS RAW MATERIALS IN FUNCTIONAL FOOD PRODUCTION	507
A. Petrović, R. Marković, D. Božić CARBON NANOTUBES AS POTENTIAL MATERIAL FOR WASTEWATER TREATMENT - A REVIEW	514
M. Marić, A. Ivković, B. Ivković, A. Janošević Ležaić, S. Uskoković-Marković, J. Savić, M. Milojević-Rakić, D. Bajuk-Bogdanović REMOVAL OF METHYLENE BLUE FROM AQUEOUS SOLUTIONS USING AN IRON-RICH SOIL	519
R. Marković, V. Gardić, R. Kovačević, Zoran Stevanović, A. Isvoran, V. Marjanović, A. Petrović BOR DISCRICT RIVERS WATERCOURSES CONTAMINATION BY Cu AND Ni IONS	524
P. Kekarjawlekar, N. Kamal, K. Maniyar, B. Deo, P. Nanda, P. Malakar, R. Manchanda DEVELOPING SAFE OPERATING PRACTICES (SOP) FOR POSTCOMBUSTION CHAMBER IN A SPONGE IRON PLANT	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. Goukoudis, 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
<b>ABSTRACTS</b>	<b>607</b>
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

D. Žnidarič THE ENERGY CRISIS AND THE EXPLOITATION OF MINERAL RESOURCES IN THE LIGHT OF INCREASING LOADS IN SPACE	613
S. Zeković A NEW GLOBAL CHALLENGES AND REGULATION FOR SUSTAINABLE SPATIAL DEVELOPMENT OF MINING	614
P.M. Angelopoulos, P. Oustadakis, G. Anastassakis, M. Georgiou, N. Kountouris HYDROTHERMAL TREATMENT OF BAUXITE RESIDUE FOR IRON RECOVERY ENHANCEMENT BY MAGNETIC SEPARATION	615
O. Ayoglu, M. Sinche-Gonzalez, M. Moilanen TEXTURAL MINERALOGICAL UNDERSTANDING OF MAGNETITE LIBERATION CONTAINING COPPER INCLUSIONS	616
M. Sinche-Gonzalez MASTER IN MINERAL PROCESING (EMJM-PROMISE) IN THE CONTEXT OF DEMAND OF CRITICAL MATERIALS AND ENERGY TRANSITION	617
<b>ADVERTISING MATERIALS</b>	<b>619</b>
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

## COPPER ORE BIOLEACHING FROM ECOLOGICAL POINT OF VIEW

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**ABSTRACT** – Microorganisms in bioleaching processes are characterized by their oxidative effect on iron ions and forms of reduced sulfur species in acidic environments. To oxidize metal sulfides found in copper ores and concentrates using microorganisms, copper leachate is oxidized as copper sulfate. The bioleach solution is extracted through extraction technologies, after which the technology of electrodeposition of copper, obtaining the final product a copper cathode of high purity.

**Keywords:** Bioleaching, Eco Friendly Technology, Base Metal, Sulfide Ore, Concentrate.

### INTRODUCTION

The mineral industry has suffered in recent year's two significant impacts: The raise on energy cost and more strict environmental regulations were in place for the metallurgical processing of sulfide ores and concentrates, mainly those containing arsenic. These impacts moved the mineral industry to develop alternative processes to roasting and smelting and searching for alternative processes to avoid the high energy consumption, grinding operation and flotation of sulphide minerals. Bioleaching must compete with alternative approaches for extracting metals from ores and concentrates. The main obstacle is the time required for metal extraction, which ranges from days, in the case of bioreactor leaching, to one or more years in the case of bio-piles and waste rock dumps. On the other hand, bioleaching is generally a much more ecological ("green") approach, requiring operation at much lower temperatures, thus energy costs are lower. Microorganisms in oxidation processes are autotrophs, i.e. they consume carbon dioxide like plants. Large amounts of CO<sub>2</sub> are emitted during melting. Bioprocessing also works at atmospheric pressure and at relatively low temperatures (20–80 °C). An external heat source is usually not needed because, like the oxidation of sulphide minerals, it is an exothermic process. Indeed, excess heat is generated where oxidation rates are intense (eg stirred tank operation) and systems need to be cooled to maintain the appropriate temperature. Bioprocessing also has advantages where, first of all, the ore or concentrate contains significant amounts of arsenic (which is released in gaseous emissions during smelting but remains in the liquid and solid phase in (bio)hydrometallurgical processing) and secondly, for the processing of low-quality and complex polymetallic ore.

In the Mining and Metallurgy Institute Bor (MMI Bor) Serbia Figure 1., two continuous facilities for the treatment of bioleaching raw materials were installed in

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order to evaluate the techno-economic drivers that regulate the application of this technology. Topics covered include choosing between tank and pile bioleaching, microbiology and process operating temperature selection, influence of ore mineralogy on process options, environmental considerations, and metallurgical test design programs.



**Figure 1** Conventional pyrometallurgical treatment of mineral raw materials in Bor

## EXPERIMENTAL

### Evolution of bioleaching technology

Microbes that play a very important role in the leaching processes of copper minerals are: *At. Thiooxidans*, which was isolated in 1922 by (Waksman and Joffre), then *At. Ferrooxidans* isolated in 1947 by (Colmer and Hinkler) and *Ferroobacillus Ferrooxidans* isolated in 1954 by (Leathen and Breley). Their ability is reflected in the ability to oxidize iron with the formation of ferric iron (the main oxidant of sulphide minerals) and the formation of sulfuric acid, which accelerates the dissolution of minerals.

The first forms of leaching in situ, dump leaching and heap leaching are replicated to the improved procedures of heap bioleaching arranged drained piles, for providing oxygen, carbon dioxide and microbes, universally adapted, such as plastic membranes covers, to capture heat and preventing water evaporation, drainage tubes to collect the solutions, network of drippers to irrigate the heap with solutions leaving behind the sprinklers, on/off irrigation system, and slowly adding more instrumentation to monitor the process [1].

### In situ leaching

This process allows the extraction of metals from a porous ore body without the need for conventional mining involving drill and blast, open cut or underground mining.

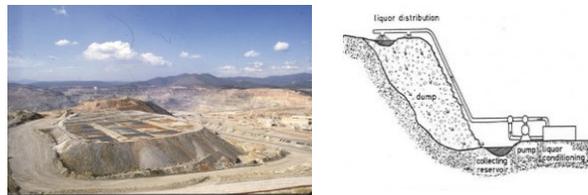
Microorganisms may be induced to release the metals into solution without any mechanical mining of the metal-bearing rocks. If the ore is not porous, holes are drilled in the ore deposit. Explosives are also used for easier penetration of the solution. The leaching solution is pumped into the deposit where it comes into contact with the ore. The leach solution is then pumped to the surface and processed, Figure 2.



**Figure 2** In situ leaching

### Dump leaching

The leaching of landfills begins with the leaching of tailings from large surface mines, the leaching time of which is measured in years. The ore is crushed and piled, then subjected to a continuous spray of water containing biomining microbes. The leaching solution is collected from the bottom and after metal extraction is used again for washing, Figure 3.



**Figure 3** Dump leaching

### Heap leaching

The ore is placed in orderly heaps on a water impermeable membrane. The leaching solution is pumped to the top of the pile and the leachate is collected and processed for metal recovery, Figure 4.



**Figure 4** Heap leaching

### Mechanism of bioleaching

Bioleaching of the ore body of copper ore is presented in Figure 5. Acidic iron-rich fluid is injected through the borehole into the fractured ore body, where it oxidizes the copper sulfide minerals. A liquid rich in copper and iron is pumped to the surface, the copper is extracted by the SX-EW process. The barren solution is regenerated in a bioreactor containing acidophilic cultures that oxidize iron  $\text{Fe}^{2+}$  to  $\text{Fe}^{3+}$ .

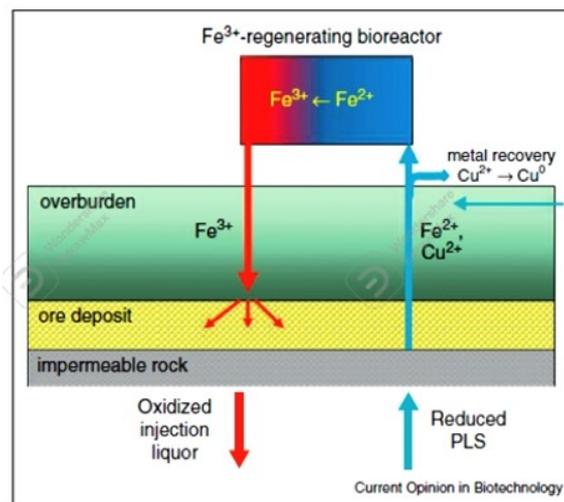


Figure 5 Indirect bioleaching mechanism ore body

### Factors affecting the extraction of metals from minerals

#### Particle size

Ores and concentrates during the leaching process serve as substrates, so that the leaching activity is proportional to the available surface. Reducing the particle size means increasing the total surface area of the particles so that a higher metal yield can be achieved. This means that the surface area plays an important role. The particle size used in bioleaching processes of 20-75 $\mu\text{m}$  of about 42 $\mu\text{m}$  is considered optimal for bioreactor leaching, while the particle size is different from minerals in heap and landfill leaching in inches.

To carry out the bioleaching operation, it is necessary that the raw material be ground as finely as possible so that it does not destroy the microbes and that the microbes overcome it as easily as possible. On the other hand, research shows that 5% of the world's total energy production is spent on mining ore bodies and grinding ore.

#### Pulp density

An increase in mineral surface area can be accompanied by an increase in pulp density. Usually, the content of the solid phase in the pulp used in bioleaching

processes is up to 20% (w/v). An uncontrolled increase in pulp density has a negative effect on the diffusion of gases, mixing and therefore on the activity of the organism.

It can also lead to the dissolution of certain compounds that have an inhibitory or even toxic effect on the growth of bacteria.

### **Temperature**

The optimal temperature growth and development mesophilic microorganisms *At. ferrooxidans* and *At. thiooxidans* is between 28-30 °C. The required temperature for the growth and development of moderate thermophiles such as *Sulfolobus*, *Acidiphilum*, *Thiobacillus caldus* is 45-55 °C. Extreme thermophiles have the greatest activity at temperature 60-90 °C.

### **pH**

Necessary condition for the growth of acidophilic bacteria is the pH value, which ranges from pH 1.8 to 2.2. Adjusting the pH value in leaching processes is also one of the important factors for metal solubility.

### **Eh**

The Eh-redox potential in bioleaching processes ranges from 350-700 mV. With the dissolution of iron and the increase in the concentration of  $Fe^{3+}$  ions, the redox potential increases. It is very important to maintain the redox potential to optimize metal dissolution and control iron deposition.

### **O<sub>2</sub> and CO<sub>2</sub>**

The concentration of carbon dioxide in the air is not sufficient for the growth of microbes, so it is necessary to add it. As bacteria are aerobic in nature, an adequate supply of oxygen is a prerequisite for a high degree of leaching.

### **Nutrients**

Microbes need inorganic compounds for growth and development, which they otherwise acquire from nature, such as ammonium sulfate, dipotassium hydrogen phosphate, potassium chloride, magnesium sulfate, and calcium nitrate.

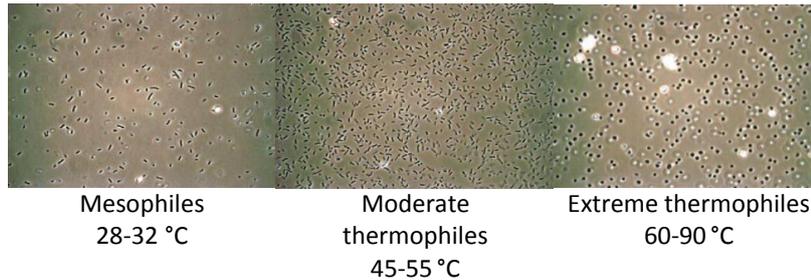
## **RESULTS AND DISCUSSION**

### **Types of microbes and isolation**

Mesophilic microorganisms *At. ferrooxidans* and *At. Thiooxidans*, Figure 6., can be isolated from open pit water presented in Figure 7., underground water that is collected in pits and from ore in Bor, Serbia and these are their natural habitats. Moderate thermophiles can be isolated from the warmer habitats of South Africa. Extremely thermophiles bacteria can be isolated example from hot springs [5].

The increase in the number of bacteria is achieved in a standard nutrient solution of mineral inorganic salts (KCl,  $(\text{NH}_4)_2\text{SO}_4$ ,  $\text{K}_2\text{HPO}_4$ ,  $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$ ) in an incubator at the required temperature for the growth of the selected bacterial culture, Figure 8.

After the development of microorganisms, it is very important that the microorganisms first adapt to the leaching conditions in the shaker, Figure 9., for the later successful management of the bioleaching process.



**Figure 6** Spaces of microbes that participate in bioleaching processes



**Figure 7** Inoculum isolation from open pit



**Figure 8** Incubator



**Figure 9** Shaker

With the help of adapted microbiological culture, bioleaching tests are performed in bioreactors with  $\text{CO}_2$  gas and air supply. Monitoring of the bioleaching process is carried out by daily sampling, in order to control the pH value, redox potential and concentration of leached metals.

The intensity of the oxidation process during bioleaching increases due to the increase in the number of bacteria, the concentration of iron ions, the increase in the acidity of the solution and the redox potential of the solution Eh.

Intensive bioleaching occurs when the basic parameters of the process (pH, Eh, pulp density, concentration of metal ions in the solution, as well as the activity and number of microorganisms) are stabilized.

Bioleaching is a slow process, but by adapting microbes to mineral raw materials and establishing continuous bioleaching in a series of bioreactors after determining the residence time it is possible to continuously obtain leached pulp every day.

#### **Small scale continuous bioleach reactors**

Mintek believes that for tank bioleaching, much more value can be derived from continuous testing, as opposed to batch testing [3]. This is simply because batch tests do not provide the reliable kinetic data that can be obtained from continuous test work. The retention time in the continuous bioleaching process is usually six days. Taking into account the start-up time and residence time for the process to achieve stable operation, it takes about three weeks to complete the test. One of the biggest problems with this is that the amount of sample required to conduct such testing becomes very large.

In order to avoid this, at MMI Bor (Institute for Mining and Metallurgy in Bor) a set of reactors for continuous bioleaching of small scales, with a total process volume of up to 6 L per reactor, was designed and established, which enable continuous tests to be carried out without consumption of large quantities of (usually scarce) concentrate samples. This is particularly useful in the early stages of a metallurgical testing work program and increases the value of the data that can be provided to the client at scope study or pre-feasibility study level. The bioreactor continuous system is shown in Figure 10.



**Figure 10** Small scale continuous bioleach reactors of ore with a capacity of 1L pulp/day

### Integrated bioleach Pilot plant

For larger-scale piloting, usually conducted to provide data for a feasibility study, an integrated pilot plant incorporating several downstream process unit operations was developed with the help of Mintek Company from Johannesburg (South Africa) at the Institute of Mining and Metallurgy Bor, as shown in Figure 11. This plant can provide detailed design information for the bioleaching process, as well as solid-liquid separation, iron removal and solution purification, SX -EW, and metal hydroxide precipitation.

In South Africa is initially processed 14 tons concentrate/day, while now being produced 55 t/day. In Kazakhstan on Suzdal BIOX plant are produce 192 t gold concentrate/day in sub-zero temperatures, Figure 12.



Figure 11 Integrated bioleach Pilot plant facility, capacity 20L pulp/day



Figure 12 Bioleaching tanks of refractory gold in a) South Africa, b) Kazakhstan

### Solvent extraction

Extraction of copper by solvent extraction, Figure 13, is based on the interphase transfer of copper from the aqueous phase to the organic phase. The transfer takes place at the interphase boundary, where the kinetics of the process depends on the

intensity of agitation of the two phases (flow of phases through the agitator-precipitator). The process then continues with phase separation, whereby agitators-settlers are used in hydrometallurgy. During the interphase transfer, cupric ions move to the organic phase and hydrogen ions to the aqueous phase, and copper forms an organometallic complex with the extractant according to the reaction:



in which two moles of oxime (active component) in the organic phase and one mole of copper release two moles of hydrogen ions in the pH range of 0.5 - 3.5.

Extractants based on 5-nonyl-salicylic-aldoxes are capable of reacting with the stoichiometric amount of copper from alkaline solutions up to 35 g/L  $Cu^{2+}$  and a minimum acidity of pH 1.4. The extractant itself forms a very strong organometallic complex from which copper is difficult to extract using the output electrolyte with a composition of 30 g/L Cu and 190 g/L  $H_2SO_4$ . This problem is solved by adding a suitable modifier to the extractant. Specific modifiers for certain extracts are nonyl phenol, tridecanol and ester modifier.



**Figure 13** Laboratory plant for leaching, solvent extraction and electrowinning  
A1 - reactor for leaching, B1 - feed tank for bioleach solution, C1 - tank for organic solution, D1 - mixer - settlers, E1 – electrowinning cell, F1 - control panel

For copper extraction, organic reagent M.5640 is used. Reagent M.5640 from Acorga is an ideal extractant for extracting copper from solution due to the high selectivity of copper extraction compared to iron. The laboratory solvent extraction system for copper extraction is composed of 5 identical mixer-settlers there of 3 in extraction and 2 in stripping. The process of solvent extraction is followed by the process of electrolytic extraction.

### Electrolytic extraction of copper

Electrolytic extraction of copper using insoluble anodes can be described as the deposition of copper from a copper-bearing electrolyte due to the passage of a direct current. The overall reaction is represented as follows:



according to which copper is deposited on the cathode and oxygen is released on the anode. PVC electrolytic cell equipped with Ti cathodes and Pb/Sn/Ca anodes.

### ACKNOWLEDGEMENT

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### CONCLUSION

By applying biotechnology in the metal extraction process, energy consumption is reduced, almost any risk of air pollution is eliminated, and the extracted metals of interest as well as potential pollutants are translated into an aqueous solution that can be easily further treated. Compared to pyrometallurgical processes, biotechnology is better for the environment and human health.

New technologies and scada software that are installed in reactor systems enable all information about the operation of the instruments and the monitoring of the technological parameters of the process to be sent wirelessly to the operator. At the same time, precise correction of process parameters can lead to a reduction in process management costs and an increase in recovery.

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