A two-stage bacterial pretreatment process for double refractory gold ores

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Abstract

Double refractory gold concentrates were subjected to a two-stage microbial process to destroy both sulfides and carbonaceous matter. In the first stage, the well-known sulfide biooxidation process, which utilizes chemolithotrophic bacteria was used to oxidize sulfides and in the second stage carbonaceous matter is destroyed using the bacterium Streptomyces setonii. After biooxidation of sulfides in the first stage, cyanidation resulted in 81.1% gold extraction. The action of Streptomyces setonii in the second stage led to a reduction in the content of carbonaceous matter, which reflected positively in the preg-robbing and leaching behavior of the sample. Degradation of carbonaceous matter was affected by pulp density, temperature and retention time. After degradation of carbonaceous matter, gold extraction increased by 13.6% resulting in an overall extraction of 94.7%. The results depict a novel two-stage microbial process to degrade both sulfides and carbonaceous matter and increase gold recovery from double refractory ores.

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1. Introduction

Refractoriness in gold ores may be caused by several factors including the presence of sulfides, tellurides, cyanides and carbonaceous matter (Boyle, 1979; Guay, 1981). When it is due to the presence of both sulfides and carbonaceous matter (CM), the ore is said to be double refractory (Nyavor and Egiebor, 1992). In such ores, gold particles may sometimes be occluded or included in the sulfide minerals and pretreatment is necessary to decompose the mineral structure to liberate gold for subsequent recovery. The CM acts as a preg-robber during cyanidation and therefore has to be eliminated or passivated before gold dissolution (Henley, 1975; Osseo-Asare et al., 1984; Demopoulos and Papangelakis, 1987; Afenya, 1991; Linge, 1991).

The pretreatment processes used for such refractory sulfide ores include roasting, chlorination, pressure oxidation and bacterial oxidation (Arriagada and Osseo-Asare, 1984; Berezovsky and Weir, 1989; Marsden and House, 1992). Bacterial oxidation utilizes chemolithotrophic bacteria to decompose the sulfide matrix to release gold particles. A number of bacteria are used in biomining but the prominent ones that are known to be involved in the oxidation of sulfide ores include Thiobacillus ferrooxidans, Thiobacillus thiooxidans and Leptospirillum ferrooxidans. (Brierley and Brans, 1994; Brierley, 1995; Hackl, 1997; Rawlings, 1998).

Due to the bacteria’s interaction with the minerals, ferrous iron in the ore is converted to the ferric state and the sulfide sulfur is ultimately converted to sulfate and sulfuric acid. Gold is also released from the sulfides. Unfortunately, carbonaceous materials are not oxidized by this pretreatment step and continue to serve as preg-robbers in the subsequent gold leaching process.

Some studies on the microbial degradation of CM have been reported. Brierley and Kulpa (1992) and Kulpa and Brierley (1993) showed that a consortium of heterotrophic bacteria, many of which are from the Pseudomonas family and naturally associated with gold ores, could deactivate the active sites on carbonaceous components leading to increase in gold recovery during cyanidation. Portier (1991) used other heterotrophic bacteria and some fungi to degrade CM and reported increases in gold recovery due to microbial action.
In this study, biooxidizing the carbonaceous material with an actinomycete, *Streptomyces setonii*, to enhance gold recovery is investigated. Our results suggest a two-stage process for the biooxidation and destruction of sulfides and CM. Chemolithothrophic bacteria are to be used in the first stage to oxidize sulfides and the degradation of CM is done in the second stage using *S. setonii*. This microorganism is known to solubilize lignin and some grades of coal (Antai and Crawford, 1981; Strandberg and Lewis, 1988; Quigley and Dugan, 1989). The biooxidation of both sulfides and carbonaceous material would significantly improve gold recovery in the subsequent cyanidation step.

2. Experimental

2.1. Ore characterization

Flotation concentrate was obtained from a plant that processes double refractory gold ores. The particle size was 80% passing 75 μm. Sulfur and carbonaceous matter (CM) in the samples were determined using the Leco combustion volumetric method. A LECO titrator SC-444DR was used in this study. The grade of gold was determined by conventional fire assaying. The main sulfide minerals were pyrite and arsenopyrite. The grade of some important constituents of the flotation concentrate used is shown in Table 1.

2.2. Microorganisms and inoculum preparation

The bacteria used were *Thiobacillus thiooxidans* (ATCC 15494), *Thiobacillus ferrooxidans* (ATCC 19859), *Leptospirillum ferrooxidans* (ATCC 53992) and *Streptomyces setonii* (ATCC 39116). *T. thiooxidans*, *T. ferrooxidans*, *L. ferrooxidans* were grown together to form a mixed culture.

The mixed cultures were maintained in a medium containing 0.5 g/l of (NH₄)₂SO₄, K₂HPO₄, MgSO₄·7H₂O, 0.1 g/l KCl and 0.01 g/l Ca(NO₃)₂. The rest are 15.0 g/l FeSO₄·7H₂O, 1.0 g/l sulfur and 0.25 ml/l of Wolfe’s solution. Transfer into fresh medium was done every 6 weeks. Cultures for biooxidation experiments were prepared by transferring 10% (v/v) of maintenance culture into fresh growth medium containing 0.5 g/l of (NH₄)₂SO₄, K₂HPO₄, MgSO₄·7H₂O, 0.1 g/l KCl and 0.01 g/l Ca(NO₃)₂.

*S. setonii* were maintained on tryptone and yeast extract agar plates at 4 °C and by periodic transfer of 10% (v/v) of a liquid culture into fresh growth medium containing 5 g/l tryptone and 3 g/l yeast extract, supplemented with 0.5 g/l KCl, MgSO₄·7H₂O, 0.1 g/l FeSO₄·7H₂O and K₂HPO₄ as inorganic nutrients. Cultures for destruction of CM had a similar composition.

2.3. Microbial-mineral interactions

The microbe, *S. setonii*, is a neutrophile while the others are acidophiles, hence it was not possible to carry out the process in a single stage. A two-stage degradation process was adopted in the study.

Biooxidation of sulfides is currently a well-known technique and the operational parameters have been well established (Brierley and Kulpa, 1992; Kulpa and Brierley, 1993; Hackl, 1997; Rawlings, 1998). The sulfide concentrates were biooxidized in a reactor at 42 °C over a period of 5 days at a pulp density of 20% solids using a mixed culture of already grown chemolithotrophic bacteria *T. thiooxidans*, *T. ferrooxidans* and *L. ferrooxidans*. The initial pH was adjusted to between 1.2 and 1.8 with sulfuric acid.

The products of sulfide biooxidation were filtered and washed several times with de-ionized water. Several portions of the oxidized material were weighed out into 250 ml Erlenmeyer flasks containing 80 ml of a culture of *Streptomyces setonii* for destruction of the CM. The pulp densities were between 5% and 40% and the flasks were agitated on an orbital shaker at 150 rpm. The parameters monitored in these experiments were temperature, time and pulp density. At the end of the contact period, the ore samples were filtered, washed with water and dried. Duplicate experiments were run and the differences in values were within 4%.

In order to ascertain the state to which CM was converted, a chemical scrubber was mounted on one flask to remove carbon dioxide from the inlet air and a barium hydroxide trap was used to detect any carbon dioxide evolution. Visual observations were also conducted.

2.4. Post-bacterial pretreatment investigations

2.4.1. Determination of changes in content of CM

Reduction in the percentage of CM was determined quantitatively using the Leco volumetric combustion technique. To prevent the organic carbon in the bacte-

<table>
<thead>
<tr>
<th>Component/grade</th>
<th>Sulfide sulfur (%)</th>
<th>Sulfate sulfur (%)</th>
<th>Total sulfur (%)</th>
<th>Au (g/t)</th>
<th>Carbonaceous matter (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>11.9</td>
<td>Trace</td>
<td>11.9</td>
<td>65.3</td>
<td>6.1</td>
<td></td>
</tr>
</tbody>
</table>

Table 1
Results of partial chemical analysis of flotation concentrate used
rial cells from influencing the determination of carbon, the biomass was dissolved from samples of pretreated material before carbon analysis. After digestion was done using 5% hypochlorite for 30 min as described by Berger et al. (1989) and Ramsay et al. (1990), samples were rinsed with distilled water.

2.4.2. Evaluation of gold extraction after microbial degradation

Preg-robbing and cyanidation tests were used to evaluate the gold extraction properties of products obtained from the microbial pretreatment processes. All pretreated samples used in these experiments were washed with water and dried before evaluation.

Preg-robbing tests were conducted on both pretreated and untreated ore samples. Five-gram samples were placed in 20 ml solution of potassium gold cyanide containing 4.5 mg Au/l in 100-ml flasks. The pH was kept at 10.5 and free cyanide concentration was negligible, hence no gold dissolution took place in the course of the preg-robbing tests. The samples were agitated on an orbital shaker at 175 rpm for 24 h. The ore was then separated from the solution and the final concentration of gold in solution determined using an atomic absorption spectrophotometer. The difference in gold concentration before and after the solution-ore contact is the gold preg-robbing percentage.

The effect of bacterial pretreatment on gold recovery was determined by cyanide leaching. Cyanidation was conducted on 100 g each of ore after biooxidation of sulfides and after both biooxidation of sulfides and destruction of CM. Samples were leached at a pulp density of 40% by weight for 24 h at pH 10.5–11. The pH was adjusted using 0.1 M sodium hydroxide and cyanide strength was 10 kg/t. The dissolved gold concentration was determined using atomic absorption and the remaining gold in the residue was determined by conventional fire assay method.

3. Results and discussion

3.1. Biooxidation of sulfides

Biooxidation of sulfides using the chemolithotrophic bacteria is currently a standard practice and has been applied in industry for some years. Bacteria such as *T. thiooxidans*, *T. ferrooxidans* and *L. ferrooxidans* are known to oxidize ferrous sulfides to ferric sulfate and sulfuric acid (Brierley and Kulpa, 1992; Kulpa and Brierley, 1993; Hackl, 1997; Rawlings, 1998). The oxidation of sulfides in the sample using *T. thiooxidans*, *T. ferrooxidans* and *L. ferrooxidans* for 5 days at 42°C resulted in 72.3% oxidation of sulfur from a head grade of 11.9%.

There was a progressive increase in the ferric: ferrous ratio over 5 days (Fig. 1), which indicates that ferrous iron present in the sulfide minerals, was oxidized to the ferric state. There was total conversion of ferrous iron to ferric before the reaction was terminated. The ferric iron is a strong oxidizing agent, which promotes the indirect chemical oxidation reactions of ferrous sulfides. Accordingly there was an increase in redox potential to a maximum value above 600 mV.

3.2. Bacterial degradation of carbonaceous matter

The components of carbonaceous matter associated with gold ores include hydrocarbons, humic acids and elemental carbon. Maturity of the elemental carbon fraction ranges from high rank lignite to anthracite and the distribution of these components vary from one deposit to another (Radtké and Scheiner, 1970; Osseo-Asare et al., 1984; Hausen and Bucknam, 1984; Stenebraten et al., 1999, 2000). Analysis of samples from a deposit similar to the one used in this study revealed the presence of hydrocarbons, humic acid and elemental carbon (Afena, 1976; Osseo-Asare et al., 1984).

The actinomycete *S. setonii* is known to degrade some types of coal, which contains all the components present in the CM. In this investigation, bacterial metabolic activity led to an increase in pH from 7.0 to above 9.0. A similar increase had been observed by Strandberg and Lewis (1988) and Quigley and Dugan (1989) in their investigations using coal. The authors suggested that the production of alkaline metabolites was responsible for coal degradation. The filtrates obtained after degradation of CM were much darker than the original cultures, which indicate that some components have been solubilized. The barium hydroxide trap mounted also indicated the evolution of carbon dioxide during degradation.
3.2.1. Carbon analysis before and after hypochlorite digestion of biomass

The carbon content of samples was determined directly after the interaction of ore and microorganisms and significant reductions were observed (Table 2). The values were reduced further after the biomass was digested with hypochlorite. When a sample that had not been contacted with \textit{S. setonii} was digested with hypochlorite, there was only a 0.15% reduction in carbon content. This indicates that the decrease in CM after treatment with \textit{S. setonii} was not due to hypochlorite digestion but rather to microbial activity. When pure silica flour was contacted with bacteria and digested the same way, samples retained 0.068% of the carbon introduced by the biomass. The residual carbon content from biomass was therefore assumed negligible.

\begin{table}[h]
\centering
\begin{tabular}{|c|c|c|}
\hline
Sample number & Before biomass digestion & After biomass digestion \\
\hline
1 & 3.67 & 2.54 \\
2 & 4.19 & 3.20 \\
3 & 3.62 & 2.85 \\
\hline
\end{tabular}
\caption{Carbon content of some samples before and after digestion of biomass}
\end{table}

Original carbon content of sample was 7.03%.

3.2.2. Effect of pulp density

There was a marked increase in decomposition of CM as the pulp density decreased (Fig. 2). The CM was reduced by about 80% at a pulp density of 5% within 14 days. For the same period, the decrease of CM at 40% solids was 38.2%. As pulp density increases, the concentration of CM would also increase and since the bacteria are aerobic, the rate of oxygen consumption would increase. This could result in oxygen limitation at higher pulp densities giving rise to lower conversions. Indeed dissolved oxygen (DO) concentration decreased as pulp densities increased (Fig. 2).

3.2.3. Effect of contact time

To determine the effect of contact time on the degradation of CM, pulp densities of 5% and 20% solids were exposed to \textit{S. setonii} over 56 days. At 20% solids, 59.4% of CM was removed after 14 days and about 80% by day 56. At a pulp density of 5% solids, about 80% of the CM was degraded within 14 days with a slight increase to 89% at the end of 56 days (Fig. 3).

In a batch system such as the one used in this study to degrade CM, bacterial growth and hence metabolic activity increases to a maximum then decreases beyond that point. However, in a continuous system, the growth phase is sustained indefinitely (Shuler and Kargi, 1992). It is therefore likely that the residence time could be reduced in a continuous system while maintaining a high percentage of degradation.

3.2.4. Effect of temperature

There was no appreciable change in degradation of CM with increase in temperature from 23 to 37°C (Fig. 4). Within this temperature range the bacteria degraded...
an average of 59.4% of the CM at 20% solids pulp density and about 80% at 5% solids. There was an increase in CM degraded at 45°C with about 76% reduction achieved at a pulp density of 20% solids and a maximum of 85.7% at a pulp density of 5% solids. This suggests that metabolic activity of the microbe was greater at 45°C leading to a higher rate of reaction. Unfortunately, it was not possible to investigate higher temperatures since *Streptomyces* usually do not survive beyond 50°C (Crawford et al., 1984; Hirsch and McCann-McCormick, 1985).

3.3. Effect of bacterial action on preg-robbing and gold extraction

There was a much lower preg-robbing activity after bacterial destruction of CM (Table 3) and a low sorption value of 8.2% was obtained for the sample that was pretreated for 14 days at 45°C. The sample pretreated at 23°C for 56 days also recorded a low adsorption value of 9.8%.

In the recovery of gold by cyanidation after biooxidation of sulfides, the initial gold dissolution was very fast with over 50% extraction by the second hour (Fig. 5). After 24 h, 81.1% extraction was achieved. When compared with the two-stage process of sulfide biooxidation followed by destruction of CM, the second bacterial pretreatment had an enhancing effect on leaching and gold extraction increased to 94.7%. The increase in recovery during cyanide leaching can be attributed to the reduction in percentage of CM.

4. Processing proposal

The results of this investigation constitute a novel technical process for recovering gold from double refractory ores. As indicated on the flow diagram (Fig. 6), sulfides in flotation concentrate are subjected to biooxidation using the chemolithotrophic bacteria

![Flow diagram](image)

Fig. 6. Proposed flow sheet for the two-stage bacterial pretreatment of double refractory gold ores.

![Graph](image)

Fig. 5. Gold extraction after the first pretreatment stage (before CM degradation) and after the two-stage pretreatment (after degradation of CM).

<table>
<thead>
<tr>
<th>Sample description</th>
<th>Final gold concentration, ppm</th>
<th>% Preg-robbing</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sample after bacterial oxidation of sulfides (B)</td>
<td>2.17</td>
<td>51.8</td>
</tr>
<tr>
<td>B. <em>after degradation of CM at 20% solids pulp density</em></td>
<td></td>
<td></td>
</tr>
<tr>
<td>14 days at 23°C</td>
<td>3.37</td>
<td>25.1</td>
</tr>
<tr>
<td>56 days at 23°C</td>
<td>4.06</td>
<td>9.8</td>
</tr>
<tr>
<td>14 days at 45°C</td>
<td>4.13</td>
<td>8.2</td>
</tr>
</tbody>
</table>

Original concentration of gold solution was 4.5 ppm.
T. thiooxidans, T. ferrooxidans and L. ferrooxidans. The oxidation product is washed and wastewater neutralized using lime before disposal as practiced in biooxidation plants. The solid product of biooxidation is transferred for bio-destruction of carbonaceous matter using S. setonii. After washing, gold in the solid residue can then be leached using the well-known process of cyanidation and the dissolved gold recovered.

The technical advantages of this proposal compared with the current biooxidation process is that the two-stage pretreatment process leads to a drastic reduction in the preg-robbing behavior of the ore and an increase in gold recovery during cyanidation. The process is also environmentally compatible.

5. Conclusions

From the results and discussions above, it can be concluded that this two-stage microbial process for double refractory ores lead to a substantial increase in gold extraction. The three well-known chemolithoautotrophic biomining bacteria oxidized sulfides in the first stage and S. setonii, a coal-degrading microbe, degraded the carbonaceous matter in refractory gold ores. The combined effects of these steps resulted in an overall gold recovery of 94.7% after cyanidation. This shows an increase of 13.6% over the single stage sulfide biooxidation process.

References


