

# COMBINATION OF CHEMICAL AND BIOLEACHING PROCESS FOR Cu AND Zn RECOVERY FROM THE SEDEX TYPE ORE

Vesna Conić<sup>1</sup>, Suzana Dragulović<sup>1</sup>, Dragana Božić<sup>1</sup>, Dragan Milanović<sup>1</sup>, Ivana Jovanović<sup>1</sup>, Srđan Stanković<sup>2</sup>, Jelena Avdalović<sup>3</sup>

<sup>1</sup>Mining and Metallurgy Institute Bor, Zeleni bulevar 35, 19210 Bor, Serbia, vesna.conic@irmbor.co.rs

<sup>2</sup>Federal Institute for Geosciences and Natural Resources, Stilleweg 2, 30655 Hannover, Germany <sup>3</sup>University of Belgrade, Institute of Chemistry, Technology and Metallurgy, Njegoševa 12, 11000 Belgrade, Serbia

#### Abstract

The "Two Stage Leaching Process" described in this paper consists of the classic acid leaching followed by a bioleaching step. Acid leaching serves to leach the oxide minerals, but when  $O_2$  is introduced as an oxidant, a partial oxidation of sulfide minerals is expected. Bioleaching serves to leach the sulfide minerals. The use of the two-stage leaching process could increase the metal recoveries of partially exploited or un-exploited ore, such as: standard and polymetallic ore containing sulfide, mixed sulfide and oxide minerals; the Sedex ore, such as the sulfide types of ore with very fine impregnated mineral structures; ore containing harmful elements such us As, Hg and Cd. To ensure the maximum metal recovery from minerals such as chalcopyrite during the tank bioleaching processes, fine grinding of sample to the particle sizes between 10 and 20 µm is often required. Acid leaching in combination with bioleaching could result in the improved exposure of mineral surfaces to the leaching reagents resulting in deeper and easer bacterial attack on sulfide minerals. Due to this reason, the good metal recoveries could be achieved for a grain size of  $80\% < 30 \mu m$ . The ability to operate at a larger particle size could lead to the energy saving and lower consumption of balls during the milling step. It was shown that a combination of acid leaching and bioleaching "Bobija" polymetallic type of ore resulted in the higher Cu and Zn recoveries than what could be achieved using either the bioleaching or bioleaching followed by the acid leaching. Since the Fe extraction is significantly lower using this process, the Cu and Zn losses will be substantially lower as a result of Fe co-precipitation. Solutions, obtained by the chemical leaching and bioleaching, can be combined and after iron precipitation be treated by the solvent extraction and electrowinning.

Keywords: polymetallic ore, Sedex type ore, acid leaching, bioleaching, At. ferrooxidans

# **1 INTRODUCTION**

In Serbia, the polymetallic off-balance ore contains: copper, zinc, lead, gold and silver that occur in quantities meeting and even exceeding the needs of the country. Deposit of the complex polymetallic sulfide ore t "Bobija", located in western Serbia, consists of several ore bodies of differential morphological and structural texture characteristics. Polymetallic paragenesis is mostly formed of sulfides with a huge content of pyrite. There are lead, zinc and copper with addition the mixture of arsenic, antimony, gold, silver, bismuth, calcium minerals and barite. An analysis of the massive sulfide ore samples has shown a high content of the basic metals (>10%Zn and Pb) as well as the precious metals contents. Bioleaching of these types of ore or concentrates is an attractive alternative treatment option, especially for the low-grade ore or complex minerals [1-3]. The processing of polymetallic concentrates by the bioleaching can have commercial benefits compared to the conventional pyrometallurgical processing method [4].



# **2 EXPERIMENTAL**

In the previous experiments [5], it was shown that without adaptation of the mixed culture, maximum recovery of 83% Cu and 89% Zn could be achieved over a period of 40 days, with around 60% Fe extraction achieved. In the subsequent experiments, a bacterial culture adapted to a grow on concentrate was used in the bioleaching experiments [6]. Bioleaching of a polymetallic sulfide concentrate (from the Bobija open pit, Ljubovija, west Serbia) was carried out at  $30^{\circ}$ C in three aerated bioleaching reactors in the presence of the adapted mesophilic mixed bacterial culture containing At. ferrooxidans, At. thiooxidans, and Leptospirillum ferrooxidans, with the addition of heterotrophic acidophilic culture Acidifilium cryptum. The T-RFLP analysis was used to identify the heterotrophic acidophilic culture. Acidifilum cryptum efficiently metabolizes the organic compounds, facilitating the growth and activity of L. ferrooxidans [7]. The fourth reactor was not inoculated and run as a control one. The bacterial culture was isolated from acid water at the sampling site. The reactors were filled with, 9K nutrient medium and have the following composition: FeSO<sub>4</sub>x7H<sub>2</sub>O - 44.8 g/l;  $(NH_4)_2SO_4 - 3g/l$ ; KCl - 0.1g/l; MgSO<sub>4</sub>×7H<sub>2</sub>O - 0.5g/l; K<sub>2</sub>HPO<sub>4</sub> - 0.5g/l;  $Ca(NO_3)_2 \times 4H_2O - 0.01g/l; Na_2SO_4 \times 10H_2O - 0.15g/l, 10\%$  adapted culture and pH of solution adjusted to 2. The concentrate was milled to a particle size of 80% d < 30 $\mu$ m, and added to the reactors at pulp density of 10% (w/v).

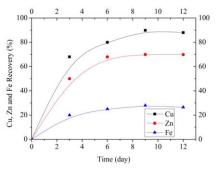


Figure 1 Cu, Zn and Fe recovery vs. time (with pulp density of 10% (w/v))

The bioleaching results showed that over a period of 12 days, the maximum recoveries of 88% Cu, 70% Zn and 30% Fe, could be achieved (Figure 1). The recovery of Zn was relatively low and did not exceed 70%. Fe recovery of about 30% that occludes in precipitation, and Cu and Zn thus reducing their recovery. On the pH=3.5 (t= $30^{\circ}$ C), 32% Zn and 39% Cu were occluded. On the pH=3 (t= $30^{\circ}$ C), 13.5% Zn and 17.8% Cu were occluded.

In the control sample (acid leaching), the chemical analysis has confirmed recovery of 72% Zn, 66.7% Cu and 4.6% Fe than in the bioleaching reactors. In this control sample, the acidity and redox potential were also measured, and their values were pH=2.12 and Eh=300.8mV.

### **3 RESULTS AND DISCUSSION**

### 3.1 Two-stage bioleaching and acid leaching

With the aim to reduce the Fe recovery, two experiments were performed. In the first experiment, a combination of bioleaching and acid leaching was carried out. In the second experiment, an acid leaching, followed by the bioleaching, was performed.



The same methodology was used as described above. In the first experiment, the bioleaching stage was interrupted on the ninth day, Figure 2. The bioleaching pulp was filtered and solution chemically analyzed. The solid residue was further treated in an acid leaching using 2% H<sub>2</sub>SO<sub>4</sub>. At the start of acid leaching, the pH was 1.15 at phase ratio of S: L=1: 5. Sulfuric acid is used during leaching, so that at the end of the acid leaching process the pH value was 1.4.

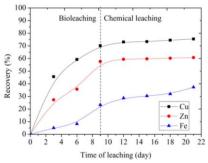


Figure 2 Combination of the bioleaching and chemical leaching with the air addition

By the chemical analyses of the bioleaching solution, it was confirmed that the recovery of Cu, Zn and Fe on the 9<sup>th</sup> Day was 70%, 55% and 23%, respectively, while at the end of the acid leaching step, the cumulative recoveries for Cu, Zn and Fe were 75%, 60% and 35%, respectively. The two-stage process did not produce the higher Cu and Zn recoveries.

#### 3.2 Two-stage acid - bioleaching process

In an attempt to further reduce the Fe extraction and increase Zn and Cu recoveries, a combination of an acid leach, followed by a bioleach step was investigated. After 7 days of acid leaching at the same conditions as previously described recoveries for Cu, Zn and Fe were 56%, 65% and 3.9%, respectively, Figure 3. At the start of the acid leaching using 2%  $H_2SO_4$ , the pH was 1.3 and at the same time the redox potential was measured as it was 200mV. At the end of acid leaching, the pH and Eh was about 1.8 and 350mV, respectively.

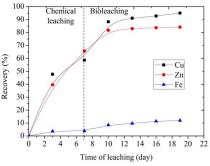


Figure 3 Combination of the chemical leaching with the air addition and bioleaching

After the acid leaching, the pulp was filtered and liquid phase chemically analyzed. By the acid leaching, a less quantity of Fe is leached in the produced pregnant solution and, in comparison to the bioleaching, gives a greater Zn concentration in it. On the other hand, for the next stage of bioleaching, the better opened ore particles will be and less remaining quantity of Cu and Zn for bioleaching. Due to that in the produced pregnant bioleach



solution, the concentration of ferric ions will be less. The solid residue was further treated by the bioleaching process in reactors filled with 9K nutrient medium at pH 2, 10% inoculum and using 10% (w/v) of pulp density. The cumulative recoveries recorded were 95%, 85% and 12% for Cu, Zn and Fe, respectively, Figure 3. The results of all these conditions gave the less total quantity precipitate of ferric ions, due to a smaller amount of leached iron. The precipitate of Fe(OH)<sub>3</sub> was less, and consequently the less quantity occluded ions of Zn and Cu, what would represent a loss. Total duration time of both leaching processes is somewhat longer in comparison to the separate acid or bioleaching, but this is all for reason to increase the Zn recovery and reduce leaching of Fe. It is considered that the acid treatment step, opened the crystalline lattice exposing the mineral grain to the attack of bacteria. The measured grain size specific surfaces of solid before and after chemical treatment -acid leaching showed 0.243 m<sup>2</sup>/g and 0.318 m<sup>2</sup>/g, respectively. The specific surface increasing of about 30%, after acid leaching, shows on better grains surface liberation for the subsequent bioleaching process.

# **4 CONCLUSION**

Using a combination of acid and bioleaching, it was demonstrated that higher Cu and Zn recoveries could be achieved than using only bioleaching or bioleaching followed by the acid leaching. Since the Fe extraction is significantly lower using this process, it is expected that the Cu and Zn losses will be substantially lower as a result of Fe co-precipitation. The solutions obtained by the chemical leaching and bioleaching can be merged and after iron precipitation be treated by the solvent extraction and electrowinning.

### ACKNOWLEDGEMENTS

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