TWO STAGE LEACHING PROCESS FOR Cu AND Zn RECOVERY FROM SEDEX TYPE ORES: PART 1

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Abstract

The "Two Stage Leaching Process" described in this paper consists of 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 partial oxidation of sulphide minerals is expected. Bioleaching serves to leach the sulphide 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 sulphide, mixed sulphide and oxide minerals;

Sedex ore, such as sulphide types of ore with very fine impregnated mineral structures;

Ores containing harmful elements such us As, Hg and Cd.

To ensure maximum metal recovery from minerals such as chalcopyrite during tank bioleaching processes, fine grinding of the sample to particle sizes between 10 and 20μm is often required. Acid leaching in combination with bioleaching could result in improved exposure of the mineral surfaces to leach reagents resulting in deeper and easer bacterial attack on sulphide minerals. Due to this reason, good metal recoveries could be achieved for a grain size of 80% < 30 μm. The ability to operate at a bigger particle size could lead to energy saving and lower consumption of balls during the milling step.

It was shown that a combination of acid- and bioleaching resulted in higher Cu and Zn recoveries than what could be achieved by using either bioleaching or bioleaching followed by acid leaching. Since the Fe extraction is significantly lower using this process, Cu and Zn losses will be substantially lower as a result of Fe co-precipitation. The solutions obtained by chemical leaching and bioleaching can be combined and after iron precipitation be treated by solvent extraction and electrowinning.

Keywords

Polymetallic ore, sedex type ore, acid leaching, bioleaching, At.ferrooxidans

INTRODUCTION

In Serbia, the polymetallic off-balance ore that contains: copper, zinc, lead, gold and silver occurs in quantities that meet and even exceed the needs of the country. Deposit of the complex polymetallic sulphide ore deposit "Bobija" located in western Serbia consists of several ore bodies of differential morphological and structural texture characteristics.

Polymetallic paragenesis is mostly formed of sulphides 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 ores or concentrates is an attractive alternative treatment option, especially for low-grade ores or complex minerals [1-3]. The processing of polymetallic concentrates by bioleaching can have commercial benefits compared to the conventional pyrometallurgical processing method [4].

RESULTS AND DISCUSSION

In previous experiments 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 [5]. In subsequent experiments, a bacterial culture adapted to grow on the concentrate was used in the bioleaching experiments [6]. Bioleaching of a polymetallic sulphide concentrate (from the Bobija open pit, Ljubovija, west Serbia) was carried out at 30^{0}C in three aerated bioleach reactors in the presence of the adapted mesophilic mixed bacterial culture containing Acidithiobacillus ferrooxidans, Acidithiobacillys thiooxidans, and Leptospirillum ferrooxidans, with the addition of heterotrophic acidophilic culture Acidifilium cryptum. T-RFLP analysis was used to identify the heterotrophic acidophilic culture. Acidifilum cryptum efficiently metabolizes organic compounds, facilitating the growth and activity of L. ferrooxidans [7]. The fourth reactor was not inoculated and run as a control. 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: $(NH_4)_2SO_4$ – 3 g/l; KCl – 0.1 g/l; $MgSO_4{\times}7H_2O$ – 0.5 g/l; K_2HPO_4 – 0.5 g/l; $Ca(NO_3)_2{\times}4H_2O$ – 0.01 g/l; $Na_2SO_4{\times}10H_2O$ – 0,15 g/l, 10% adapted culture and the pH of the solution adjusted to 2. The concentrate was milled to a particle size of 80% d < 30μm, and added to the reactors at a pulp density of 10% (w/v).

The bioleaching results showed that over a period of 12 days, maximum recoveries of Cu, Zn and Fe, of 88%, 70% and 30%, respectively could be achieved (Fig.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^{0}C), 32% Zn and 39% Cu were occluded. On the pH=3 (t=30^{0}C), 13.5% Zn and 17.8% Cu were occluded.

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

2.1 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 leach followed by bioleaching was performed.

The same methodology was used as described above. In the first experiment, the bioleaching stage was interrupted on the ninth day, Fig. 2. The bioleach pulp was filtered and the solution chemically analyzed. The solid residue was further treated in an acid leach using 2% H_2SO_4. At the start of acid leaching pH was 1.15 at a phase ratio of S:L = 1:5. Sulfuric acid is consumed during the leaching, so that at the end of the acid leaching process pH value was 1.4.

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

2.2 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, Fig.3.

At the start of the acid leaching by using 2%H_2SO_4, pH was 1.3 at the same time was measured redox potential and was 200mV. At the end of acid leaching pH and Eh was about 1.8 and 350mV respectively.

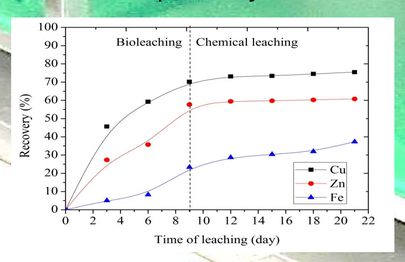

Figure 1 – Cu, Zn and Fe recovery vs. time (with pulp density of 10% (w/v))

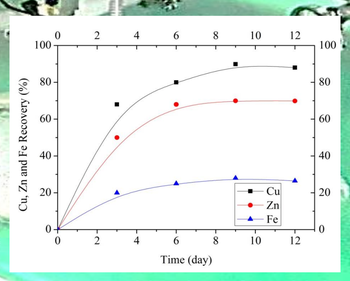

Figure 2 – Combination of the bioleaching and chemical leaching with the air addition

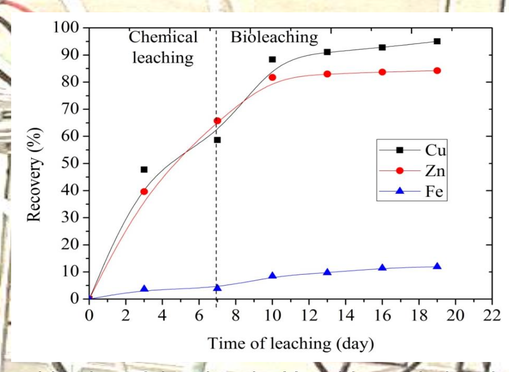

Figure 3 – Combination of the chemical leaching with the air addition and bioleaching

After the acid leaching, the pulp was filtered and the liquid phase chemically analyzed.

By the acid leaching, a less quantity of Fe is leached in the produced pregnant solution and in comparison with 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 a 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, Fig. 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 $(OH)_3$ 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 with the separate acid or bioleaching but this is all for reason to increase the Zn recovery and to reduce leaching of Fe.

It is considered that the acid treatment step, opened the crystalline lattice exposing the the mineral grain to the attack of bacteria. Measured grain size specific surfaces of solid before and after chemical treatment-acid leaching showed 0.243 m^2/g and 0.318 m^2/g respectively. Specific surface increasing of about 30%, after acid leaching, shows on better grains surface liberation for subsequent bioleaching process.

In acidic medium by using acid leaching with introduction O_2 from air, possible chemical reactions sulfides are (1-4):

$$Cu_2S + 4H^+ + O_2 \rightarrow 2Cu^+ + S^0 + 2H_2O \quad \text{Chalcocite} \quad (1)$$

$$FeS_2 + \frac{7}{2}O_2 + H_2O \rightarrow Fe^{2+} + 2SO_4^{2-} + 2H^+ \quad \text{Pyrite} \quad (2)$$

$$Fe^{2+} + \frac{1}{4}O_2 + H^+ \rightarrow Fe^{3+} + \frac{1}{2}H_2O$$

$$FeS_2 + 2Fe_2(SO_4)_3 \rightarrow 3FeSO_4 + 2S^0$$

$$CuFeS_2 + O_2 + 4H^+ \rightarrow Cu^{2+} + Fe^{2+} + 2S^0 + 2H_2O \quad \text{Chalcopyrite} \quad (3)$$

$$CuS + \frac{1}{2}O_2 + H_2SO_4 \rightarrow CuSO_4 + S^0 + H_2O \quad \text{Covellite} \quad (4)$$

Similar reactions will proceed for presents zinc sulphide minerals by which sulphur can be formed.

In acidic medium by using bioleaching with introduction O_2 from air, possible chemical reactions for sulfides are (5-8):

$$FeS_2 + 3{,}5\,O_2 + H_2O \xrightarrow{\text{At.thiooxidans and At.ferrooxidans}} FeSO_4 + H_2SO_4 \quad (5)$$

$$2FeSO_4 + 0{,}5O_2 + H_2SO_4 \xrightarrow{\text{At.ferrooxidans}} Fe_2(SO_4)_3 + H_2O \quad (6)$$

$$CuFeS_2 + 4Fe^{3+} \rightarrow Cu^{2+} + 5Fe^{2+} + 2S^0 \quad (7)$$

$$S^o + \frac{3}{2}O_2 + H_2O \xrightarrow{At.thiooxidans} 2H^+ + SO_4^{2-} \quad (8)$$

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 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 chemical leaching and bioleaching can be merged and after iron precipitation be treated by solvent extraction and electrowinning.

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