Minerals Engineering 129 (2018) 47–53

Contents lists available at ScienceDirect

Minerals Engineering

journal homepage: www.elsevier.com/locate/mineng

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

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ARTICLE INFO

Keywords:
Biological pretreatment
Flotation tailings
Chloride leaching
Cyanidation

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., 2007). 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 (Ozkan 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 no 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

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https://doi.org/10.1016/j.mineng.2018.09.012
Received 12 July 2018; Received in revised form 6 September 2018; Accepted 10 September 2018

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 (H_2SO_4), and ferrous to ferric iron (Fe^{3+}). H_2SO_4 and Fe^{3+} 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 (Fe^{2+}) to ferric iron (Fe^{3+}), ferric ion 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).

$$Fe_7S_8 + 7H_2SO_4 \rightarrow 7FeSO_4 + 7H_2S + S \quad (1)$$

$$Fe_7S_8 + H_2O + 15.5O_2(g) \rightarrow 7FeSO_4 + H_2SO_4 \quad (2)$$

$$Fe_7S_8 + O_2(g) \rightarrow 7FeSO_4 + S \quad (3)$$

$$Fe_7S_8 + 31Fe_2(SO_4)_3 + 32H_2O \rightarrow 69Fe(SO_4) + 32H_2SO_4 \quad (4)$$

$$Fe_7S_8 + 7Fe_2(SO_4)_3 \rightarrow 21FeSO_4 + 8S^0 \quad (5)$$

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; Kinnunen, 2004). 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 chloride leaching, targeted for gold and copper.

Table 1
Working temperature of acidophilic microorganisms in bioleaching processes (modified from Deveci et al., 2003; Holanda et al., 2016).

Microorganism type	Culture	Working temperature (°C)
Mesophilic	*Acidithiobacillus (At.) ferrooxidans* *Leptospirillum (L.) ferrooxidans* *At. thiooxidans* *Acidibacillus (Ab.) ferrooxidans**	20–40
Moderate thermophilic	*Sulfobacillus (Sb.) thermosulfidooxidans,* *Sb. acidophilus* *At. caldus*	40–45
Extreme thermophilic	*Sulfolobus-like archaea* *Sulfolobus. metallicus* *Acidianus. brierleyi*	55–85

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

Table 2
Mineral salts and elements in 0 K medium (modified 9 K medium without ferrous iron, Silverman and Lundgren, 1959).

Chemical	Amounts (g/L)
$(NH_4)_2SO_4$	3
KCl	0.1
K_2HPO_4	0.5
$MgSO_4 * 7H_2O$	0.5
$Ca(NO_3)_2 * 4H_2O$	0.14

2. Materials and methods

2.1. Microorganisms and adaptation

The mixed acidophilic culture, which contains *Acidithiobacillus ferrooxidans*, *Acidithiobacillus thiooxidans/albertensis*, *Acidithiobacillus caldus*, *Leptospirillum ferrooxidans*, *Sulfobacillus thermosulfidooxidans*, *Sulfobacillus thermotolerans* 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 (H_2SO_4, 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 H_2SO_4 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 3
Solid concentration and leaching time of the bioleaching experiments.

Experiment ID	Solid concentration (w/v, %)	Leaching time (days)
B1	5	15
B2	7.5	11
B3	10	15
B4	12.5	11