LEACH-SX-EW COPPER REVALORIZATION FROM OVERBURDEN OF ABANDONED COPPER MINE CEROVO, EASTERN SERBIA

Z. Stevanović*#, M. Antonijević**, R. Jonović*, Lj. Avramović*, R. Marković*, M. Bugarin* and V. Trujić*

*Institute for Mining and Metallurgy 19210 Bor, Serbia
**University of Belgrade, Technical faculty in Bor, 19210 Bor, Serbia

Abstract

Hydrometallurgical processes for copper revalorization from overburden of abandoned mine Cerovo in Eastern Serbia were studied. Paper contain results of percolation leaching tests, performed with acidic mine waters accumulated in the bottom of the former open pit, followed by solvent extraction (SX) and electrowinning (EW) processes on achieved copper pregnant leach solutions. Usage of accumulated waste waters was objected to minimizing the environmental hazard due to uncontrolled leaking of these waters in nearby creeks and rivers. Chemical composition of acidic mine waters used for leaching tests was: (g/dm^3): Cu – 0.201; Fe – 0.095; Mn – 0.041; Zn – 0.026; Ni - 0.0004; pH value - 3.3. Copper content in overburden sample used for leaching tests was 0.21% from which 64% were oxide copper minerals. In scope of leaching tests were examined influence of leaching solution pH values and iron (III) concentration on copper recovery. It was established that for 120 hours of leaching on pH=1.5 without oxidant agents, copper concentration in pregnant leach solutions enriched up to $1.08g/dm^3$ which was enough for copper extraction from solution with SX-EW treatment. As extraction reagent in SX circuit was used LIX-984N in a kerosene diluent. Cathode current density in electrowinning cell was $220Am^{-2}$ while electrolyte temperature was kept on 50 ± 2^oC. Produced cathode copper at the end of SX-EW process has purity of 99.95% Cu.

\# *Corresponding author: zoran.stevanovic@irmbor.co.rs*

1. Introduction

At present, there are basically two main methods used worldwide in order to process copper ores for metal production. First one is the "conventional" – pyro-metallurgical method, comprised by numerous types of shaft and flash technologies. Treatment process is consisted of crushing, grinding, flotation, smelting-refining and electro-refining stages. This method is applied to sulphide copper ores and is economically feasible for copper richer feeds [1,2].

A second method, "hydrometallurgical", is applied to the rest of the world's primary copper production, objected mainly on oxide and/or low grade copper ores due to significantly lower operating costs [3,4,5]. Treatment chain in hydrometallurgy processes are usually consisted of crushing, leaching (non-oxidative leaching, atmospheric leaching or pressure leaching), solvent extraction and electrowinning. Hydrometallurgical processing can be effectively applied for oxidized ores, containing CuO, Cu_2O, carbonates and some silicates, and rarely for sulphide ores with chalcocite and covellite as predominant copper minerals [6, 7]. Hydrometallurgical methods are used in countries having readily available deposits with low copper content and with surplus of oxidized forms at the same time (USA, Chile, Australia, and Peru). The most important development in copper hydrometallurgy, with respect to the growing number of its applications as well as for its future potential, has been solvent extraction process. It became the achievement which revolutionized copper production all over the world and enabled to introduce hydrometallurgy for industrial scale [8].
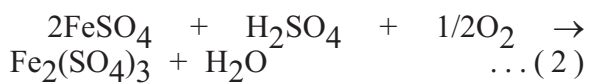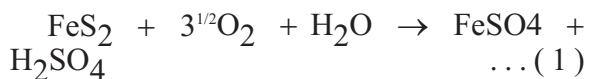
Beginning of solvent extraction process development, objected on metal extraction from leach solutions, date from the late 60's of last century. Beforehand, solvent extraction processes were used in analytical chemistry assaying [9], while large scale usage was mostly for uranium extraction from sulphuric acidic leach solutions [10]. Achieved experiences in uranium extraction processes initiated some of leading mining Companies to start researching of copper extraction from different solutions by solvent extraction process usage. One of them was Generally Mills which already had developed and commercialized ALAMINE® 336, as an SX reagent for the recovery of uranium from sulphuric acid leach liquors, [11] and believed that a similar technology for copper recovery would be welcome. However, pioneering operations of the Bluebird Mine and Bagdad Mines in Arizona, USA in the late 60's of last century, which used selective organic extraction reagents for metal concentration from leach solution in order to make possible the commercial production of pure copper metal by electrowinning processes, represent the beginning of the SX-EW technology as we know it today [12].

Mining & Smelting Complex Bor represent largest copper producer in Serbia where mining and processing of copper and other precious metals have history of over one century. Mining production started in 1903 with the exploitation of the underground mine, followed by opening of 3 open pits in the Bor area (from 1912, 1979 and 1991 – Bor, Veliki Krivelj and Cerovo respectively). The industrial activities in Bor, in particular those by the mining and smelter complex, have resulted in negative impacts on the environment of the region (including air, water, and soil) as well as having raised serious concerns about associated health effects of the pollution at large [13]. From

the influence width point of view, water pollution certainly represents one of the strongest environmental impacts which further induce water and soil pollution in wider area.

Significant part of water pollution arises by Acid Mine Drainage (AMD) originated by percolation of atmospheric waters through dumped overburden. After excavation and delaying of overburden, present sulphide mineralization has been exposed to influence of air and atmospheric which have as a result oxidation processes, especially of pyrite, and making AMD`s. Generally, the oxidation of pyrite from mining wastes under weathering conditions, and further formation of iron (III) could be represented by the following reactions [14-16]:

$$FeS_2 + 3^{1/2}O_2 + H_2O \rightarrow FeSO4 + H_2SO_4 \qquad \dots (1)$$

$$2FeSO_4 + H_2SO_4 + 1/2O_2 \rightarrow Fe_2(SO_4)_3 + H_2O \qquad \dots (2)$$

Products of pyrite oxidation are sulphuric acid and iron (III) which further induce oxidation of other sulphide minerals and generation of contaminated Acid Mine Drainages (AMD) with low pH value (2.5-4.5) and increased content of SO_4 and metals ions (Cu, Zn, Pb, As, Cd, Ni i Mn), metalloids, etc. [17, 18]. Originated AMD`s mobilize and disseminate metals ions in nearby rivers making strong negative environmental impact, reflected through long term contamination of surrounding soil, as well as surface and underground water system.

Main sources in scope of Mining and Smelting Complex Bor for AMD origination from overburden are three open pit mines (Cerovo, V. Krivelj and Bor) located as illustrated on Fig.1.
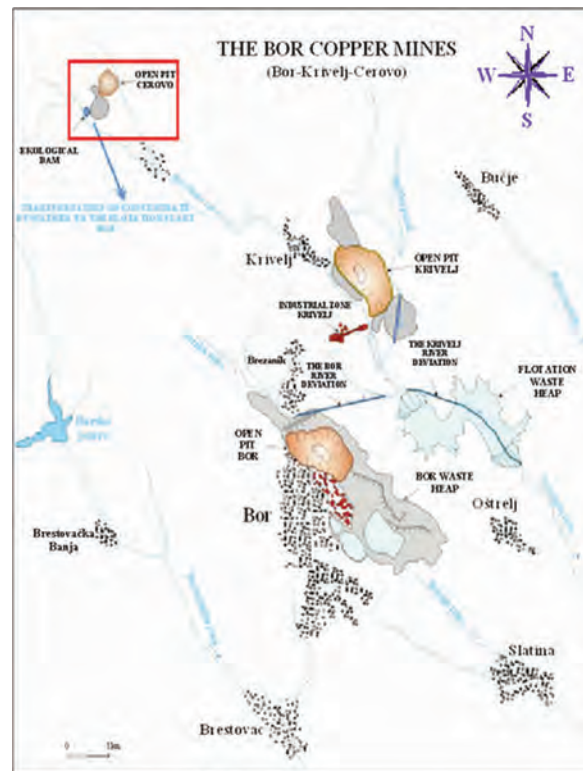

Fig. 1. Locations of open pit mines in scope of Mining & Smelting Complex Bor

Copper mine Cerovo is the youngest mine in scope of Mining and Smelting Complex Bor, opened in 1991 and include open pit mining and processing plant with crushing stage (three stadiums), grinding stage (two stadiums) and formed pulp thickening up to 36% of solid contents. The thickened pulp was pumped by three serial linked slurry pumps through steel pipeline up to the Bor flotation plant, which is located 13.3 km far away from Cerovo mine. Operating period of Cerovo mine was very short, from 1991 up to 2002 and during this time, all wastewaters from open pit and Cerovo processing plant were collected into "ecological dam" and from it, used back as technological water in processing plant. Since mine closure in 2002, atmospheric waters was continued to flow into the area of open pit making water

accumulation in the bottom of open pit with about 400 m^3 of water characterized by low pH value and high concentration of residual metals and metalloids. Existing "ecological dam" does not preserved a sufficiently high protection for surroundings soil and water streams from further pollution, mainly because of huge average atmospheric precipitation on annual level, calculated at average of around 550 m^3 per day which flow into open pit area. Whereas mine Cerovo is the first spot from the North side, in scope of Mining and Smelting Complex Bor (Fig.1), where was mining activities, surrounding cricks (Valja Mare and Cerova River), as illustrated on Fig.2, have upstream water quality of I and II category and downstream are highly polluted by AMDs through disorganized natural system of surface and underground water system.

Owing to dumped overburden quantity of around 25.000.000 tons with average copper content of 0.21% and increased content of pyrite, it could be expected that AMD origination will last very long time causing a lot of environmental problems. However,
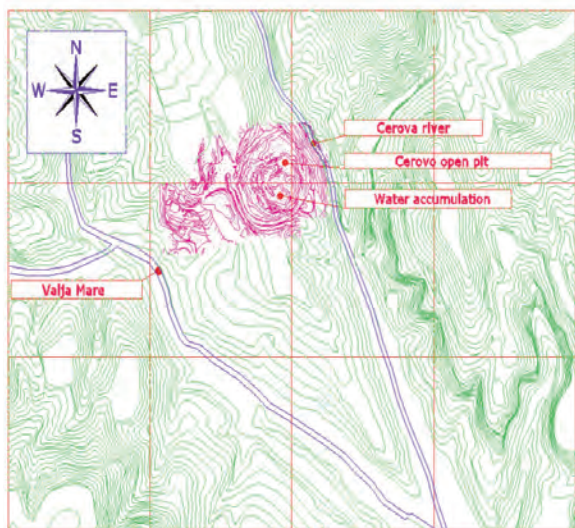
apart from being the source for AMD`s origination and pollution, overburden also could be source for copper revalorization because AMD`s have some appearance with copper content of over 1g/dm^3, which could be extracted by usage of up to date SX-EW processes. Therefore, the aim of this paper was to make a contribution to defining possibility for environmental protection on Cerovo location with making economic benefits through copper revalorization by leaching and SX-EW technologies usage.

According to proposed aim, we perform leaching experiments of overburden sample using adjusted mine waters from Cerovo open pit accumulation followed by SX-EW treatment of pregnant leach solution objected to metal copper producing. The intention was to determine optimum process parameters for eventual large scale process on mine site where all mine waters will be collected and treated.

Results of presented investigations have to route direction of further steps for defining possibilities of this issue resolving and also to induce Mining and Smelting Complex Bor management to consider implementation of SX-EW processes on other similar resources in scope of Bor Copper Mines.

Fig. 2. Cerovo open pit Mine area with surrounding rivers

2. Experimental

2.1. Particle sizes determination and chemical analyzing

Overburden sample particle sizes determination was performed on standard Tyler sieve series by dry method. Chemical analyzing was performed on overburden and mine waters samples as well as on pregnant leach solutions, SX-EW solutions and produced cathode copper.

Analyzing elements in overburden sample and mine waters samples were firstly heavy metals with limitation concentration for soils and waters by law regulations of Serbia Republic (Gazette 23/94). All chemical analyzes was determined by AES method on Atomic Emission Spectrometer with Induced Coupled Plasma (ICP-AES). Overburden samples are firstly homogenized by standard mixing procedure from which is afterward taken smaller sample quantity in mass of 20g, by "chess field" method. Reduced quantity of samples was homogenized one more time after which was taken samples in quantity of 0.5g for respective chemical analyses. Samples for chemical analyzing were dissolved by using 10ml $(HCL:HNO_3=3:1)$ solution. Dissolved samples were transferred in normal vessel of 25ml volume which is afterward supplemented with redistilled water up to the mark of 25ml. Solutions prepared by described procedure were, by peristaltic pump, introduced in induced coupled plasma flame (T=7000K) of ICP where is performed atomization and ionisation of elements. Finally detection of elements concentrations were done through CCD detector of ICP. Mine waters and pregnant leach solutions samples were analyzed on same equipment and by same procedure but directly without preparation due to already homogenize characteristics of solutions.

Solution samples from SX-EW circuit were taken in quantity of 10ml by measuring flask and afterward supplemented with redistilled water up to the 50ml. Copper was analysed by Gravimetric method (G), sulphuric acid by titration standard procedure (VT) and iron by Atomic Absorption Spectrophotometer (AAS) (Perkin-Elmer – 403). Cathode copper deposit obtained during the electrowinning process was analyzed by Atomic Absorption Spectrophotometer (AAS) (Perkin-Elmer – 403) according to Standard BS 6017 requirements.

2.2. Cerovo overburden sample characteristics

During operating period between 1991-2002 Cerovo copper mine produced 19.950.000 tons of copper ore and 24.800.000 tons of overburden. Copper ore was treated in Bor flotation plant while overburden (open pit tailing) was dumped on west - southwest side of the open pit Cerovo.

Overburden sample was taken on west side of the open pit in total quantity of 200kg. Due to easier manipulation, entire sample was crushed up to 85% -30mm. Overburden sample chemical composition and particle sizes characteristics are presented in Table 1 and Fig.3 respectively.

2.3. Cerovo mine waters sample characteristics

Mine waters in the accumulation on the bottom of open pit Cerovo, with total volume of $400m^3$, are collected from underground waters and surface waters which are originated from atmospheric precipitations

Table 1. Chemical composition of overburden sample

Elements content													
Cu_{tot} (%)	Cu_{ox} (%)	Fe^{2+} (%)	Fe^{3+} (%)	Mg (%)	Mn (%)	Ca (%)	Zn (%)	Cd (%)	As (%)	SiO_2 (%)	Al_2O_3 (%)	Ag (g/t)	Au (g/t)
0.210	0.136	1.68	3.87	1.53	0.027	2.02	0.009	/	<0.003	62.98	17.07	0.50	0.02

Fig. 3. Particle sizes characteristics of overburden sample

Fig. 4. Water accumulation on the bottom of the open pit Cerovo

and gravitate into Cerovo open pit area. Due to geographical position of open pit Cerovo (Fig.2), surface waters from north, west and southwest side gravitate into open pit while surface waters from east and southeast side flow into Cerova River. Image of water accumulation on the bottom of open pit Cerovo, generated by using GEMCOM v.6.2 software tools, is presented on Fig.4.

Mine water sample, used for leaching solutions preparation, was taken from described accumulation in total volume of 150dm3. Characteristics and chemical composition are presented in Table 2.

2.4. Experimental setup

2.4.1. Leaching

Equipment for leaching experiments was consisted of Plexiglas column with diameter 150mm and height of 900mm, 5dm^3 volume dosing tank with flow regulation valve, 15 dm^3 volume collecting tank for enriched solution and peristaltic pump. Experimental setup of leaching tests is illustrated on Fig.5.

After homogenization and quantity reducing, overburden sample in mass of 8.3kg with copper content of 0.21% were placed in column. Over the sample was mount inert silicon dioxide bed, thickness of about 1cm, due to uniform distribution of leaching solution. Below the sample, in the bottom of column, was placed linen for very fine particles filtration.

Volume of leaching solution for experiment was 15dm^3 with introduction speed in column of 0.300dm^3/h which was calculated based on solutions flow through porous media during copper ores leaching [19,20]. pH values were adjusted by addition of sulphuric acid to leaching solutions before experiments and to output solutions before recirculation. In experiments with oxidant, iron (III) sulphate was only added in leaching solution after pH value adjustment on the beginning of experiment. Total time of experiment was 120h with recirculation of leaching solution.

Table 2. Mine water characteristics and elements content

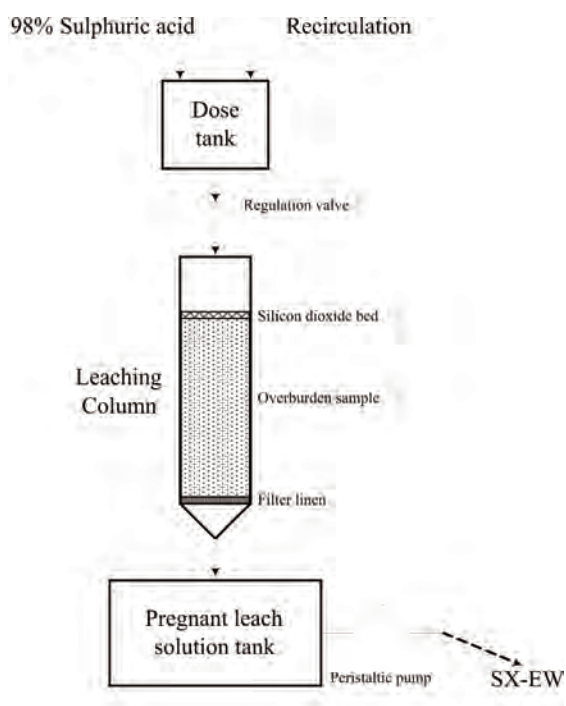| Characteristics and elements content									
T (°C)	Color	Odour	pH	Cu (g/dm^3)	Fe (g/dm^3)	Ni (g/dm^3)	As (g/dm^3)	Zn (g/dm^3)	Mn (g/dm^3)
18	red	/	3.3	0.201	0.095	0.0004	/	0.026	0.041

Fig, 5. Leaching experiments setup

In scope of leaching tests were performed two experiments series for examination of leaching solution pH values and iron (III) concentration influence on copper recovery. pH influence on copper recovery was examined with following values (pH=1; pH=1.5; pH=2). During analyzing the influence of iron (III) in leaching solution with pH=1.5 (source of iron is iron (III) sulphate), concentrations of Fe^{3+} ions were 1.0, 5.0 and 10.0 g/dm^3. All experiments were performed at atmospheric conditions. Copper pregnant leach solution, from leaching process with selected optimal parameters at the end of leaching examinations was treated by SX-EW process.

2.4.2. SX-EW

SX-EW equipment was consisted of linked solvent extraction and electrowinning laboratory units. SX unit was Mixer – Settler POLUX C Type with mixer volume of $85 cm^3$ and settler volume of 175 cm^3. EW unit was rectangular electrolytic cell, with 1.5 dm^3 capacity, made from Polypropylene. The cap of the cell was also rectangular with kerfs witch permitting the parallel arrangement of the electrodes and holes for inflow and overflow of electrolyte. The supply glass reservoir with volume of $1 dm^3$ was equipped with flow regulation valve and pipe heater. Electrolytic cell was connected by busbar to the galvanostate, model 5B (IRM-Bor, Serbia), with characteristics: max. electrical current 5A and max. voltage 5V. Flow rate of linked SX-EW equipment was $1 dm^3$/h. Schematic illustration of SX-EW experimental setup is given on Fig.6.

Due to closing linked SX-EW circuit at the experiments beginning was prepared synthetic $CuSO_4$ solution as spent electrolyte with contents of copper (31 g/dm^3) and sulphuric acid (198 g/dm^3).

Pregnant leach solution from leaching stage with pH=1.5, contents of copper (1.08 g/dm^3) and iron (1.11 g/dm^3) was introduced into SX unit by peristaltic pump. Owing to high selectivity characteristics of copper over iron in high acidic media (pH=1.8) and faster kinetics (rate of reaction) [21], as extraction reagent in extraction circuit was used LIX-984N (5%) in kerosene diluents. SX circuit were consisted of two extraction stages and one stripping stage. Organic-Aqueous ratio in extraction stage was 1:1, while in stripping stage was 5:1 [22]. Organic and aqueous phases are mixed in mixers until equilibrium is reached and then separated in settlers. After the extraction and stripping stages were performed sampling of aqueous phases from settler overflow and analyzed on copper, iron and sulphuric acid content.
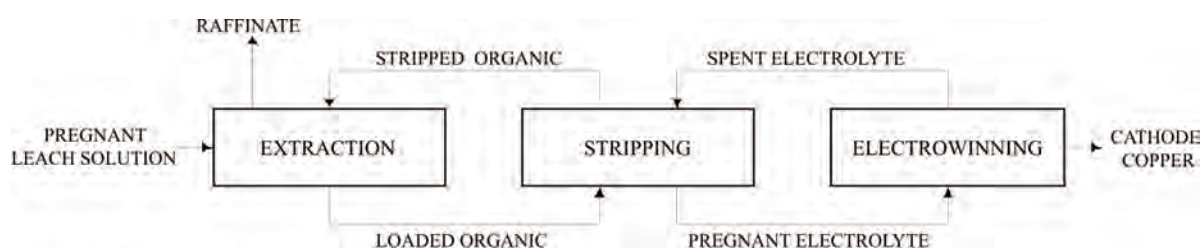
Fig. 6. Schematic illustration of SX-EW experiments setup

Electrowinning of pregnant electrolyte from stripping stage was performed in electrolytic cell with maintaining electrolyte temperature on 50 ± 2°C. Pregnant electrolyte working volume for EW stage was 15 dm^3 with flow rate of 1dm^3/h. Concentration of the main components in pregnant electrolyte from stripping stage was (g/dm^3): Cu – 36.1, H_2SO_4 - 182.41 and Fe – 0.015. In order to reduce corrosion of the lead anode and due to lower lead content in the copper cathode was added cobalt sulphate. Two starter cathode sheets and three anodes were inserted into the cell with 20 mm interraxial distance between two various electrodes. Electrode organization was anode – cathode – anode. Starter cathode sheets was prepared from cathode copper plate, produced in Mining and Smelting Complex Bor - Electrolytic Refinery Plant with following content (ppm): As < 3; Sb < 2; Bi < 1; Fe < 5; Pb < 2; Ni < 1; Si < 9; Ag < 5; Te < 0.1; Sn < 2; Zn < 5; Al < 10; Se < 0.7 and Cu = 99.95 %. Total active surface of all cathodes which were immersed into the electrolyte was 0.0225m2. Cast antimonial lead anodes (6 % antimony) were used as anode material in a form of plate. Anode and cathode dimensions were similar. The EW test was carried out in galvanostatic operations at cathodic current density of 220Am^{-2} and I=4.95A and this value was function of specified Cu content in spent electrolyte [23]. Corresponding cell voltage was measured with differential

electrometer. The solution samples were taken on each 60 minutes from the cell overflow due to analyzing of Cu, Fe and sulphuric acid concentrations. Cathode copper deposit obtained during the electrowinning process was analyzed on copper purity at the end of experiment. Spent electrolyte was returned in a SX unit for copper striping from the loaded organic.

3. Results and discussion

3.1. Leaching

3.1.1. The effect of leaching solution pH value

Obtained results from examination of pH solution value (pH=1.0, pH=1.5 and pH=2.0) influence on Cu and Fe leaching rate from overburden samples are presented on Figs. 7, 8 and 9 respectively. Experiments were performed without oxidants addition at atmospheric conditions.

By increasing the pH value of leach solution in range of 1.0–2.0, after 120 hours of leaching, copper content in output solutions was increased from 0.99g/dm^3 to 1.11g/dm^3 with copper recoveries from 68% to 79% respectively. Although oxidants were not added during the experiments, except for the oxygen from the air, a relatively high copper dissolution values were achieved indicating the presence of readily leachable

copper oxides in the overburden. Since overburden have been exposed to weathering for over 10-15 years, and knowing from the other side that copper deposit on Cerovo location was consisted partly from oxide copper minerals, oxidation of some copper sulphides and formation of secondary copper minerals such as:

cuprite Cu_2O, tenorite CuO, chalcanthite $CuSO_4 \cdot 5H_2O$, azurite $2CuCO_3 \cdot Cu(OH)_2$, malachite $CuCO_3 \cdot Cu(OH)_2$ and chrysocola $CuO \cdot SiO_2 \cdot 2H_2O$ which are easy leachable is expectable.

At pH 2 (Fig.9), copper content is the lowest ($0.99g/dm^3$) which could be consequence of iron hydroxide formation on higher pH values and reducing of Fe(III) concentration who represent main oxidant agent for sulphide oxidation and H^+ ions generation [24,25].

Also, H^+ ions concentration increasing sensibly correlates with the iron dissolution, at pH 2 iron concentration after 120 hours leaching reached $0.54g/dm^3$ (Fig.9), while at pH 1 iron concentration increased up to $2.28g/dm^3$ (Fig.7) which could be obstacle during solvent extraction stage.

Consequently, leaching solution of acidity pH 1.5 can be selected as optimal one for further investigations considering the obtained results (Fig. 8). Copper concentration of $1.08g/dm^3$ with recovery of 76% is slightly lower than at pH 1.0 ($1.11g/dm^3$) with copper recovery of 79% (Fig.7), but however, iron concentration is significantly lower ($1.11g/dm^3$) than at pH 1.0 ($2.28g/dm^3$) which is advantage for pregnant leach solution treatment in SX circuit.

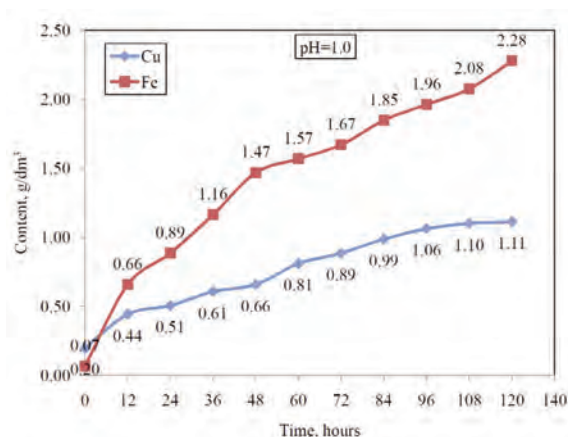### 3.1.2. The effect of Fe (III) concentration

Fig. 7. Dependence of copper and iron concentrations on time during leaching at pH=1
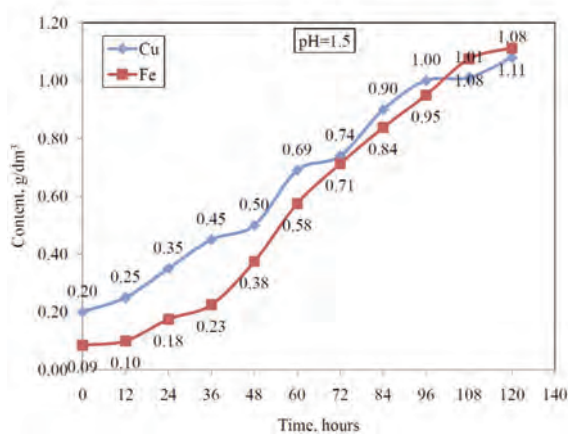

Fig. 8. Dependence of copper and iron concentrations on time during leaching at pH=1.5
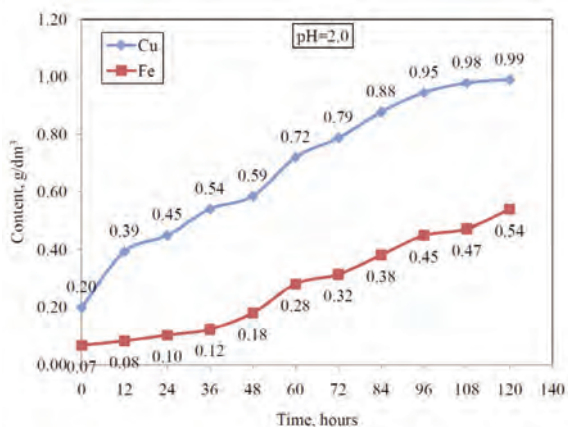

Fig. 9. Dependence of copper and iron concentrations on time during leaching at pH=2

Even it is known that increased concentration of iron in pregnant leach solution can balk solvent extraction process we performed preliminary experiments of iron (III) concentration influence on copper recovery. Intention was only to determine is it possible to make significant increasing of copper recovery and concentration in pregnant leach solution by oxidants, which will indicate on presence of easier leachable copper sulphide minerals. Obtained results from examination of Fe (III) concentration at varied concentrations (Fe^{3+} = 1.0, 5.0 and 10.0 g/dm^3) influence on copper leaching rate from overburden samples are presented on Fig. 10. Experiments were performed at pH 1.5 and at atmospheric conditions.

The presented results indicate that the presence of Fe^{3+} ions in the leach solution has very small effect on copper dissolution. The obtained copper concentrations for 120 hours of leaching are approximately the same and differ for only ±0.03g/dm^3 (Fig.10) or by only ±3% from the copper recovery point of view (76%-79%). Possible reason for achieved results could be that present iron in overburden, released during pyrite and other iron minerals oxidation, is enough for leaching of available copper oxides, so introduction of additional Fe (III) have no significant effect.

From the other side, achieved copper recoveries of over 75% mean that present oxide copper in process feed (64%, Tab.1) and partially sulphides were recovered. Among all copper sulphide minerals on Cerovo deposit chalcopyrite is dominant, and knowing that chalcopyrite oxidation rate was marginally dependably on the concentration of iron (III) [26-27], presented results could be quite logical and satisfactory, even without the addition of oxidants. Therefore, pregnant leach solution
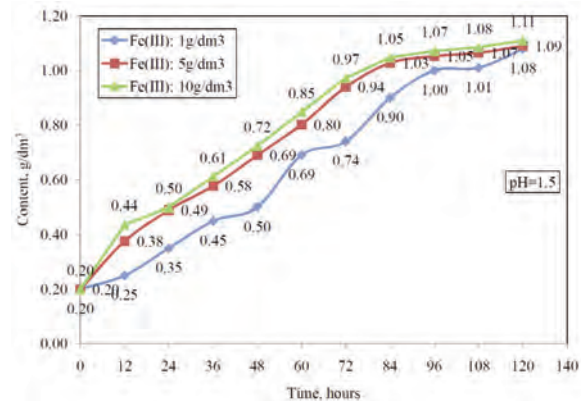

Fig. 10. Dependence of copper concentrations on time during leaching at various Fe (III) concentrations

for SX-EW circuit was prepared by leaching at pH 1.5 without oxidants addition.

3.2. Solvent extraction

Pregnant leach solution from leaching stage has copper concentration of 1.08$g/dm3$ with copper recovery of 76%, iron concentration of 1.11g/dm^3, and pH value of 1.5. SX circuit were consisted of two extraction stages and one stripping stage with usage of LIX 984N (5%) in kerosene diluents as extraction regent.

Extraction stage parameters were:
• aq/o ratio= 1/1
• Aqueous phase: Pregnant leach solution Cu=1.08$/dm^3$, Fe=1.11$/dm^3$, pH=1.5
• Organic phase: LIX-984N (5%) in kerosene
• Stages: 2
• Copper recovery: 98%

Stripping stage parameters were:
• aq/o ratio= 1/5
• Aqueous phase: Spent electrolyte Cu^{2+}=31g/dm^3, H_2SO_4=198g/dm^3
• Organic phase: Loaded organic
• Stages: 1

Obtained pregnant electrolyte for EW

process has content of
    Cu^{2+}=36.1g/dm^3,
    Fe^{3+}=0.015g/dm^3 and
    H_2SO_4=182.41g/dm^3.

Presented SX results indicate that LIX 984N, as extraction reagent in this case, show good performances in point of high selectivity of copper over iron and acids during the extraction process, high transfer capacity of the copper on the extractant, fast kinetics and good phase separation after mixing. Therefore, our sense is that LIX 984N would be quite suitable for the eventual industrial scale process which naturally should be confirmed through further researching or pilot plant testing.

3.3. Electrowinning

During EW process, copper was deposited by using constant galvanostatic puls from actual pregnant electrolyte at 50±2°C at the current value of I=4.95A and constant flow rate of 1 dm^3/h. Dependence of copper concentration on process duration is presented on Fig.11.

From the Fig. 11 could be seen that during all the time of process Cu concentration in spent electrolyte was in a range of 30.83-32.65g/dm^3 which was lower than the starting value of 36.1g/dm^3.

Calculated theoretical mass of cathode copper for process duration of fifteen hours is m$_o$=88.06g while measured mass of produced electrowon copper has value of m=82.78g. Current efficiency which is calculated in relation to difference of copper deposit masses from beginning to end of test is ø = 94%.

Dependence of sulphuric acid concentration on process duration is presented on Fig.12.

Results presented on Fig. 12 shows that H_2SO_4 concentration is higher than starting value of 182.41g/dm^3. Sulphuric acid concentration in spent electrolyte samples during time was in range of 193.6-194.6g/dm^3 which is in accordance with the values for the Cu concentration in electrolyte (Fig. 11). For the lower value of copper concentration, value for sulphuric acid is higher. Iron concentration was constant during the process.

Values of cell voltages, measured with differential electrometer during time, were used for average value calculation (average calculated=2.34V). This value was used for the calculation of specific energy consumption Es (kW h kg^{-1}) according to
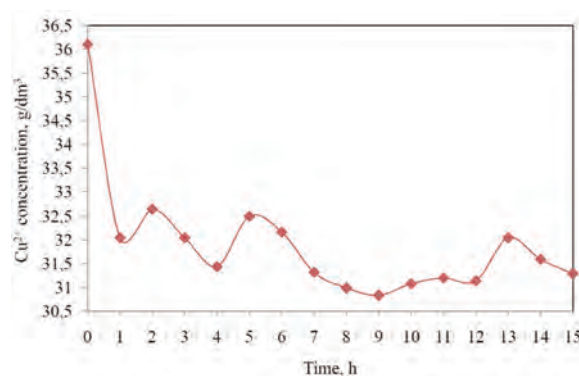

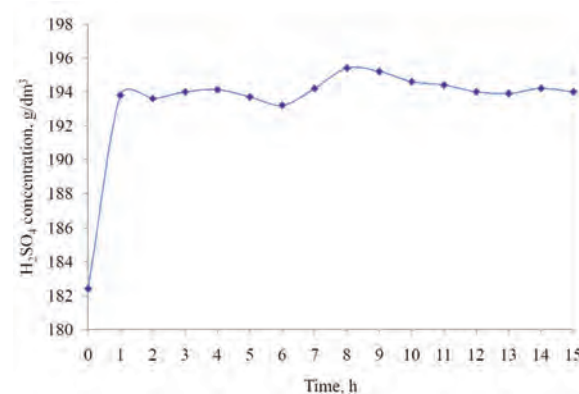*Fig.11. Cu concentrations in spent electrolyte during time*

Fig. 12. H_2SO_4 concentrations in spent electrolyte during time

the following equation [28]:

$$E_S = 100 \; x \; q \; x \; E_{cell} / m \; x \; ø$$

$$= 2.23 \text{kW h kg}^{-1} \qquad \ldots (3)$$

Where are:
q: Electric charge (kA h);
Ecell: Cell voltage (V);
m: Weight of deposited metal (kg) and
ø: Current efficiency (%).

Final chemical analyzes of electrowon copper confirmed that copper purity is in accordance with standard BS 6017 [29].

4. Conclusion

On the basis of the results presented in this work, the following conclusions can be drawn:

• pH value of leaching solution has effects on the copper recovery from Cerovo overburden. By acidity increasing from the pH value of 2.0 to 1.0, after 120 hours of leaching, copper recovery increased from 68% to 79%.

• H^+ ions concentration increasing sensibly correlates with the iron dissolution. At pH 2 iron concentration after 120 hours leaching reached 0.54g/dm^3, while at pH 1 iron concentration increased up to 2.28g/dm^3 (Fig.7).

• Addition of Fe (III) as oxidant in the leach solution has no significant effect on copper dissolution. Differences in copper concentration with 10g/dm^3 of Fe (III) and without oxidants are 0.03g/dm^3 or only 3% from the copper recovery point of view (76%-79%) which indicate on significant presence of chalcopyrite among sulphide copper minerals.

• As extraction reagent, LIX 984N show good performances in solvent extraction circuit with achieved copper recovery of 98% from pregnant leach solution.

• Current efficiency in electrowinning stage was 94% with produced electrowon copper in accordance with standard BS 6017.

• Copper recoveries through leaching and SX-EW processes were 76%, 98% and 94% respectively, resulting with total copper recovery for entire process of 70% which indicate on possible industrial scale process with positive economic results.

• Achieved total copper recovery of 70%, and possibility for solving problem of water system pollution by AMDs on Cerovo location, induce necessity for performing pilot scale tests objected to copper revalorization and environmental protection which will contribute to sustainable development of mine activities in scope of Mining and Smelting Complex Bor.

References

1. M.G. King, JOM Vol.59, No2 (2007) 21.

2. F. Habashi, Journal of Mining and Metallurgy, Section B. Metallurgy, 43(1)B (2007) 1.

3. M. R. Vanhanen, The Finnish Environment Institute, Finland, 1999, p.71.

4. W.H. Dresher, How Hydrometallurgy and the SX-EW Process Made Copper the "Green"

Metal, (2001), h t t p : / / w w w . c o p p e r . o r g / publications/newsletters/innovations/2001/08/hy drometallurgy.html

5. G.A. Kordosky, The Journal of the South African Institute of Mining and Metallurgy, 11/12 (2002) 445.

6. M.M. Antonijević, M.D. Dimitrijević, Z. O. Stevanović, S.M. Šerbula, G.D. Bogdanović, Journal of Hazardous Materials, 158 (2008) 23.

7. T. McWaters, Mining Eng., September (1990) 1075.

8. K. Rotuska and T. Chmielewski, Physicochemical Problems of Mineral Processing, 42 (2008) 29.

9. G. Morrison and H. Freiser, Solvent Extraction in Analytical Chemistry, John Wiley and Sons, Inc., New York, 1957.

10. A.M. Ross, Mining Engineering, 9 (1957) 21.

11. K.L. Power, Operation of the First Commercial Copper Liquid Ion Exchange and Electrowinning Plant, Copper Metallurgy, R.P. Ehrlich, ed., AIME, New York 1970, p.1.

12. G.W. Seward, Leaching, SX-EW Production of Copper – A Global View. Zeneca-China-Symposium, Acorga Ltd. Technical Library (www.acorga.com), 1997, p.10.

13. T. Marjanović, M. Trumić, Lj. Marković (Eds.), Lokalni ekološki akcioni plan opštine Bor, Bor, (2003) 40. (*in Serbian*).

14. P. C. Singer and W. Stumm, Science, 167 (1970) 112.

15. G. Kamei and H. Ohmoto, Geochim. Cosmochim. Acta, 64 (1999) 2585.

16. M.J. Borda, D.R. Strongin and M.A. Schoonen, Geochim. Cosmochim. Acta, 68 (2004) 1807.

17. G. Parker and A. Robertson, Australian Minerals & Energy Environment Foundation, 1999, p.11.

18. H.M. Conesa, A. Faz and R. Arnolds, Science Total Environmental, 266 (2006) 1.

19. J.F. Munoz, P. Rengifo and M. Vauclin, Journal of Contaminant Hydrology, 27 (1997) 1.

20. E. Cariaga, F. Concha and M. Sepúlveda, Chemical Engineering Journal, 111(2-3) (2005) 151.

21. C.R. Merigold, LIX® Reagent Solvent Extraction: Plant Manual for Small and Medium Size Leach-Solvent Extraction-Electrowinning Copper Recovery Operations, Henkel Corporation – Minerals Industry Division, Tucson Arizona, USA, 1996, p.1.

22. R.V. Stevanović, S. Čupić, R.R. Jonović, Lj.R. Avramović, R.T. Marković, In Book of Abstracts, 47th Meeting of the Serbian Chemical Society, Belgrade, Serbia, 2009, p.51.

23. A.M. Alfantazi, and D. Valic, Journal of Applied Electrochemistry, 33 (2003) 217.

24. L. Stjernaman Forsberg and S. Ledin, The Science of the Total Environment, 358 (2006) 21.

25. M. Gleisner and R.B. Herbert Jr.,J. Geochem. Explor., 76 (2002) 139.

26. P.B. Munoz, J.D. Miller and M.E. Wadsworth, Metall. Trans., 10B (1979) 149.

27. J.E. Dutrizac, Metall. Trans., 12B (1981) 371.

28. P. Fornari and C. Abbruzzese, Hydrometallurgy, 52(3) (1999) 209.

29. B. Čađenović, R. Marković and A. Milosavljević, Journal Copper Bor, 1 (34) (2009) 69.