



Bioleaching of copper, nickel and cobalt from the low grade sulfidic tailing of Golgohar Iron Mine, Iran



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ABSTRACT

This study was conducted to establish the possible application of bioleaching to recover valuable metals from the sulfidic tailing of Golgohar Iron Mine (Kerman, Iran). Shake flask leaching experiments were carried out in the presence of a mixed culture of moderately thermophilic microorganisms at a stirring rate of 150 rpm and a temperature of 45 °C, with the addition of yeast extract (0.02 (w/w)). The influence of bacterial inoculation, pH, nutrient medium type and pulp density on the recovery of copper, nickel and cobalt from the tailing was investigated. The results showed that 55.0% of copper, 98.2% of nickel and 59.5% of cobalt could be extracted from the tailing through the bioleaching process after 30 days at 5% (w/v) pulp density. The recovery of valuable metals from the tailing in the presence of microorganisms was approximately three times higher than that in the un-inoculated leaching experiment under similar conditions. It was also found that the recovery of copper at the initial pH of 1.2 was 17% higher than that at the pH of 1.8, while nickel and cobalt recoveries were 37% and 23% more at the pH of 1.8, respectively. It was also revealed that the recoveries of valuable metals were approximately similar in both 9 K and Norris nutrient media. Moreover, the results showed that in both nutrient media, copper recovery at the higher pulp density was significantly higher than that at the lower pulp density; this was mainly attributed to the lower redox potential. On the other hand, nickel and cobalt recoveries were higher at the lower pulp density, probably due to the higher redox potential values. A two-stage bioleaching process in which the redox potential is controlled at a low level in the primary reactors, followed by the secondary reactors with a high redox potential is supposed to achieve the maximum recovery of valuable metals.

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1. Introduction

Due to the depletion of high-grade and simple ores, the growing demand for valuable metals and the development of new hydrometallurgical technologies, extensive efforts have been made to recover valuable metals from low-grade ores and tailings. These lean materials can account for up to three quarters of the total reserves of certain metals (Xie et al., 2005).

Golgohar Iron Ore (Kerman Province, Iran) is one of the largest deposits in Iran with a probable reserve of 1350 Mt. The main harmful element of the ore is sulfur, which is present as metal sulfides such as pyrite and chalcopyrite. These sulfide minerals are mainly separated from iron oxides by a reverse flotation process in which a low grade copper–nickel–cobalt bearing material is produced as the floated portion. Unpublished preliminary investigations showed that this

tailing could not be upgraded by conventional physical or physicochemical methods.

Bioleaching has a great potential to recover valuable metals from low grade, polymetallic and complex sulfide ores due to its technical ability, relative simplicity, environmentally eco-friendly process and low capital and operational cost requirements (Brierley and Brierley, 2001; Rawlings et al., 2003; Lavalle et al., 2008; Anjum et al., 2012). The recovery of valuable metals using microorganisms is now a worldwide established biotechnological process (Vera et al., 2013). Up to date, bioleaching has been applied successfully for the extraction of copper from secondary and to some extent, primary copper sulfides, as well as the oxidation of refractory gold ores in both uncontrolled dumps and designed bioheaps (Watling, 2006; Pradhan et al., 2008; Gentina and Acevedo, 2013). Stirred tank bioleaching has also been commercialized for cobalt recovery and the biooxidation of refractory gold concentrates (Olson et al., 2003; Morin and d'Hugues, 2007; van-Aswegen et al., 2007). However, in the case of chalcopyrite ores and concentrates, the process has not been commercially applied widely. The leading processes operate at relatively high temperatures around 80 °C (Batty and Rorke, 2006). At these high temperatures,

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difficulties such as the low solubility of air, the high rate of evaporation, the high corrosion of construction materials and the low mechanical resistance of living cells (limiting the increase in pulp density) occur. However, these are not as much of a problem at lower temperatures. Leaching reactions of metal sulfides are exothermic, raising the temperature of stirred tanks to 40–50 °C, which is the optimum range for the growth of moderate thermophilic microorganisms (Cancho et al., 2007). In addition to possibly improving sulfide oxidation with the higher temperature, operation of stirred reactors at 50 °C reduces process-cooling requirements (Olson et al., 2003). So, in many cases, the industry has preferred these moderate thermophilic microorganisms because they are more resistant to higher pulp densities and higher heavy metal concentrations than extreme thermophiles (Cancho et al., 2007; Olson et al., 2003).

Recently, several investigations on the extraction of copper, cobalt and nickel from low grade sulfide ores have been reported (Watling, 2008; Watling et al., 2009; Zhen et al., 2009; Yang et al., 2011). However, a few publications have been presented on the recovery of these valuable metals from tailings. Xie et al. (2005) studied the recovery of nickel, copper and cobalt from low-grade sulfide tailings. They found that by mixed nitric–sulphuric acid solutions at ambient temperature and atmospheric pressure, recoveries up to 91.5%, 85.0% and 54.6% for nickel, copper and cobalt were achieved under laboratory conditions, respectively. Watling (2008) reviewed the bioleaching of nickel–copper sulfides. Watling et al. (2009) also studied the bioleaching of a low-grade copper–nickel sulfide ore using isothermal columns. The recovery of nickel and copper was 70% and 20% after about 200 days, respectively. Likewise, Zhen et al. (2009) investigated the column bioleaching of a low grade nickel-bearing sulfide ore using a mixed culture of mesophilic microorganisms and found a nickel recovery of 91% and a cobalt recovery of 81% in 312 days. Chinese researchers (Yang et al., 2011) also found that using mesophilic microorganisms, a recovery of 94% of nickel, 62% of cobalt and 70% of copper was achieved after 68 days in flask bioleaching experiments. However, a recovery of 46% of nickel, 39% of cobalt and 13% of copper was achieved within 139 days of column leaching. Heap bioleaching was successfully applied for processing Talvivaara black schist deposit in Finland as one of the largest nickel deposits in the world (Brierley and Brierley, 2013). Kondrat'eva et al. (2012) investigated percolation bioleaching for the extraction of copper, zinc and gold from the flotation tailing of a sulfide ore and concluded that a good recovery of valuable metals could be obtained after 134 days. In addition, Turkish researchers (Onal et al., 2012) studied the recovery of copper, cobalt, nickel and magnetite from the iron ore tailing of Divriji Mine through a sequence of flotation, roasting, acid leaching and sulfide precipitation processes.

Bioleaching of low-grade and complex copper–nickel–cobalt bearing sulfidic tailings was not found in the technical literature. Such a material could be considered as a good candidate to supply the related metals in the future. Hence, in the present study, a low-grade copper–nickel–cobalt bearing sulfidic tailing from Golgozar Iron Complex was subjected to shake flask bioleaching by a mixed culture of iron- and sulfur-oxidizing moderately thermophilic microorganisms. The aim of the present research was to assess the amenability of bioleaching to recover valuable metals from the tailing and also, to investigate the influence of some chemical and operational parameters on the process efficiency.

2. Materials and methods

2.1. Minerals

A sulfidic tailing obtained from the floated portion of reverse flotation cells in Hematite Recovery Plant (HRP) of Golgozar Iron Complex (Kerman province, Iran) was used in experiments. Chemical analysis of the representative sample by ICP-OES showed 0.16% of Cu, 0.078% of Ni and 0.044% of Co (Table 1). X-ray diffraction analysis of the sample showed pyrite (FeS₂) and magnetite (Fe₃O₄) as the major phases and talc (Mg₃Si₄O₁₀(OH)₁₀) and antigorite (Mg₃Si₂O₅(OH)₄) as the minor ones. Based on the wet screening analysis, the particle size of the sample was 80% below 50 µm. Mineralogical studies performed by optical microscopy (model: Leica DLMP) of the polished specimen showed that copper present as chalcopyrite (CuFeS₂) was mostly locked with magnetite and pyrite minerals (Fig. 1). Individual nickel and cobalt minerals were found neither in the mineralogical images nor in the X-ray analysis.

Further mineralogical analysis was conducted using an electron probe micro-analyzer (EPMA). Fig. 2 shows the images and the related elemental analyses of the representative sample. The analysis showed that nickel was partially occluded in pyrite grains. No nickel sulfide was observed in the polished specimen; thus it was assumed that nickel occurred in solid solution in pyrite. Talc and magnesium–calcium bearing minerals (A and B grains) did not contain nickel and cobalt. A chrome–nickel bearing iron-oxide phase containing about 9.5% of nickel and 12.5% of chromium was found in the sample.

2.2. Microorganisms

A mixed culture of iron- and sulfur-oxidizing microorganisms, including *Leptospirillum ferriphilum*, *Acidithiobacillus caldus*, *Sulfobacillus* sp. and *Ferroplasma* sp., was used in the experiments. This mixed culture was originally obtained from the microbial cell bank of Sarcheshmeh Copper Mine (Iran, Kerman). The microbial identification had been previously performed through 16S rRNA gene sequencing. The culture was enriched in shake flasks using the sulfidic tailing (5% w/v) as the substrate in an iron-free 9K nutrient medium (Silverman and Lundgren, 1959) at the stirring rate of 150 rpm, the initial pH of 1.8 and the temperature of 45 °C. The nutrient medium had the following composition: 3 g/L of (NH₄)₂SO₄, 0.1 g/L of KCl, 0.5 g/L of K₂HPO₄, 0.5 g/L of MgSO₄·7H₂O, 0.01 g/L of Ca(NO₃)₂. Norris nutrient medium (Norris and Barr, 1985) with the composition of 0.4 g/L of (NH₄)₂SO₄, 0.4 g/L of K₂HPO₄ and 0.5 g/L of MgSO₄·7H₂O was used in some experiments.

2.3. Experimental

Bioleaching experiments were conducted in 500 mL Erlenmeyer flasks with a suspension volume of 200 mL in an iron-free basal salt medium supplemented with 0.02% (w/v) yeast extract. Each flask was inoculated with a bacterial solution (15%, v/v) and then incubated at 45 °C on a rotary shaker at 150 rpm. To inoculate bacteria to a fresh medium, the bacterial solution was added to the flask containing the required fresh nutrient solution (at the desired pH). After mixing the resulting slurry, the pH was adjusted and the redox potential was recorded. All experiments were inoculated from a stock bacterial

Table 1
Chemical analysis of the representative sample by X-ray fluorescence (XRF).

Element or component	P ^a	Fe ^a	SiO ₂	TiO ₂	Al ₂ O ₃	CaO	MgO	MnO	Cu ^a	Ni ^a	Co ^a	S ^b
Content (%)	0.027	56.82	4.97	0.05	0.23	0.27	2.75	0.05	0.16	0.078	0.044	24.5

^aDetermined by ICP-OES; ^bdetermined by LECO analyzer; other compounds: determined by X-ray fluorescence (XRF).

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