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Smith, Sarah; Grail, Barry; Johnson, David

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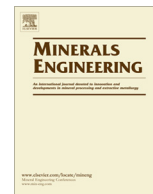
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## Reductive bioprocessing of cobalt-bearing limonitic laterites



Sarah L. Smith\*, Barry M. Grail, D. Barrie Johnson

College of Natural Sciences, Bangor University, LL57 2UW, UK

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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 *Acidithiobacillus ferrooxidans* and *Sulfobacillus thermosulfidoxidans*).

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### 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<sub>2</sub>) 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; Nancuqueo 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.

\* Corresponding author at: Brambell Building, Deiniol Road, Bangor LL57 2UW, UK.

E-mail address: [Sarah.Smith@bangor.ac.uk](mailto:Sarah.Smith@bangor.ac.uk) (S.L. Smith).

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<sup>3</sup> (*The geology, geomaterials 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 (Ñancucheo et al., 2016), 1 mM ferrous sulfate and 2 g elemental sulfur. The consortium contained *Acidithiobacillus* (*At.*) *ferrooxidans*<sup>T</sup>, *At. ferriphilus*<sup>T</sup>, *At. ferridurans*<sup>T</sup>, *Acidibacillus* (*Ab.*) *sulfuroxidans*<sup>T</sup>, *Sulfobacillus* (*Sb.*) *thermosulfidooxidans*<sup>T</sup> 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<sub>2</sub>SO<sub>4</sub> 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  $\sim 1\text{--}5 \times 10^8 \text{ mL}^{-1}$  (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'-GGGCGGWTGTACAAGC-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 colorimetrically 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<sup>®</sup> CS5A column and an AD25 absorbance detector (Ñancucheo 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*<sub>H</sub> 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

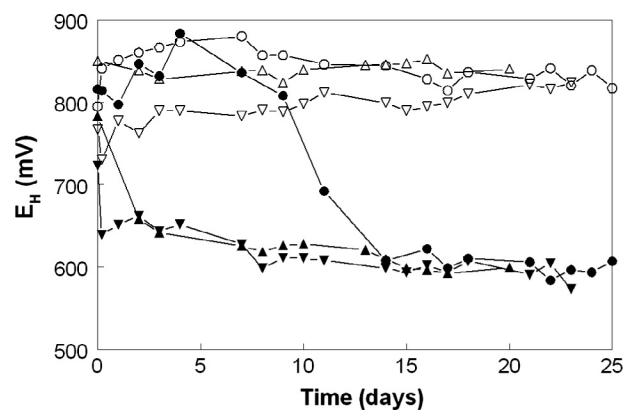


Fig. 1. Changes in redox potentials during bio-processing of limonitic ores under anaerobic (solid symbols) and aerobic conditions. Key: (▼, ▽) SHLM7; (▲, △) SHLM11; (●, ○) Acoje limonite.

differences (of between 200 and 250 mV) in redox potentials between parallel bioreactors. The decline in  $E_H$  values was much slower in the case of the Acoje limonite than with the Shevchenko limonites, taking  $\sim 14$  days for the value to stabilise at  $\sim +600$  mV, compared to 4–6 days for the latter two.

Cobalt was leached effectively from all three limonitic ores under reducing conditions (Fig. 2). The maximum concentrations of soluble cobalt in these bioreactors (87, 93 and 30 mg L<sup>-1</sup> from ore samples SHLM7, SHLM11 and Acoje, respectively) corresponded to extraction of >99%, 88.5% and 90% of cobalt from the ores. Most of the manganese present in all three of the limonite samples was also extracted under reducing conditions (Fig. 2). With two of the limonites (SHLM11 and Acoje) there were large differences in the amounts of cobalt and manganese extracted under reducing compared to oxidising conditions, though in the case of the SHLM7 limonite, differences were more marginal (Fig. 2). In all cases (oxidative and reductive bio-processing of the three limonite samples) there was strong correlation between the amounts of cobalt and manganese that were extracted; regression coefficients were >0.97, but there was evidence of secondary

precipitation of both metals with protracted bioprocessing of the Acoje limonite.

Fig. 3 shows data of nickel and iron extraction from the limonite samples in the same experiments. Again there were differences between the SHLM7 and the other two limonites, in that >70% of the Ni was solubilised in the former but far less with the latter ( $\sim 50\%$  for SHLM11 and 40% for the Acoje sample). More nickel was extracted by reductive than oxidative leaching, especially in the case of SHLM7. Differences in oxidative and reductive bioleaching of iron were marginal with iron for SHLM11 and Acoje samples, and were not apparent in the case of the SHLM7 limonite; the extent of iron solubilisation from all of the limonite ores was low.

With the SHLM7 limonite, addition of acid was required from the onset of reductive bioleaching to maintain the pH at 1.8, whereas alkali was required in the case of oxidative bioleaching (Fig. 4). In contrast, addition of acid was required in the early stages of both oxidative and reductive bioleaching of SHLM11 limonite, and alkali addition (for oxidative bioleaching) was only necessary after 9 days of bio-processing. A similar scenario was observed with the Acoje limonite, though in this case addition of

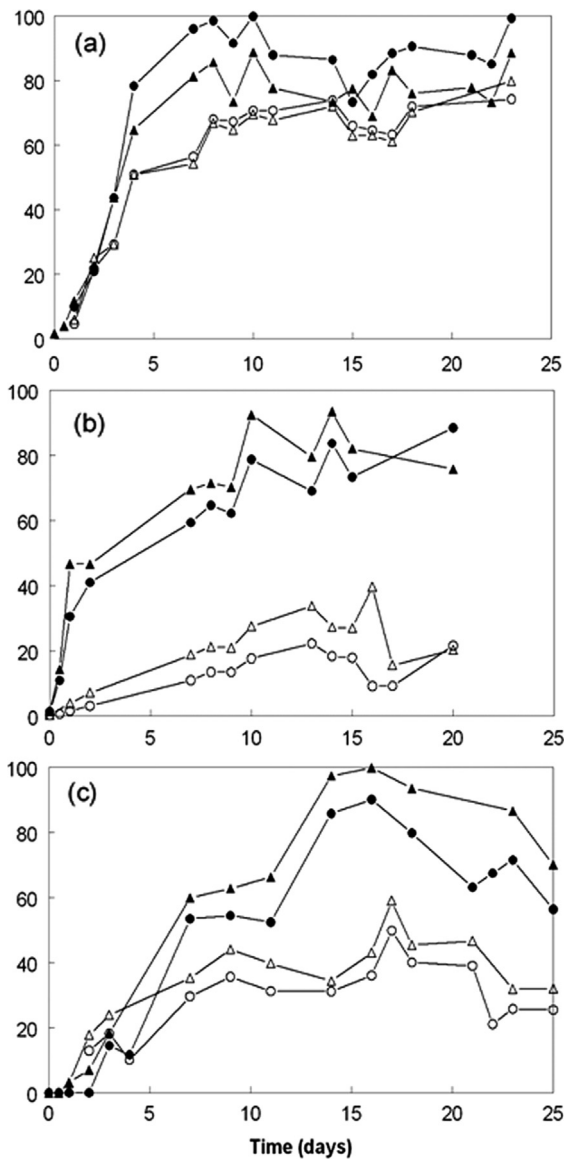


Fig. 2. Comparison of the amounts of cobalt (●, ○) and manganese (▲, △) extracted by bio-processing of (a) SHLM7, (b) SHLM11, and (c) Acoje limonites under anaerobic (solid symbols) and aerobic (hollow symbols) conditions.

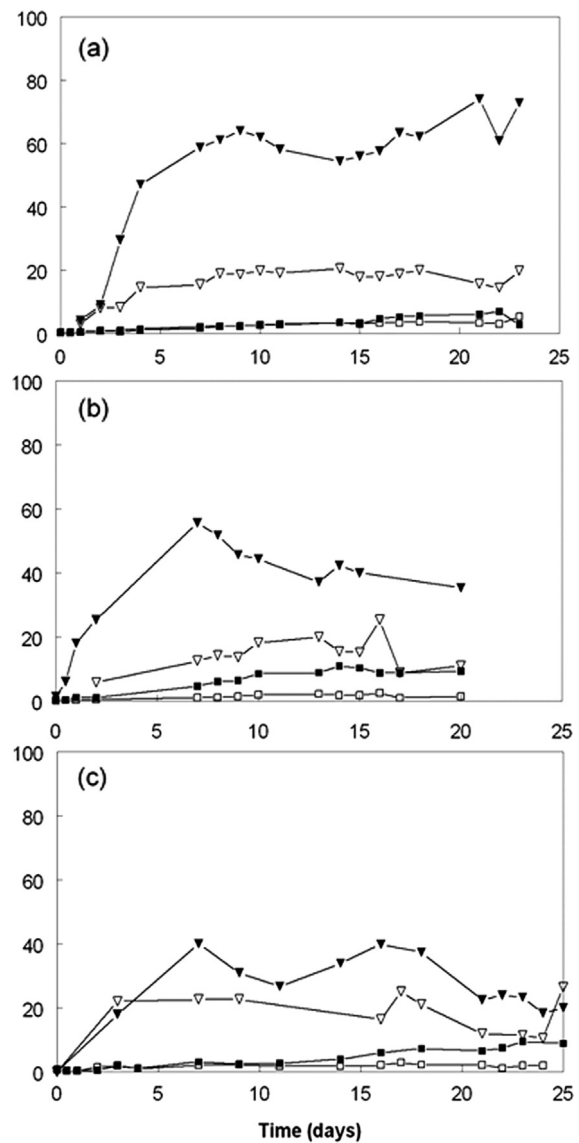
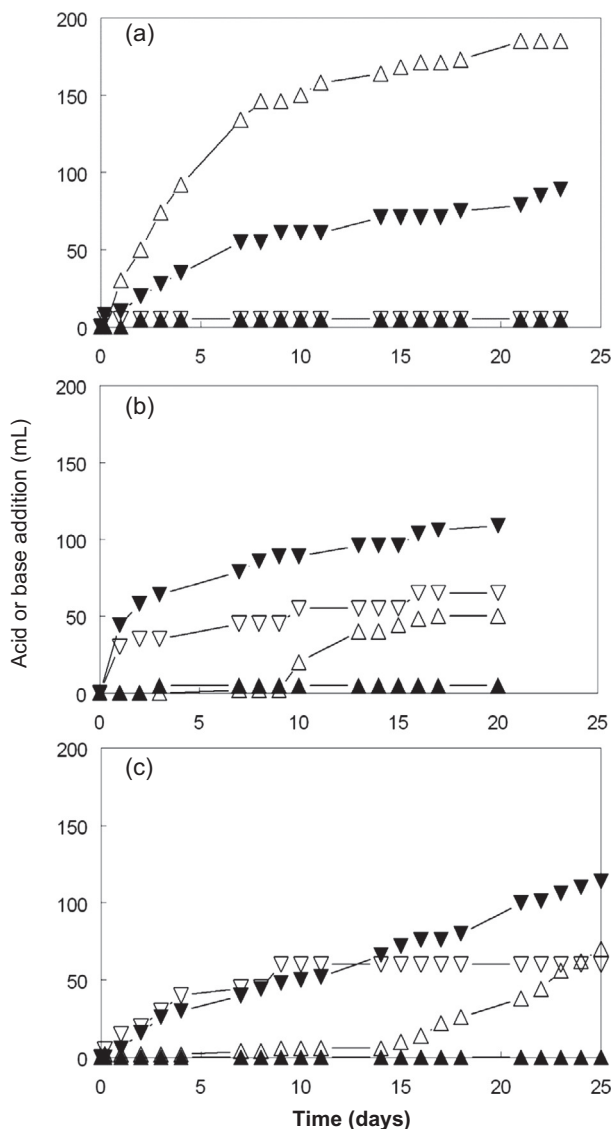


Fig. 3. Comparison of the amounts of nickel (▼, ▽) and iron (■, □) extracted by bio-processing of (a) SHLM7, (b) SHLM11, and (c) Acoje limonites under anaerobic (solid symbols) and aerobic (hollow symbols) conditions.



**Fig. 4.** Cumulative volumes of 1 M  $\text{H}_2\text{SO}_4$  (▼, ▽) and 1 M NaOH (▲, △) to maintain bioreactors at pH 1.8 during bio-processing of (a) SHLM7, (b) SHLM11, and (c) Acoje limonites. Solid symbols denote bioreactors gassed with OFN, and hollow symbols those gassed with atmospheric air.

alkali (for oxidative bioleaching) started 14 days into mineral bio-processing (Fig. 4). Alkali was not required to maintain the set pH when bio-processing any of the three limonites under reducing conditions.

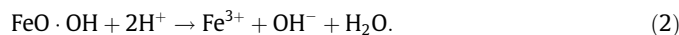
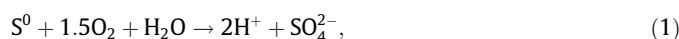
The bacterial communities present at the end of the bioleaching periods were far less diverse than those present in the initial inocula. *At. ferrooxidans* and *Sb. thermosulfidooxidans* were detected in both SHLM11 and Acoje limonite leachates, bio-processed under reductive and oxidative conditions, while only *At. ferrooxidans* was detected at the end of bioleaching of the SHLM7 limonite, again in both aerobic and anaerobic bioreactors. It is likely that the decrease in bacterial community diversity occurred during the initial sulfur oxidation phase of the experiment, where conditions would have been favourable for the aerobic sulfur-oxidising bacteria added to the initial consortium.

#### 4. Discussion

The abundance of limonitic laterite ores, particularly in tropical areas, represents a significant, though currently unexploited,

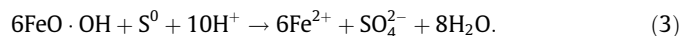
reserve of cobalt. In contrast to sulfidic cobalt ores, these are generally dominated by oxidised iron and manganese minerals, such as goethite ( $\alpha\text{FeO}\cdot\text{OH}$ ) and asbolane  $(\text{Ni},\text{Co})_x\text{Mn}(\text{O},\text{OH})_4\cdot n\text{H}_2\text{O}$  (Dalvi et al., 2004; Johnson et al., 2013). Nickel is usually the main target metal in lateritic ores, and these represent greater global reserves of this metal than accessible sulfidic ores, even though most nickel is currently obtained from the latter. Both the Caron process (chemical reduction of the dried ore at  $\sim 750^\circ\text{C}$  and extraction of the metal from the calcine produced with ammoniacal ammonium sulfate; Asselin, 2011) and the PAL process (a high pressure and temperature ( $\sim 250^\circ\text{C}$ ) process in which nickel is solubilised and goethite transformed to haematite; Taylor, 2013) have been used to recover nickel from limonitic ores, while other options, such as leaching with concentrated acids, have also been considered (Johnson and du Plessis, 2015). The Acoje limonite ore (from the Philippines), investigated in this study, was previously been exported to China (and elsewhere) for the production of ferromanganese, although an acid heap leaching was also trialled. Technologies such as atmospheric tank leaching, heap leaching and smelting had also been considered for processing the Shevchenko laterite (Barcza, 2009). Limonitic ores have previously been shown to be amenable to reductive bioleaching, though nickel and copper, rather than cobalt, were the primary target metals in those studies (Hallberg et al., 2011; Johnson et al., 2013; Nancucueo et al., 2014). Results from the present study have demonstrated the effectiveness of reductive bioleaching applied to limonitic laterite ores where the main objective was to extract cobalt.

Bioreactors, operated in parallel, allowed the direct comparison of oxidative and reductive bioleaching, both carried out using acidic solutions, for each limonite sample. In the presence of oxygen, sulfuric acid generated by the microbial oxidation of elemental sulfur (Eq. (1)) is responsible for the dissolution of minerals such as goethite (Eq. (2)):

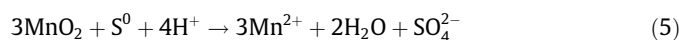
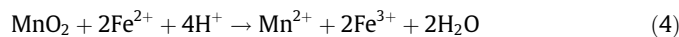


Since alkali addition was required to maintain pH at 1.8 throughout the oxidative bio-processing of SHLM7 limonite, reaction (1) appeared to be more rapid than reaction (2) during the entire experiment. In contrast, there was an initial phase of acid consumption with both the SHLM11 and Acoje limonites (i.e. reaction (2) was more rapid at that time), and only later in the experiment was alkali addition required to maintain pH homeostasis.

Addition of sulfuric acid was required to maintain pH homeostasis in all reductive experiments. This was anticipated since, as shown in Eq. (3), the reductive dissolution of goethite is highly consumptive of protons:



The reductive dissolution of manganese (IV) minerals is also an acid-consuming reaction (Eq. (4), illustrating indirect reduction by ferrous iron, and Eq. (5) which depicts direct reductive dissolution coupled to sulfur oxidation) whereas acid dissolution (involving no redox change in the metal) is only moderately acid-consuming (Eq. (6); Swain et al., 1975):



Dissolution of several of the gangue minerals that comprise the Shevchenko and Acoje limonites present another source of acid consumption; these include serpentine, antigorite, amphibole,

clinochlore, smectite and montmorillonite. Acid consumption is a major potential cost associated with the reductive bioprocessing of limonitic ores. However, as illustrated in the present study, it should be possible to balance acid consumption and acid production in a sulfur/limonite slurry by controlling access to oxygen, either by intermittent aeration or by maintaining concentrations of dissolved oxygen at low levels. This issue will be investigated in future studies.

Cobalt was very effectively solubilised from all three limonites under reducing conditions. The strong correlation between cobalt and manganese release suggests that the former was mostly associated with manganese (IV) minerals such as asbolane, as previously described by Johnson et al. (2013) for a different limonite ore, rather than with goethite. The reductive dissolution of manganese (IV) minerals could have been mediated either indirectly by ferrous iron generated by the microbial reductive dissolution of goethite (combination of Eqs. (3) and (4)) or directly by bacteria present in the bioreactors (Eq. (5)). Although the percentages of iron solubilised from all three limonites were relatively small in all the bioreactors, the large contents of goethite in the ores meant that ferrous iron concentrations were always well in excess of those of manganese (II). For example, the maximum ferrous iron concentration recorded in bioleachates of the Acoje limonite was 2068 mg L<sup>-1</sup> while that of manganese (II) was 227 mg L<sup>-1</sup>. Recent evidence has suggested that Mn(IV) oxides can also serve as direct electron acceptors for iron-reducing *Acidithiobacillus* spp. (coupled to sulfur oxidation) in the absence of both oxygen and an iron shuttle (E. Pakostova and D.B. Johnson, unpublished data). Interestingly, the difference between cobalt extracted under reductive and oxidative conditions from the SHML7 ore was far more marginal than for the two other samples that were bio-processed, suggesting that manganese minerals present in the SHLM7 limonite were more amenable to acid leaching alone (Eq. (6)), and that ferrous iron-catalysed or direct microbial dissolution was of relatively minor importance. Alkali consumption was significantly greater during the oxidative leaching of the SHLM7 limonite, compared to during the oxidative leaching of the SHLM11 and Acoje limonites. The enhanced acid generation in the SHLM7 limonite oxidative experiment may have also been, in part, responsible for the more similar percentages of metals leached from the oxidative and reductive experiments, compared with the other two ores.

The dissolution of manganese (IV) minerals, whether mediated by reductive bioprocessing, by acid or a combination of both, appears therefore to be the *sine qua non* where the prime objective is the extraction and recovery of cobalt (as opposed to nickel) in limonitic laterite ores.

There were interesting differences between the bioleaching of two other transition metals (nickel and iron) from the three limonite ores tested. Microbially-mediated extraction of nickel was significantly greater for both the Shevchenko limonites when bioleached under reducing conditions, but similar yields of soluble nickel were obtained by bioleaching the Acoje limonite under either oxidative or reductive conditions. The percentage of iron leached from the ores (generally <10%) under reducing conditions was small compared to the percentage of other transition metals that were leached. This was perceived as a positive phenomenon, as the potential for efficient leaching of target metals (cobalt and nickel) while at the same time minimizing the amount of ferric iron minerals solubilised is advantageous both in terms of sulfur consumption and downstream-processing (soluble iron has to be removed at least partially in a flow circuit; du Plessis et al., 2011). Also, generating a low redox potential, ferrous iron-dominated, pregnant leach solution (PLS) is beneficial in terms of downstream metal recovery, as Fe(II) precipitates at a higher pH than Fe(III), minimizing the loss of other metals as a result of coprecipitation with Fe(III) (Marrero et al., 2015).

## 5. Conclusions

This work has demonstrated that it is possible to effectively bioleach cobalt from limonitic ores under acidic, relatively low temperature, reducing conditions, using bacteria that couple the oxidation of elemental sulfur to the reduction of oxidised cobalt-bearing minerals. Extraction of cobalt was far more efficient in anaerobic than in aerobic bioreactors, and appeared to be closely correlated with the dissolution of manganese (IV) minerals present in the limonites. The cobalt that was extracted was soluble in the reduced acidic leach liquors, facilitating its downstream recovery. A microbial processing approach for extracting base metals from oxidised ores such as limonites has many potential advantages (for example, in terms of environmental impact and carbon footprint) over current high pressure/temperature processing technologies.

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