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Reductive bioprocessing of cobalt-bearing limonitic laterites

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ABSTRACT

Demand for cobalt is increasing worldwide, primarily as a result of its use in rechargeable batteries, super-alloys, and the chemicals industry. Extraction and recovery of cobalt from primary ores and waste materials using (novel) bioprocessing approaches has been suggested to have significant potential as a means to secure the supply of this critical metal in future years. While bioleaching of cobalt-bearing sulfide ores has been carried out in one full-scale operation (at Kasese, Uganda), bioprocessing of cobalt-bearing oxidised ores, such as limonitic laterites, has hitherto received little attention. In the present work, reductive bioleaching of three limonitic laterite ores was carried out in anaerobic bioreactors, maintained at pH 1.8 and 35 °C, and compared with oxidative acid leaching in control aerobic bioreactors. Elemental sulfur was added as electron donor for the acidophilic bacteria used in both aerobic and anaerobic bioreactors. Reductive bioleaching enhanced the extraction of cobalt from all three ores, by a factor of up to 6-fold, compared to acid leaching under aerobic conditions. Extraction of cobalt from the ores closely paralleled that of manganese, suggesting that the most of the cobalt was liberated via the reductive dissolution of manganese (IV) minerals present in the limonites, catalysed directly and/or indirectly by the bacteria present (predominantly *Acidithiobacillusferrooxidans* and *Sulfobacillusthermosulfidooxidans*).

1. Introduction

Significant increases in the demand for cobalt, which had a global market value of ~$2.1 billion (US) in 2013, are occurring as a result of its use in super-alloys, rechargeable batteries and a range of catalytic processes (British Geological Survey, 2009). Cobalt is often obtained as a by-product during the processing of copper and nickel (Roberts and Gunn, 2014), and current processing technologies for cobalt-bearing ores mostly involve high temperatures and pressures, and are therefore energy intensive. This provides both incentive and opportunity to develop new and environmentally-benign (bio-)processing options to extract and recover what is frequently regarded as a strategic metal.

Bioprocessing has previously been used to extract cobalt from mineral tailings deposited as waste material during copper mining of a sulfidic ore in Kasese, Uganda (Morin and d'Hughes, 2007). This involved bioleaching the tailings in stirred tanks at ~40 °C in the presence of acidophilic bacteria and archaea that catalysed the oxidative dissolution of pyrite (FeS_2) with which the cobalt was intimately associated. The cobalt released remained soluble in the acidic leach liquors, and was recovered downstream by solvent extraction and electrowinning, generating a high-grade metal product. The operation continued until the tailings had become depleted. Cobalt can also occur in oxidised ores, such as limonitic laterites. In these, cobalt is generally present in far smaller concentrations than the primary base metal targeted for extraction (nickel), and limonites have not generally been considered as economically-viable sources of cobalt. Processing of nickel limonites conventionally involves the use of high pressures and temperatures, such as in the Caron process (Asselin, 2011). However, it has been demonstrated that limonitic ores are also amenable to bio-processing at relatively low temperatures (around 30 °C; Hallberg et al., 2011; Johnson et al., 2013; Ñancucheo et al., 2014; Johnson and du Plessis, 2015; Marrero et al., 2015). While the microorganisms that mediate this are similar to those used in conventional biomining operations, a major difference is that, when bioleaching oxidised ores, they are usually constrained to operate under anaerobic conditions in order to catalyse the reductive dissolution of oxidised minerals. While much of the nickel in limonitic ores is associated with ferric iron minerals such as goethite, Johnson et al. (2013) reported that there was a strong correlation between cobalt and manganese solubilised by reductive bio-processing of a nickel limonite, and that the cobalt present was associated with manganese (IV) minerals, such as asbolane.

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Here we describe experiments in which three cobalt-containing limonite ores, two originating from central Asia and the other from eastern Asia, were subjected to both reductive and oxidative bio-processing in pH- and temperature-controlled bioreactors, at pH 1.8 and 35 °C.

2. Methods

2.1. Limonite ores

Three cobalt-bearing limonitic laterite ores were bio-processed at low pH and mesophilic temperatures in the current study. Two of the ores were obtained from Shevchenko, Kazakhstan (SHLM7 and SHLM11), and the third from the Acoje mine in the Philippines, by partners in the COG[3] (*The geology, geometallurgy and geomicrobiology of cobalt resources leading to new product streams*) project (http://www.nhm.ac.uk/our-science/our-work/sustainability/cog3-cobalt-project.html). Goethite was the dominant iron mineral present in the ores. The major transition metals present were iron (16.7–31%) manganese (0.46–0.92%), nickel (1.0–1.54%), zinc (0.03–0.04%), in addition to cobalt (0.07–0.19%). Prior to bioleaching, the dried ores were crushed and sieved to <2 mm.

2.2. Bacterial cultures

A mixed culture consortium containing mesophilic and thermo-tolerant species of iron-oxidising, iron-reducing, and sulfur-oxidising acidophilic bacteria was set up and grown in a shake flask containing 200 mL of liquid medium, comprising basal salts and trace elements (Ňancucheo et al., 2016), 1 mM ferrous sulfate and 2 g elemental sulfur. The consortium contained *Acidithiobacillus* (*At.*) *ferrooxidans*[T], *At. ferriphilus*[T], *At. ferridurans*[T], *Acidibacillus* (*Ab.*) *sulfuroxidans*[T], *Sulfobacillus* (*Sb.*) *thermosulfidooxidans*[T] and *Sb. acidophilus* (strain BOR1), and the shake flask starter culture was grown at 30 °C and pH 1.8.

2.3. Reductive bioleaching of limonitic laterite ores

Two bioreactor vessels (2.3 L), both coupled to modular units that controlled pH, temperature and agitation (Electrolab, UK), were operated in parallel in each experiment, using one of the three limonite ore samples. Basal salts/trace elements solution (1.9 L; adjusted to pH 1.8 and containing 1 mM ferrous sulfate) was put into each reactor vessel, followed by 25 g of elemental sulfur and 100 mL of the sulfur-grown inoculum (Section 2.2. The pH in the bioreactors was maintained at 1.8 by automated addition of 1 M H_2SO_4 or 1 M NaOH, the temperature fixed at 35 °C, and the reactors were stirred at 150 rpm. Both bioreactors were initially aerated with atmospheric-air, but once cell numbers had reached $\sim 1–5 \times 10^8$ mL^{-1} (7–10 days after inoculation of the bioreactors) the gas supply to one of them was switched to oxygen-free nitrogen (OFN) to promote anaerobic conditions while the second bioreactor was continued to be gassed with sterile air, to retain aerobic conditions. Limonite ore samples (100 g) were then added to each of the bioreactors. Liquid samples were withdrawn from each vessel on a daily basis for chemical analysis, and the volumes of acid and alkali added to each vessel required to maintain the pH values at 1.8 were recorded and collated. Bioleaching of the three ore samples was carried out for 20–31 days. At the end of each experiment, the mineral leachates (pregnant leach solutions; PLS) and solid residues were harvested and separated from each other. The PLS were stored at 4 °C, while the solid residues were washed with acidified water, dried and weighed.

2.4. Biomolecular analysis

The composition of the bacterial communities in PLS at the end of the bioleaching periods were determined by filtering liquid samples through sterile 0.2 μm nitrocellulose membrane filters (to collect biomass), cutting these into strips and extracting DNA using MoBio ultraclean soil DNA isolation kits. 16S rRNA genes were amplified from DNA using the primer sets 27F: (5′-AGAGTTT GATCCTGGCTCAG-3′ (Lane, 1991) labelled with the fluorochrome Cy5) and 1387R: (5′-GGGCGGWGTGTACAAGGC-3′; Marchesi et al., 1998). Terminal restriction enzyme fragment length polymorphism (T-RFLP) analysis of the amplified 16S rRNA genes involved digesting them with the restriction enzymes AluI, CfoI, HaeIII and EcoRI. Gene fragments were separated by capillary electrophoresis, and their lengths and fluorescence intensity were measured using a Beckman CEQ8000 Genetic Analysis System, and identified by comparison with those present in the Bangor University database.

2.5. Chemical analytical techniques

Ferrous iron in solution was determined colorometrically using the Ferrozine assay (Stookey, 1970). Total soluble iron was also determined using the Ferrozine assay, following reduction of soluble ferric iron present to ferrous using an excess of ascorbic acid. Concentrations of transition metals in leachates were measured using ion chromatography, using a Dionex-320 chromatograph fitted with an IonPAC® CS5A column and an AD25 absorbance detector (Ňancucheo and Johnson, 2010). pH and redox potential measurements were made off-line. pH values were measured using a pHase electrode (VWR, UK); redox potentials measurements using a platinum/silver-silver chloride electrode (Thermo Scientific, UK) and were adjusted to be relative to a standard hydrogen electrode (i.e. E_H values). Both electrodes were coupled to an Accumet 50 pH meter.

3. Results

In each of the three experiments, two bioreactors were operated in parallel – one gassed with OFN to induce anaerobic conditions and the other maintained as an aerobic system, though all other operational parameters (temperature, agitation etc.) were identical. Changing the gas supply from air to OFN resulted in a major change in solution chemistry, from one that was oxidising (dominated by soluble ferric iron) to one that was reducing (dominated by ferrous iron). As shown in Fig. 1, this was reflected in large

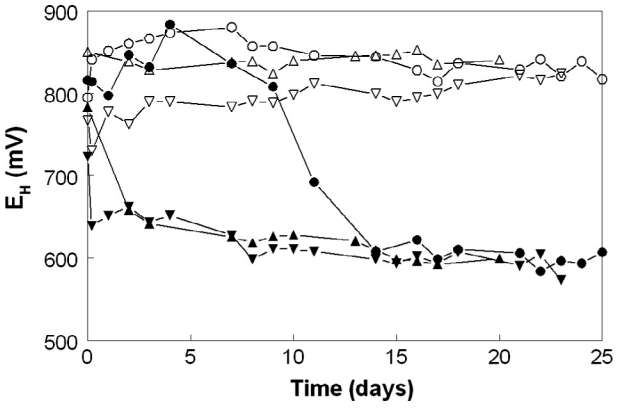

Fig. 1. Changes in redox potentials during bio-processing of limonitic ores under anaerobic (solid symbols) and aerobic conditions. Key: (▼, ▽) SHLM7; (▲, Δ) SHLM11; (●, o) Acoje limonite.