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Effect of biological pretreatment on metal extraction from flotation tailings for chloride leaching

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ABSTRACT
This study focuses on investigating the extraction of gold, copper, iron, nickel, cobalt, and zinc present in the flotation tailings. The studied sample contained iron (3.56%), copper (0.09%), and gold (0.2 ppm) as major target elements, whereas cobalt (0.04%), nickel (0.03%) and zinc (0.04%) were trace elements of interest. Primarily, bioleaching with mixed acidophilic culture was applied as a pretreatment process for the recovery of nickel, cobalt, and zinc, as well as for iron removal. The effect of solid concentration (5–12.5%) in bioleaching was investigated at pH 1.8 and the temperature was kept at 32 °C. The highest extractions of nickel, cobalt, zinc, and iron at 5% and 7.5% solid concentrations in the bioleaching experiments were 90%, 60%, 86% and 67%, respectively. Dissolution of gold and copper was not observed. The residues from bioleaching pretreatment were applied for chemical chloride leaching to extract gold and copper into the solution. In chloride leaching, the highest extractions of copper and gold were 98% and 63%, respectively. In addition, residual nickel, cobalt, and zinc were dissolved into the solution with the extraction of 99%, 80%, and 90%, respectively. In all chloride leaching experiments, the highest extractions of iron, copper, gold, nickel, cobalt, and zinc were observed with biologically pretreated feed. Alternatively, residues from bioleaching were also subjected to conventional cyanide leaching. Dissolutions of copper, nickel, cobalt and zinc were shown to be higher in chloride solution, however, 7%-unit more of gold could be extracted by cyanidation. With these findings, it appears that the combination of biological pretreatment and chloride leaching can provide a non-toxic process for improved valuable metals extraction from low-grade tailings.

1. Introduction

Mining industry has challenges to produce pure metals due to decreasing grade and complexity of ores. Thus, new processes for the extraction and recovery of metals from mine tailings are of interest. However, tailings can contain not only valuable metals, such as gold, copper, nickel, cobalt, and zinc, but also hazardous metals like arsenic, lead, and cadmium which may cause harm to the environment (Xie et al., 2005; Hao et al., 2016). With the aim to decrease environmental concerns and to increase metal recovery from tailings, improved and economical technologies are essential (Liu et al., 2005). Metals in sulfide tailings are mostly present as very fine particles and enclosed in sulfide matrix, and the extraction of these metals into leaching solution can be very challenging (Ozkank et al., 1998; Marsden and House, 2006).

There are several pre-treatment processes for sulfide ores/concentrates to improve the metal extraction. Roasting can be used as a pre-treatment process to remove harmful components by oxidation and it releases gold and/or precious metals from sulfide matrix before conventional cyanide leaching. However, the roasting process has some challenges due to a low metal recovery and environmental pollution concerns (Lawrence and Bruynesteyn, 1983). Pressure oxidation allows sulfide oxidation in autoclave and has been applied during the last couple of decades in the industrial scale (Aylmore and Jaffer, 2012). Bioleaching is one of the alternative pretreatment processes which is potentially economic, environmentally friendly and effective in leaching various metals from sulfide tailings, without any requirement for high temperature, pressure, and with no gaseous emissions (Lee and Pandey, 2012). In the past couple of decades, the extraction of gold, copper, nickel, zinc, and uranium by heap bioleaching and bio-oxidation (Outotec BIOX®) from sulfide ores/concentrates in large/industrial scales has been of great interest.
scale has obtained more attention (van Aswegen et al., 2007; Erust et al., 2013).

Bioleaching utilizes acidophilic sulfur and/or ferrous iron oxidizing microorganisms, which can convert reduced sulfur compounds to sulfuric acid (H₂SO₄), and ferrous to ferric iron (Fe³⁺). H₂SO₄ and Fe³⁺ leach sulfide minerals, releasing encapsulated metal, and enabling the dissolution of metals into the leaching solution (Aromaa et al., 2013; Sand et al., 2001; Suzuki, 2001). The following reactions (1–5) show the bioleaching of pyrrhotite mineral. Pyrrhotite can be oxidized by oxygen, ferric ion or by acid. Furthermore, oxygen feed oxidizes ferrous iron (Fe²⁺) to ferric iron (Fe³⁺), ferric iron being also excellent oxidant for pyrrhotite (Garg et al., 2015; Arpalahti and Lundström, 2018). The oxidation of ferrous iron with just oxygen is very slow at low pH, however presence of microorganisms, oxidation process can be boosted significantly more than a million times (Brierley, 1982; Morrow 2001).

\[
\begin{align*}
\text{FeS} + 7\text{H}_2\text{SO}_4 \rightarrow 7\text{FeSO}_4 + 7\text{H}_2\text{S} + \text{S} \\
\text{FeS} + \text{H}_2\text{O} + 15.5\text{O}_2(g) \rightarrow 7\text{FeSO}_4 + \text{H}_2\text{O} \\
\text{FeS} + \text{O}_2(g) \rightarrow 7\text{FeSO}_4 + \text{S} \\
\text{FeS} + 31\text{Fe}(\text{SO}_4)_2 + 32\text{H}_2\text{O} \rightarrow 69\text{Fe}(\text{SO}_4) + 32\text{H}_2\text{SO}_4 \\
\text{FeS} + 7\text{Fe}(\text{SO}_4)_2 \rightarrow 21\text{FeSO}_4 + 8\text{S}^0
\end{align*}
\]

Table 1 presents the working temperature of acidophilic microorganisms, which can participate in the dissolution of sulfide minerals. Operating temperature of mesophilic microorganisms in bioleaching of sulfide minerals is maximum 40 °C. Also, moderately and extremely thermophilic microorganisms are used for improving the dissolution rate of sulfide minerals from chalcopyrite at higher process temperature. The reason of effective chalcopyrite leaching with the extremely thermophilic microorganisms can be that passivating sulfur layers which occur during the leaching are less stable at higher temperature (Stott et al., 2000; Rodríguez et al., 2003; Rawlings et al., 2003; Torma, 1977). Also, processes using thermophilic microorganism can run up to 85 °C (Deveci et al., 2003; Rawlings et al., 2003). Torma (1977) mentioned that bioleaching of most of the sulfide minerals runs at the optimum pH level of 1.5–2.3. However, industrial applications such as BIOX® (van Aswegen et al., 2007) and BacTech® (Miller et al., 1999) have lower pH level than optimum conditions (1.2–1.8 and 1.3–1.5, respectively).

Due to the toxicity of cyanide, many alternative processes have been developed to recover gold, precious metals from primary and/or secondary materials. Chloride is one of the most promising alternatives, being non-toxic, allowing fast extraction kinetics and, low environmental impact, less gold passivation, and furthermore, being able of dissolving also refractory ores (Lampinen et al., 2017; Marsden and House, 2006; Soo Nam et al., 2008). Thus, the objective of this work was to investigate a new method to extract, copper, nickel, cobalt, and zinc from low grade flotation tailings by biological pretreatment prior to cyanide free chloridle leaching, targeted for gold and copper.

2. Materials and methods

2.1. Microorganisms and adaptation

The mixed acidophilic culture, which contains Acidithiobacillus ferroxidans, Acidithiobacillus thiooxidans/albertensis, Acidithiobacillus caldus, Leptospirillum ferrooxidans, Sulfbacillus thermosulfidooxidans and some Alicyclobacillus species was originally enriched from a sulfide ore mine (Halinen et al., 2009). The culture was adapted to the studied material in duplicate 250 ml Erlenmeyer flasks with 100 ml working volume. The flasks were inoculated with acidophilic mixed culture (10 ml) into 0 K cultivation medium (Table 2) (modified 9 K medium without ferrous iron, Silverman and Lundgren, 1959) (90 ml) followed by tailing sample addition (1–10 g/L). Shake flask experiments were run in a rotary shaker at 32 °C, which was chosen according to the most dominant microorganism in the mixed culture (L. ferrooxidans) (Table 1). Rotary speed was kept constant at 150 rpm, and pH was adjusted to 1.5 with concentrated sulfuric acid (H₂SO₄, 95%). Oxygen and carbon dioxide were supplied from air throughout the 22 days experiments.

In the adaptation experiments, the effect of solid concentration (w/v) (1–10%) was studied. The pH and redox potential (mV vs. Ag/AgCl in 3 M KCl) were measured every second day. Samples were taken after 1, 5, 10, and 22 days from the solution and analyzed after the filtration. In addition to the adaptation experiments, chemical control leaching experiments were carried out in shake flasks without inoculum, where only 0 K medium was added and H₂SO₄ was used to adjust pH to 1.5. Prior to the chemical control experiments, feed material was dried in the oven at 60 °C for 3 days.

2.2. Bioleaching in reactors

Bioleaching experiments of flotation tailings were operated with 5 L total solution in a titanium reactor. The solution contained 4500 ml 0 K medium (Table 2) with the adapted microbial culture as inoculum (500 ml). The effect of solid concentration (w/v) (5%, 7.5%, 10% and 12.5%) on metal extraction was investigated at 32 °C and 300 rpm

<table>
<thead>
<tr>
<th>Table 1</th>
<th>Working temperature of acidophilic microorganisms in bioleaching processes (modified from Deveci et al., 2003; Holanda et al., 2016).</th>
</tr>
</thead>
<tbody>
<tr>
<td>Microorganism type</td>
<td>Culture</td>
</tr>
<tr>
<td>Mesophilic</td>
<td>Acidithiobacillus (At.) ferroxidans</td>
</tr>
<tr>
<td></td>
<td>Leptospirillum (L.) ferrooxidans</td>
</tr>
<tr>
<td></td>
<td>Acidithiobacillus thiooxidans</td>
</tr>
<tr>
<td></td>
<td>Acidithiobacillus (Ab.) ferrooxidans</td>
</tr>
<tr>
<td>Moderate thermophilic</td>
<td>Sulfbacillus (Sb.) thermosulfidooxidans, Sb. acidophilus</td>
</tr>
<tr>
<td></td>
<td>Ac. caldus</td>
</tr>
<tr>
<td>Extreme thermophilic</td>
<td>Sulfoloba-like archaea</td>
</tr>
<tr>
<td></td>
<td>Sulfoloba. metallica</td>
</tr>
<tr>
<td></td>
<td>Acidianus. briareyi</td>
</tr>
</tbody>
</table>

*Acidibacillus ferroxidans has not yet validly published under the rules of the International Code of Nomenclature of Bacteria.

<table>
<thead>
<tr>
<th>Table 2</th>
<th>Mineral salts and elements in 0 K medium (modified 9 K medium without ferrous iron, Silverman and Lundgren, 1959).</th>
</tr>
</thead>
<tbody>
<tr>
<td>Chemical</td>
<td>Amounts (g/L)</td>
</tr>
<tr>
<td>(NH₄)₂SO₄</td>
<td>3</td>
</tr>
<tr>
<td>KCl</td>
<td>0.1</td>
</tr>
<tr>
<td>K₂HPO₄</td>
<td>0.5</td>
</tr>
<tr>
<td>MgSO₄ * 7H₂O</td>
<td>0.5</td>
</tr>
<tr>
<td>Ca(NO₃)₂ * 4H₂O</td>
<td>0.14</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Table 3</th>
<th>Solid concentration and leaching time of the bioleaching experiments.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Experiment ID</td>
<td>Solid concentration (w/v, %)</td>
</tr>
<tr>
<td>B1</td>
<td>5</td>
</tr>
<tr>
<td>B2</td>
<td>7.5</td>
</tr>
<tr>
<td>B3</td>
<td>10</td>
</tr>
<tr>
<td>B4</td>
<td>12.5</td>
</tr>
</tbody>
</table>
stirring rate for 11 or 15 days (Table 3). Aeration was provided from the bottom of the reactor at a flow rate of 3 L/min and the pH was controlled with concentrated H2SO4 (95%) in the beginning of experiments to 1.8. Samples were taken after 1, 4, 7, 11, and 15 days for analyzing from solution and solid residue. Experiments were monitored by pH, redox potential (mV vs. Ag/AgCl in 3 M KCl), and dissolved Fe (mg/L). Consort C3040 electrochemical analyzer was used for both pH and redox measuring. Manufacturer and model of pH and redox potential electrodes were Van London Phoenix PH7V110-10B-300 and Van London Phoenix RP75130-10B-300, respectively.

### 2.3. Chloride leaching

Chloride leaching experiments were run with the residues (B1 and B2) from the bioleaching tests in 21 titanium reactor at Outotec Research Center, Pori, Finland. The effect of microbial pretreatment was investigated with as-received (d80 = 150 µm) and ground (d80 = 26 µm) materials with the addition of an external oxidant (cupric ion) (copper II chloride hydrate, CuCl2·2H2O, VMR chemicals, technical grade) (30 g/L, Cu2+) and in the absence of additional oxidant in 250 g/L sodium chloride (NaCl) (MERCK, analytical grade). Table 4 shows the conditions of chloride leaching experiments. Cupric ion experiments were run for 24 h at the pH of 1.8. The experiments in the absence of cupric ions (Cu2+) were performed for 72 h at the pH of 1. Temperature (95 °C), oxygen purging (1200 LN/min), solid: liquid ratio (1:3), and stirring rate (950 rpm) were kept fixed and pH was adjusted with HCl (37%) and NaOH (20 g/L) in all leaching experiments. Samples were taken after 0, 1, 2, 4, 8, 12, 16 and 24 h and in addition after 48, 60 and 72 h in the absence of cupric ions. Metal concentrations of filtered (pore size filter, 0.45 µm) samples and solid residues were determined.

### 2.4. Cyanide leaching

Cyanide leaching (Experimental ID CN1) was run for 72 h at 2 g/L initial sodium cyanide (NaCN) concentration with bioleaching residue (B2) (d80: 150 µm) in 1 L mechanically agitated glass reactor. Experiment was conducted under the following conditions: pH = 11 (adjusted by NaOH), room temperature (22 °C), 25% of solid concentration, 500 ml/min of air feed, and 400 rpm of stirring rate. After taking samples in 0, 1, 2, 4, 8, 12, 16, 24, 48, and 72 h, filtration was applied for solid and liquid separation. Concentration of metals from samples and residues were determined.

### 2.5. Analytical methods

Chemical and mineralogical composition of the raw material was analyzed by Inductively Coupled Plasma Optical Emission Spectrometry (ICP-OES) (Thermo Scientific iCap 6000), Inductively Coupled Plasma Mass Spectrometry (ICP-MS) (Thermo Scientific iCap Q) after total dissolution. Gold was analyzed from duplicate samples by Fire Assay method. Main gangue minerals were determined with X-ray diffraction (XRD) (Bruker D8 ECO) and polished section was prepared for mineralogical study in a JEOL JSM-6490LV Scanning Electron Microscope (SEM). Concentration of Fe, Cu, Ni, Co, and Zn from leaching solution and residue samples were analyzed by ICP-OES (Thermo Scientific iCap 6000). Au was analyzed by ICP-MS (Thermo Scientific iCap Q) and Fire assay method from the solution and residues, respectively. The particle size distribution was determined with laser diffraction method by Malvern Mastersizer 3000 analyzer.

### 3. Results and discussion

#### 3.1. Material composition

The studied raw-material in the leaching was tailings originating from a flotation process. The studied sample contained iron (3.5%), copper (0.09%), and gold (0.2 ppm), whereas cobalt (0.04%), zinc (0.04%), nickel (0.03%) were the trace elements of interest. Hornblende -type amphibole, quartz, and dolomite composed 83% of the sample and phlogopite, chlorite, and magnetite occurred as accessory gangue minerals. Most abundant ore minerals were pyrrhotite (2.85%) and pyrite (1.83%), with accessory chalcopyrite (0.25%), pentlandite (0.08%), and sphalerite (0.07%). Gold was present as free milling and between 1 and 3 µm of grain size. The particle size distribution (d80) of the original sample was 150 µm and ground for 120 min grinding time to 26 µm in a laboratory ball mill at slurry density of 65 wt% and 600 rpm rotation speed.

#### 3.2. Adaptation

Fig. 1 presents the observed pH, redox potential, and dissolved iron concentration at different solid concentrations (1%, 5% and 10%). The highest redox potential (+690 mV vs. Ag/AgCl), maximum dissolved Fe (mg/L) (1310 mg/L) and pH (1.5) within five days with only 0.05 ml/L acid consumption were observed in 5% solid concentration in the presence of micro-organisms. In the absence of micro-organisms (control experiments) highest acid consumption, 0.2 ml/L, was observed at the same solid concentration. Rapid increase of initial pH in the beginning of the leaching can be inferred to the dissolution of pyrrhotite, which is an acid consuming mineral (Arpalahti and Lundström, 2018). Once pyrrhotite had oxidized, then the process started to produce acid. Therefore, pH started to decline after 5th day and later on it stayed constant.

Table 5 presents the leaching yields (%) of Ni, Co, Zn, Fe, Cu and Au after 22 days of leaching. In the control experiment with 5% solid concentration, the maximum yields of nickel, cobalt, zinc, and iron were 44%, 25%, 20%, and 60%, respectively. In the same conditions with bioleaching, up to 84%, 71%, 72%, and 72% of nickel, cobalt, zinc, and iron were extracted. Gold and most of copper remained in the leach residue. Due to the observed high metal extractions, 5% solid concentration was chosen for reactor bioleaching experiments.

#### 3.3. Effect of solid concentration on the extraction of metals in bioleaching reactors

The effect of solids concentration (5%, 7.5%, 10%, and 12.5%) on bioleaching was evaluated with four reactor experiments (B1, B2, B3, and B4). Fig. 2(a)–(d) presents the extractions of nickel, zinc cobalt, and iron, respectively. As expected, the maximum extractions for Ni, Zn, and Co (90%, 86%, and 60%, respectively) were achieved at the lowest 5% solid concentration (Experiment B1). However, the final dissolution of Fe in the test having 7.5% solid concentration (Experiment B2) was 20%-units higher than at 5% solid concentration. According to the solution analysis, gold did not dissolve. In all experiments (B1-B4) copper dissolution into the solution was below 15%. The reason for this can be as Bhatti et al. (2012) mentioned, that during the bioleaching secondary solids phases such as jarosite and elemental S can be formed on.
the surface of chalcopyrite. Low leaching kinetics of cobalt can be related to pyrite, which is the main cobalt carrying mineral and chalcopyrite, which locks pyrite and pyrrhotite in the mineral matrix. During the first 4 days the pH was above 5 in all experiments, and it was decreased with the addition of H$_2$SO$_4$ to 1.8. When the material was added to the solution, redox potential decreased to +250 mV. Redox potential started to rise after the second day until the end of the experiment and reached the maximum value of +670 mV in 5% solid concentration (Experiment B1).

Table 6 shows the chemical composition of leach residues (solids) after bioleaching experiments. Metal concentrations of the material decreased significantly in bioleaching experiments. Residues from experiments B1 and B2 were used as a feed material in the following chloride experiments.

3.4. Effect of bacterial pretreatment on metal recovery in chloride leaching

Experiments C1 and BC1 were run for 72 h in the absence of cupric ions, where only oxygen was used as oxidant, solution had 250 g/L NaCl, pH was kept constant to 1. Fig. 3 shows the copper extractions as a function of time in chloride leaching with comparison of biological pretreatment process for as-received material (d$_{80}$: 150 µm). The maximum extraction of copper in direct chloride leaching was 80% (Experiment C1). After bacterial pretreatment process, 98% of copper was extracted in chloride leaching (Experiment BC1). Based on solid analyses of leach residues, dissolution of gold into the solution in direct chloride leaching was only 30%, whereas gold extraction of 63% could be achieved after biological pretreatment in chloride leaching. Table 7 presents the metal concentrations of the feed material and final residues from chloride leaching experiments.

Experiments C2 and BC2 were run with the addition of cupric ions (30 g/L) directly or after biological pretreatment for chloride leaching, respectively. Experiments were carried out in 250 g/L NaCl, at pH 1.8, and 24 h with ground material (d$_{80}$ = 26 µm). The maximum dissolution of Ni, Co, and Zn (99%, 80%, and 90%, respectively) into the solution was achieved in the experiment BC2, which was run with biological pretreatment process. In chloride leaching without biological pretreatment, the extractions of Ni, Co, and Zn into the solution were 20–30%-units lower than with biological pretreatment. This can be seen in the Fig. 4(a)–(c), where all metal dissolutions presented are calculated only from chloride leaching stages (see Fig. 4(a)–(c)). Lower dissolution rate of cobalt can be a consequence of slow dissolution kinetics of pyrite, which is the cobalt bearing mineral in the investigated
Based on solid analyses, gold dissolutions were 50% and 30% into the solution with and without biological pretreatment, respectively.

3.5. Effect of particle size on metal extraction

Fig. 5 illustrates the effect of particle size (d80, as-received 150 µm and ground 26 µm) on metal extractions of Au, Fe, Cu, Ni, Zn, and Co in chloride leaching in the presence of biological pretreatment (Experiments BC1 and BC3). Both experiments were conducted at 250 g/L NaCl, pH 1, 95 °C for 72 h. The results indicate that the dissolution of iron, nickel, and cobalt into the solution was much higher (25–50% unit) with finer material (ground) than with coarser (as-received) material (Experiment BC1). However, the extraction of Au, Cu and Zn was somewhat higher (2–9%) with as-received material (Experiment BC3). The reason for higher extractions of nickel, zinc, and cobalt with ground material compared to as-received material can be the liberation of metals in the grinding process resulting in higher leaching kinetics.

Table 6
Chemical composition (%) of original feed material and the leach residues (labelled as *LR) from bioleaching experiments.

<table>
<thead>
<tr>
<th>Sample name</th>
<th>Fe (%)</th>
<th>Cu (%)</th>
<th>Au (ppm)</th>
<th>Ni (%)</th>
<th>Co (%)</th>
<th>Zn (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Original Feed</td>
<td>3.56</td>
<td>0.09</td>
<td>0.2</td>
<td>0.03</td>
<td>0.04</td>
<td>0.04</td>
</tr>
<tr>
<td>B1*LR</td>
<td>2.15</td>
<td>0.07</td>
<td>0.13</td>
<td>0.01</td>
<td>0.02</td>
<td>0.03</td>
</tr>
<tr>
<td>B2*LR</td>
<td>1.41</td>
<td>0.06</td>
<td>0.16</td>
<td>0.01</td>
<td>0.02</td>
<td>0.03</td>
</tr>
<tr>
<td>B3*LR</td>
<td>2.45</td>
<td>0.07</td>
<td>0.16</td>
<td>0.01</td>
<td>0.03</td>
<td>0.03</td>
</tr>
<tr>
<td>B4*LR</td>
<td>2.14</td>
<td>0.06</td>
<td>0.11</td>
<td>0.02</td>
<td>0.03</td>
<td>0.03</td>
</tr>
</tbody>
</table>

Fig. 2. The effect of various solids concentration (5, 7.5, 10, and 12.5%) on nickel (a), zinc (b), cobalt (c), and iron (d) extractions in bioleaching at 32 °C (Experiment ID B1-B4).

Fig. 3. Effect of bioleaching pretreatment on copper extraction in chloride leaching at pH 1, 95 °C, 250 g/L NaCl (Experiments C1 and BC1).
3.6. Comparison between chloride and cyanide leaching on metal extraction of biologically treated material

The extraction of Au, Fe, Cu, Ni, Co, and Zn was further investigated in cyanide solution from biologically treated material. The aim was to compare the efficiency of cyanide free chloride leaching with cyanide leaching. It was observed that in chloride leaching experiment (BC1) dissolutions of iron, copper, nickel, cobalt, and zinc into the solution were 59%, 99%, 46%, 37%, and 60%, respectively (see Fig. 6). However, extraction of these metals in cyanide leaching (CN1) were significantly lower (up to 85%-units). On the other hand, higher gold extractions (70%) could be achieved in cyanide media compared to chloride media (63%), based on solid analysis of the leach residue.

4. Conclusions

A new method combining biological pretreatment and cyanide free chloride leaching for metal recovery from flotation tailings was developed. Bioleaching was used as a pretreatment method to extract iron, copper, nickel, cobalt, and zinc from low-grade flotation tailings prior to cyanide free gold leaching in chloride media. First, bioleaching and control experiments were run in shake flasks to adapt the microorganisms to the tailings material and to determine the leaching parameters. Highest redox potentials (640–660 mV vs. Ag/AgCl) and metal extractions of Ni, Co, Zn, and Fe, (90%, 60%, 86%, and 67%, respectively) were gained at 5% and 7.5% solid concentrations. Copper and gold remained in the final residue. The dissolution of copper and gold was conducted by cyanide-free chloride leaching. The residues from bioleaching (residues of experiment B1 and B2) were used in chloride leaching as the feed material and the effect of bacterial pretreatment process on metal recovery was investigated. Besides, the effect of particle size was studied with two different particle sizes (d80), which were as-received (150 µm) and ground (26 µm). For comparison, conventional cyanide leaching was run 72 h at pH 11, 2 g/L NaCN concentration with biologically treated material to compare leaching yields (%) with chloride leaching. In all chloride leaching experiments, the highest extractions of metals were gained with the microbiologically pretreated material. The highest copper (98%) and gold (63%) extractions were gained at pH 1, 150 µm particle size, and 72 h leaching time. The maximum dissolution of Ni, Co, and Zn (99%, 80% and 90%, respectively) were achieved at pH 1.8, 26 µm particle size, and leaching time of 24 h. Also, extractions of Ni, Co, and Zn were higher up to 50%-units with ground material than with the as-received material. In cyanide leaching, 70% extraction yield of gold was observed, but the other metals (Fe, Cu, Ni, Co, and Zn) remained in the leach residue. It can be inferred that: (I) bacterial pretreatment can provide advantage over direct chloride leaching, even though direct chloride leaching was conducted at aggressive conditions such as 250 g/L NaCl, T = 95 °C for...
**Fig. 5.** Effect of grinding on the extraction (%) of metals in chloride leaching after biological pretreatment at 250 g/L NaCl concentration, pH = 1, 95 °C, and 72 h (Experiment ID BC1 and BC3).

**Fig. 6.** Extraction of Au, Fe, Cu, Ni, Co and Zn (%) in chloride and cyanide leaching from biologically treated material (Experiment ID BC1 and CN1).

leaching time of up to 72 h, (II) biological pretreatment process followed by chloride leaching is more effective for base metals extraction when compared to cyanide leaching, (III) consequently, combination of biological pretreatment and chloride leaching could provide a viable process route for improving the metal extraction and further recovery from low grade ores and tailings.

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**References**


