

## CORRELATION OF Fe<sup>2+</sup> WITH Cu<sup>2+</sup> AND Zn<sup>2+</sup> IN THE BIOLEACHING PROCESS

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### Abstract

*This paper describes the impact of adding pyrite and ferrous sulfate on the recovery of Cu and Zn in the bioleaching process of treating the polymetallic raw materials. For a period of 20 days, at temperature of 30<sup>o</sup>C, phase ratio S:L=1:5 and pH=2 with bacterial culture At. Ferrooxidans and At. Thiooxidans, higher Cu leaching was achieved with addition of pyrite compared to the addition of ferrous sulfate, and significantly lower leaching of Zn for both cases of addition pyrite and ferrous sulfate.*

**Keywords:** bioleaching, polymetallic ore, metals recovery, pyrite, ferrous-sulphate

### 1 INTRODUCTION

The deposit of complex polymetallic sulphide ore "Bobija" is located in western Serbia. It consists of several ore bodies with different morphological and structural-textural characteristics. The following mineral paragenesis occur in the deposit: barite, barite-quartz-pyrite and pyrite - polymetallic paragenesis. In addition, this mineral paragenesis is integrated, giving much more complex mineral paragenesis with very complicated structural-textural relationships. Paragenesis of barite-quartz and pyrite minerals is less present and occurs as an intermediate layer between a barite layer and pyrite polymetallic paragenesis with barite. In the mineral paragenesis, besides barite and pyrite, there is also copper, zinc, lead, arsenic, antimony, silver, gold, bismuth, calcium, etc. Earlier exploration and exploitation focused only on barite.

The associated massive sulphide mineralization associations are recognized by the REO (Real estate owned) as the SEDEX ore type.

The bioleaching treatment of these ore or concentrates is the most successful alternative in many mining projects or industrial applications, especially for the low-grade ores or complex minerals [1-3]. The processing of polymetallic concentrates by bioleaching can have the commercial benefits compared to the conventional pyrometallurgical processing method [4].

Application of the microbiological techniques have enabled the identification and understanding the different bioleach micro-organisms. This understanding of the microbiology of bioleach micro-organisms could be one of the keys to the successful process development [5,6].

Pyrite is a major companion of the sulphide copper and lead-zinc ore. It plays an important role in the biochemical processes of iron and sulfur cycling in the nature. Oxidation

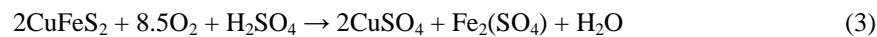
of pyrite begins with the oxidation of sulfur by oxygen to give sulfate, nonferrous iron, and acidity. The rate-limiting step is the oxidation of  $\text{Fe}^{2+}$  to  $\text{Fe}^{3+}$ , which occurs very slowly at low pH - chemically, but is catalyzed by the bacteria - biochemically.

The bacteria iron-oxidants can leach directly sulphide minerals. The process is described in the following reaction and presupposes an intimate interaction of the bacteria with the mineral substrate, what is explained by the equation (1):



Where M represents a bivalent metal, usually as sulphide (e.g., Fe and Cu).

Reaction (2) and (3) represents the microbiological oxidation of pyrite and chalcocopyrite respectively:



This paper shows the addition of iron in the form of pyrite and ferrosulfate in order to determine its influence and correlation with  $\text{Cu}^{2+}$  and  $\text{Zn}^{2+}$  in bioleaching processes.

## 2 EXPERIMENTAL

Prepared samples of ore with a particle size of 100% - 75  $\mu\text{m}$  were treated by the bioleaching process in a series of bioreactors, shown in Figure 1, with the introduction of  $\text{CO}_2$  gas and air.  $\text{FeSO}_4 \cdot x\text{H}_2\text{O}$  was added to the first two reactors 3.01g in the first, and 6.02g in the second reactor, while  $\text{FeS}_2$  was added to the other two, 3.016g in the third, and 6.032g in the fourth reactor.

A fifth separate reactor served as a control in which leaching conditions were the same only without bacterial culture.



**Figure 1** Bioreactor system

The bioleaching experiment was performed with the following parameters:

- Leaching solution                      pH=2 with 10% bacterial culture *At. Ferrooxidans* and *At. Thiooxidans* in 9K standard nutrient solution of mineral inorganic salts
- Phase ratio                                S: L=1: 5
- Leaching time                            20 days
- Temperature                              30<sup>o</sup>C

After the leaching process was completed, the resulting pulp was filtered on a Bichner funnel. The applied analytical method of metal analysis from solution was the ICP-AAS.

### 3 RESULTS AND DISCUSSION

The degrees of metal leaching, depending on the duration of bioleaching for the cases of addition of ferrous sulfate or pyrite, are showed in Table 1.

**Table 1** Degree of metal leaching depending on the duration of bioleaching for the cases of addition of ferrous sulfate or pyrite

Conditions: S: L=1:5, 30 <sup>o</sup> C	Time (days)	Metal leaching (g) and degree of leaching (%)									
		Cu		Zn		Fe		As		Cd	
		g	%	g	%	g	%	g	%	g	%
I Fe <sub>(ore)</sub> 13.85g + Fe <sup>2+</sup> (FeSO <sub>4</sub> x7H <sub>2</sub> O) 3.01g	5	0.73	79.3	1.52	54.0	1.90	13.5	0.053	33.1	0.0033	0.60
	10	0.74	80.2	1.53	54.4	2.17	15.4	0.066	41.2	0.0033	0.60
	15	0.76	82.7	1.55	55.3	3.18	22.6	0.075	46.9	0.0033	0.60
	20	0.81	88.3	1.75	62.3	5.09	36.2	0.092	57.5	0.0036	0.65
II Fe <sub>(ore)</sub> 13.85g + Fe <sup>2+</sup> (FeSO <sub>4</sub> x7H <sub>2</sub> O) 6.02g	5	0.66	72.0	1.44	51.2	1.90	13.5	0.045	28.1	0.0031	0.56
	10	0.69	75.3	1.49	53.1	3.07	21.6	0.047	29.4	0.0032	0.58
	15	0.70	76.2	1.52	54.2	3.58	25.5	0.048	30.0	0.0033	0.60
	20	0.72	79.2	1.55	55.2	5.26	37.4	0.055	34.4	0.0034	0.62
III Fe <sub>(ore)</sub> 13.85g + Fe <sub>(pyrite)</sub> 3.016g	5	0.74	81.4	1.48	52.6	1.07	6.3	0.048	30.0	0.0030	0.54
	10	0.76	83.3	1.49	53.1	1.14	6.7	0.062	38.8	0.0031	0.56
	15	0.77	84.1	1.53	54.6	1.48	8.6	0.061	38.1	0.0031	0.56
	20	0.81	88.5	1.55	55.3	1.60	9.4	0.073	45.6	0.0032	0.58
IV Fe <sub>(ore)</sub> 13.85g + Fe <sub>(pyrite)</sub> 6.032g	5	0.76	82.9	1.31	46.6	1.18	5.9	0.039	24.4	0.0027	0.49
	10	0.77	83.5	1.33	47.2	1.17	5.8	0.060	37.5	0.0027	0.49
	15	0.77	84.1	1.36	48.5	1.17	5.8	0.063	39.4	0.0027	0.49
	20	0.82	89.4	1.39	49.6	1.45	7.3	0.067	41.9	0.0030	0.54

According to the obtained and shown results from Table 1, it can be noticed that:

- higher Fe<sup>2+</sup> content in the solution when FeSO<sub>4</sub>x7H<sub>2</sub>O is added is logical, because the dissolution of ferrous sulfate in water directly occurred. In particular, FeSO<sub>4</sub>x7H<sub>2</sub>O is dissolved in both water and pH=2, while FeS<sub>2</sub> is not dissolved in either water or pH=2. In order for FeS<sub>2</sub> to dissolve, the bacterial decomposition is required. By the use of FeS<sub>2</sub>, the leaching degree of Fe<sup>2+</sup> is lower due to the slower process of pyrite dissolution;

- leaching of Cu<sup>2+</sup> is lower in the case of adding FeSO<sub>4</sub>x7H<sub>2</sub>O, because the probable suddenly high concentration of Fe<sup>2+</sup> ions in solution can slow down and block the dissolution of Cu<sup>2+</sup>. Due to this reason, it is necessary to take into account the optimal amount of Fe<sup>2+</sup> addition. It can be seen from the Table 1 that higher Cu<sup>2+</sup> leachings were obtained when FeS<sub>2</sub> was added compared to when FeSO<sub>4</sub>x7H<sub>2</sub>O was used for the same period of time. Pyrite is cheaper than FeSO<sub>4</sub>x7H<sub>2</sub>O, so this is another reason for its justified use in the bioleaching processes;

- leaching of Zn<sup>2+</sup> is very low, considering that it is more electronegative than both Cu<sup>2+</sup> and Fe<sup>2+</sup>, it was expected that its leaching would be greater than these metals. It is assumed that the reason is the specificity of mineralogical and chemical composition of raw material, which is a limiting factor in the leaching processes;

- in a separate fifth control reactor, without bacterial culture, a significant series of leaching of Cu and Zn was achieved;
- in bioleaching processes, 30-60% of arsenic is leached, which in solution can be in the form of As<sup>+3</sup> and more toxic As<sup>+5</sup>. Arsenic is a highly toxic element that can affect the metabolic functions of microorganisms [7];
- cadmium is also leached in the bioleaching processes, but usually its contents in the raw material are up to 10x lower than arsenic.

#### 4 CONCLUSION

Acidophilus microorganisms such as *At. ferrooxidans*, are the enzymatic systems that allow transferring electrons from ferrous ion to oxygen. The Fe<sup>2+</sup> ions are oxidized to Fe<sup>3+</sup> on the surface of bacteria by enzymes in the cell wall, usually associated with the exopolysaccharide, for transfer of its electron to a short electron transport chain in the cytoplasm membrane. This step may take place without the need for an intimate between the bacteria and ore substrate to be processed, which can be performed through an indirect attack of a ferric ion. Higher leaching of Cu was obtained with addition of pyrite, compared to when ferrous sulfate was added, and a significantly lower leaching of Zn were obtained for both cases of adding both pyrite and ferrous sulfate. It is assumed that the reason for low leaching of Zn is the specificity of mineralogical and chemical composition of the raw material, which represents a limiting factor in the leaching processes.

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