Biooxidation pretreatment of low grade refractory gold tailings using a sulfur-oxidizing mixotrophic bacterium

I Purnomo1, S K Chaerun1,2, and M Z Mubarok1

1Department of Metallurgical Engineering, Faculty of Mining and Petroleum Engineering, Institut Teknologi Bandung, Ganesha 10, Bandung 40132, Indonesia
2Geomicrobiology-Biomining & Biocorrosion Laboratory, Microbial Culture Collection Laboratory, Biosciences and Biotechnology Research Center (BBRC), Institut Teknologi Bandung, Ganesha 10, Bandung 40132, Indonesia

E-mail: zaki@mining.itb.ac.id

Abstract. An inefficient gold leaching in the cyanidation process from refractory gold tailings was caused by gold particle locked in specific minerals. The aim of this study was to harness the ability of a sulfur-oxidizing bacterium to oxidize iron and sulfur and its behaviour on ferrous sulfate heptahydrate (FeSO4.7H2O) and pyrite (FeS2) as the medium in the biooxidation process for gold and silver extraction. The results showed that the gold extracted in ferrous sulfate medium was 20.48%, while that in pyrite medium tended to reduce from direct cyanidation to 14%. The silver extraction increased from 80.96% to 99.26% in ferrous sulfate medium and 91.30% in pyrite medium. This result indicated that ferrous sulfate heptahydrate was more suitable than pyrite, which resulted in the higher extraction of gold.

1. Introduction
The increase of the gold demand leads to searching for more developed gold resources [1]. Most of the world gold (±2/3) are obtained from the processing of non-refractory gold ores because the ore proves to be easier to process using conventional gravity or cyanidation concentration methods. Generally, the method that is commercially undertaken is through cyanidation process. The processing of gold ore is carried out by cyanidation process followed by recovery of gold through cementation using zinc powder, adsorption with activated carbon or ion exchange resin. The problem in this process is gold losses caused by the loss of Au-Ag in fine carbon fraction, which is destroyed and carried into the tailings. In addition, the gold leaching process does not undergo optimally if gold ore that is processed is refractory. Gold minerals are called refractory when gold metal particles are very small (50 μm in diameter) and are included in carbonaceous minerals, sulfides, tellurides, and cyanicides. With the presence of these minerals, the cyanidation process becomes ineffective and tends to reduce gold recovery to below 80% even though ore particles are crushed [2]. Sulfide minerals also restrict access to leachate reagents to liberate the gold ore that is included. Hence, this refractory gold ore in its processing requires pretreatment methods before cyanidation.

Some conventional pretreatment methods such as the pre-aeration method by chlorination, roasting, pressure oxidation, ultrafine grinding, and flotation-intensive leaching are proven to be less suitable to process refractory-type gold ores because such methods have several disadvantages such as expensive investment costs, low gold recovery and environmental risks [3]. Recently, biooxidation pretreatment
that was first time introduced in 1986, has been used for about 5% of total world gold production [4]. Industries and researchers have been concerned with this method because of its lower investment costs, easier operation and more environmentally friendly way. Pretreatment of gold ores in the industry through biooxidation generally uses acidophilic bacteria, which only live at a low pH <2. These acidophilic bacteria cannot grow and move well at pH >3 and are not resistant to organic compounds. On the other hand, the mineralogy of the gold ore was found more complex, for example, gold was found to be associated with acid-consuming minerals, such as carbonate minerals and some organic carbon compounds in the ore. A previous study has reported that the gold extraction can be increased by harnessing the ability of the mixotrophic bacterium capable of oxidizing sulfur (i.e., *Citrobacter youngae*) to oxidize iron and sulfur and increase gold recovery which reached the recovery value of above 90% from high sulfides ores [5,6,7]. The bacterium has the ability to live in a wider pH range from pH 4 to 8 than chemolithotrophic bacteria. *C.youngae* uses organic and inorganic carbon as its carbon sources and can oxidize sulfur to sulfuric acid and also oxidize iron. Basically, the mechanism of iron and sulfur oxidation by bacteria occurs in two mechanisms, direct and indirect mechanism by oxidizing Fe$^{2+}$ to Fe$^{3+}$ according to the reactions in equations 1 and 2 [8].

$$2\text{Fe}^{2+} + 0.5\text{O}_2 + 2\text{H}^+ \xrightarrow{\text{bacteria}} 2\text{Fe}^{3+} + \text{H}_2\text{O}$$

(1)

$$\text{MS} + 2\text{Fe}^{3+} \xrightarrow{\text{bacteria}} \text{M}^{2+} + \text{S}^0 + 2\text{Fe}^{2+}$$

(2)

Based on these mechanisms, the iron sources could vary from any compounds such as FeSO$_4$ and pyrite. In this study, the effects of FeSO$_4$ and pyrite addition in biooxidation system on gold and silver recovery were investigated by taking into account several aspects of biooxidation and leaching processes.

2. Materials and Methods

2.1 Sample characterization

In this study, a total amount of 50 kg samples were received from a gold processing plant tailing in West Java. As received samples were mostly in fine particles of about P75-74 µm, where the coarser size was ground to get the desired size. The samples were then prepared by quartering-coning methods and subsequently sampled with riffle splitter and then prepared for mineralogical analysis. The semi-quantitative X-ray diffraction (XRD) analysis and chemical composition were showed in Table 1 and Table 2, respectively. A diagnostic leaching was conducted to determine the gold distribution in the tailing more clearly [9,10,11]. Diagnostic leaching steps were conducted using a variety of acids aimed to destroy specific minerals, followed by residual cyanidation from each stage (data not shown). At the end of the cyanidation process, dissolved gold was analyzed by using atomic absorption spectroscopy (AAS) [12,13]. The result indicated that the more than 30% particle of gold was distributed throughout pyrite mineral.

| Minerals | Weight percent |
|----------|----------------|
| Quartz   | 42.1           |
| Calcite  | 23.5           |
| Sanidine | 26.5           |
| Albite   | 6.3            |
| Pyrite   | 1.7            |
2.2 Biooxidation pretreatment
In the present study, the bacterium used was a sulfur-oxidizing bacterium (i.e., *Citrobacter youngae*) as one of our bacterial collections. This bacterium was cultured in the LB-broth medium that was sterilized by autoclave at 121°C for 20 min. For the initial condition, the pH medium was set for optimal growth of the bacterium. The pH setting was performed to control the dominant species in the biooxidation system. Also, it could maximize the oxidation rate and prevent the formation of jarosite during biooxidation [14,15].

LB-broth medium consisted of 5 g/L Na$_2$S$_2$O$_3$.5H$_2$O, 7 g/L FeSO$_4$.7H$_2$O, 3 g/L molasses, 5 g/L yeast extract, and 10 g/L NaCl.

| Element | Weight percent | Element | Weight percent |
|---------|----------------|---------|----------------|
| Si      | 60.06          | S       | 0.53           |
| Ca      | 13.53          | Mn      | 0.54           |
| Al      | 7.95           | Ti      | 0.33           |
| K       | 7.16           | Cr      | 0.07           |
| Fe      | 5.49           | Cu      | 0.06           |
| Mg      | 3.34           | Zn      | 0.06           |
| C       | 1.92           | Ni      | 0.03           |
| Au (g/t)| 0.5            | Ag (g/t)| 18             |

Table 2. Chemical composition of the sample

Before being adapted with the tailings, the bacterium was cultured until the growth reached 75% of the exponential phase (for 3 days) under aerobic condition. Bacterial adaptation included biooxidation and cyanidation processes of biooxidation residue. Biooxidation experiments were conducted in duplicate in 500 mL Schott bottles with a working volume of 350 mL. This working volume consisted of 15% (v/v) bacterial inoculum, 5% solids of the sample and medium. The composition of the medium at this stage was the same as that at the inoculation stage. The pH and redox potential of the suspensions were measured daily at the interval of 24 hours for 5 days. To evaluate the changes in the concentration of soluble Fe, the suspension (5 mL) was collected daily and centrifuged at 5000 rpm for 10 min. In centrifugation step, the supernatant was collected and prepared for AAS analysis, while the pellet was returned to biooxidation suspension by top-up solution. After 5 days, the residue of biooxidation was filtered and prepared for cyanidation step.

2.3 Leaching procedure
In the leaching step, all residues from biooxidation were leached using cyanide. A series of experiment were carried out in duplicate in the beaker glass for 24 hours and all parameters in this process were kept constant. Leaching parameters under study included NaCN concentration of 1000 ppm, pH 10.5-11, 30% solid, dissolved oxygen concentration adjusted to 7-10 ppm by H$_2$O$_2$ addition and pH adjustment by hydrated lime addition. At the end of the leaching, the slurry was filtrated and repulped by NaCN wash solution. The filter cake was then dried to determine the mass loss before a subsequent step. The analysis of Au and Ag in the residue was performed by digestion using aqua regia. In this procedure, 5 g of dried residues were dissolved in 100 ml of a mixture of concentrated HCl and HNO$_3$ and then stirred at 350 rpm at 90°C for 8 hours. The filtrate from this process was separated from silicate residue and submitted for analysis of Au and Ag by AAS. Direct cyanidation was also conducted in the same parameters to compare the result from biooxidation pretreatment.
3. Results and Discussion

3.1 Biooxidation pretreatment

Daily monitoring data of biooxidation system are presented in Figs. 1-3. Figure 1 showed the solution pH of the biooxidation system supplemented with FeSO₄ or pyrite. Both biooxidation systems showed the increase of pH values although the pH was adjusted to ~5 at the onset of the experiment. This behaviour might be caused by dissolution of alkaline minerals [16] as well as a large number of calcite mineral in the tailings (~23.50 wt.%). Calcite mineral reacted with H⁺ ions in the solution might form calcium hydroxide and carbon dioxide [17]. Therefore, the pH increase in the biooxidation system containing pyrite tended to be lower than that containing FeSO₄. This indicated that the bacterium was more capable of providing proton ions by oxidizing sulfide mineral (herein pyrite) than FeSO₄.

![Figure 1. Solution pH values of the biooxidation system supplemented with FeSO₄·7H₂O (5, 10, 15 g/L) or pyrite (2, 5, 7 g/L) using a sulfur-oxidizing mixotrophic bacterium over a period of 5 days](image-url)
Figure 2 revealed the solution Eh values of the biooxidation system supplemented with FeSO₄ or pyrite. The Eh values tended to decrease caused by physicochemical or bacterial activity. The values indicated the efficiency and bacterial activity during the biooxidation process. It is reported that non-adaptive bacteria reach solution potential under 650 mV (vs. SHE) [7]. The performance of the bacterium used in this study might be influenced by the complexity of the tailing characteristics.

**Figure 2.** Solution Eh (mV vs. SHE) values of the biooxidation system supplemented with FeSO₄·7H₂O (5, 10, 15 g/L) or pyrite (2, 5, 7 g/L) using a sulfur-oxidizing mixotrophic bacterium over a period of 5 days

Figure 3 represented soluble iron (Fe) in the biooxidation system supplemented with FeSO₄ or pyrite. The concentration of soluble Fe in the biooxidation system supplemented with FeSO₄ was higher than that with pyrite. This behaviour occurred because FeSO₄ dissolved immediately at the first day of biooxidation, whereas pyrite (in solid form) required the role of the bacterium to dissolve. The decreased concentration of soluble iron in the biooxidation system supplemented with FeSO₄ might be due to an increase in pH during the biooxidation pretreatment. It is reported that high pH values leads to an unstable condition for Fe ions, thus causing precipitation [5, 17].
Figure 3. Soluble iron (mg/L) in the biooxidation system supplemented with FeSO$_4 \cdot 7$H$_2$O (5, 10, 15 g/L) or pyrite (2, 5, 7 g/L) using a sulfur-oxidizing mixotrophic bacterium over a period of 5 days.

3.2 Cyanidation leaching
The gold and silver recovery in the biooxidation system supplemented with FeSO$_4$ or pyrite was presented in Table 3. It was demonstrated that direct leaching without biooxidation pretreatment reached the recovery of 17.85% and 80.96% for gold and silver, respectively. The extraction levels of gold and silver in the biooxidation system supplemented with FeSO$_4$ was greater than those in direct leaching, which reached an optimum recovery at 7 g/L FeSO$_4$ addition for gold and 5 g/L for silver. It appeared that an increase in FeSO$_4$ concentration (15 g/L) resulted in the decreased extraction values of gold and silver. The addition of FeSO$_4$ in high concentration increased the iron and sulfur ions soluble in bulk solution. Consequently, this condition decreased the probability of the bacterium to oxidize the associated minerals of gold because the bacterium preferred to oxidize the iron and sulfur ions. The gold recovery in the biooxidation system supplemented with pyrite tended to decrease with increasing pyrite concentration and was lower than direct leaching (without biooxidation pretreatment). This behaviour might be caused by the formation of silver sulfides between sulfide ions, which were not oxidized by the bacterium, and silver in the tailings. This silver sulfide leads to passivation layer, which can limit the access of cyanide solution and cause the lower gold and silver recovery [18].

Table 3. Gold and silver extraction from biooxidation residue

| Medium     | Concentration (g/L) | %Extraction Au | %Extraction Ag |
|------------|---------------------|----------------|----------------|
| FeSO$_4 \cdot 7$H$_2$O | 5                   | 18.97          | 99.26          |
|            | 7                   | 20.48          | 67.08          |
|            | 10                  | 17.12          | 96.90          |
|            | 15                  | 17.17          | 93.94          |
4. Conclusions

In the present study, *Citrobacter youngae* was able to increase the gold recovery from 17.85% to 23.95% under biooxidation parameters of 5% solids, FeSO₄·7H₂O concentration of 7 g/L and particle size under 200 mesh. Based on these result, *C. youngae* was able to recover gold trapped in pyrite by 20.33%, while pyrite addition tended to reduces the recovery of gold caused by passivation layer forming in the cyanidation process.

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