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Evaluation of submerged bio-oxidation concept for refractory gold ores

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ABSTRACT

As the quality of gold (Au) deposits decreases, processes which can economically extract Au from low grade ores will grow in importance to the minerals industry. *In situ*, in-place and vat leaching methods can be attractive alternatives for low grade ores that are uneconomical to process using conventional open-pit or underground mining and processing methods. The objective of this study was to evaluate at laboratory scale a submerged bio-oxidation process concept to potentially improve the recovery of Au from refractory ore bodies that may be amenable to in-place or vat processing. The process included biological generation of ferric iron in a bioreactor followed by ferric iron oxidation of pyrite in submerged upflow columns. The results showed that oxidation of pyrite is possible using ferric iron that is biologically generated either externally or using underground aeration in the ore body. The simulated underground aeration and the presence of bioleaching microorganisms clearly enhanced the oxidation of pyrite. Moreover, microorganisms decreased the accumulation of elemental-S, the presence of which may have a negative effect on subsequent gold leaching and recovery.

1. Introduction

Gold (Au) ore grades in Australia continue a long-term declining trend over time (Mudd, 2009). As the grade of Au deposits continues to decrease, it is expected that processes which can economically extract Au from low grade ores will assume greater importance in the minerals industry. Biotechnology has the potential to transform uneconomic Au reserves into mineable resources. Bioprocessing can be attractive for: 1) low grade Au ores that are uneconomical to process using conventional metallurgical techniques, and 2) refractory Au ores requiring oxidation of the sulfides to liberate the gold.

It has been demonstrated that microorganisms can mediate Au solubilisation by oxidising the sulfide matrix of refractory Au ores and by excretion of ligands capable of stabilising Au by forming Au-rich complexes and/or colloids. Moreover, microorganisms can also precipitate and accumulate Au from solution (Reith et al., 2007). In the main bio-oxidation and bioleaching techniques, such as reactor, vat, heap, dump and stope leaching the ore is removed from the ore body, whereas *in situ* and in-place leaching do not involve the removal of the ore. For *in situ* leaching the ore is leached as it is, whereas for in-place leaching the ore body is deliberately fractured, for example by blasting, to improve the permeability before leaching (Wadden and Gallant, 1985). In both cases, the leach solution is injected into the subsurface ore body to extract target metals. The pregnant (metal-bearing) leach solution is collected from production wells for metal recovery (Brierley, 2010). This type of biomining does not usually require extensive mine infrastructure and may reduce the aesthetic impact of the mining operation. However, *in situ* and in-place leaching do require extended contact times between ore minerals and fluid, well developed reservoir permeability and effective lixiviant recovery. Extensive knowledge of the hydrology and geology of the area and careful control of lixiviant (leaching) solutions are required to prevent contamination of local or regional groundwater.

The bio-oxidation of the sulfide matrix of refractory Au ores is based on the activity of acidophilic chemolithotrophic iron- and sulfur-oxidising microorganisms which obtain energy by oxidising ferrous (Fe^{2+}) to ferric (Fe^{3+}) or elemental-S or other reduced sulfur compounds to H_2SO_4 (Sand et al., 1995). The bio-oxidation is a pre-treatment process which can decrease the consumption of chemical lixiviants, such as cyanide, for Au solubilisation in subsequent parts of the operation and ultimately increase Au yields. However, since it does not actually solubilise Au, bio-oxidation needs to be used in conjunction with other methods (van Aswegen et al., 2007). The use of non-conventional lixiviants, such as thiosulfate, has recently received attention as an alternative technology to the cyanidation of gold ores due to the growing environmental and public concerns over the use of cyanide (Feng and van Deventer, 2010; Wan and LeVier, 2003). Oxide Au ores are well suited for thiosulfate leaching, while sulfide ores show low extractions. In refractory Au ores fine patches of gold are often locked in the sulfide matrix. In order to recover gold, high sulfide-containing ores require at least partial oxidation prior to thiosulfate

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leaching (Feng and van Deventer, 2010). Biooxidation pre-treatment of refractory Au ores has been applied in bioreactors and heaps, whereas *in situ*, in-place and vat applications are yet to be developed. The objective of this study was to evaluate at laboratory scale a submerged bio-oxidation concept, where the sulfide is oxidised using biologically generated ferric iron (Fe^{3+}) to potentially enhance gold recovery in an environment that is intended to resemble in-place or vat processing, although the particle size used may not be realistic for these. This work focused on the Fe^{3+} generation and pyrite oxidation steps and used laboratory scale submerged upflow columns. The subsequent leaching of the Au from the bio-oxidised ore with chemical lixiviants was out of the scope of this work.

2. Materials and methods

2.1. Ore preparation and characterisation

2.1.1. Ore

The Au- and pyrite-containing ore from Western Australia (WA) was crushed and sieved to a particle size of 1–4 mm for the pyrite oxidation studies.

2.1.2. Elemental analysis

The acid-soluble contents of various elements in the 1–4 mm size fraction of the ore were determined by inductively coupled plasma-atomic emission spectroscopy (ICP-AES) by the Analytical Services of CSIRO Process Science and Engineering at Waterford, WA. Samples of the 1–4 mm fraction were initially pulverised and thereafter digested in MLS 1200 Mega Microwave Digester from Milestone using program # 5 (25 min procedure) with *aqua regia* solution prior to analysis.

2.1.3. Sulfide-S analysis

Sulfide-S analysis was used to estimate the amount of pyrite in the 1–4 mm size fraction of the ore before and after biooxidation. The analyses were conducted by the Analytical Services of CSIRO Process Science and Engineering at Waterford, WA using a Labfit CS2000 sulfur analyser after removing sulfates with carbonate treatment. Pyrite content of the ore before oxidation was estimated by assuming that all of the sulfide in the ore was present as pyrite (verified by mineralogical analysis) and calculating the pyrite content using molecular weights (MW) as follows:

$$\text{Pyrite mass } \% = [\text{MW(pyrite)}/\text{MW(2 x sulfur)}]\text{x sulfide}-\text{S content}.$$

2.1.4. X-ray diffraction

The mineralogical composition of the 1–4 mm ore was analysed using X-ray diffraction (XRD) by Analytical Services of CSIRO Process Science and Engineering at Waterford, WA.

2.1.5. QEMSCAN

Polished thin sections were cut from the 1–4 mm ore fraction and set in epoxy resin for QEMSCAN analysis using fieldscan mode to determine minor and trace mineral abundances and exposure of pyrite. Four 30 mm thin section blocks were scanned at a 20 μm pixel spacing with the QEMSCAN instrument. The QEMSCAN data were used to calculate the contents of various elements in the ore, the deportment of Fe in the various Fe-containing minerals and the exposure of pyrite before and after acid leaching. To evaluate the effect of acid leaching, exposed acid soluble minerals were removed from the QEMSCAN images by data processing. It was assumed that the carbonate minerals calcite, ankerite, ankerite/dolomite solid-solution series and dolomite were acid soluble in that order. The minerals were removed iteratively until a stable condition was reached such that no new acid soluble minerals were exposed by the completion of the iteration.

2.1.6. Acid consumption test

Acid consumption of the 1–4 mm ore was determined by mixing approximately 10 g (accurately weighed) of the mineral with 200 mL of de-ionised water and titrating the pH of the slurry to an equilibrium pH of 1.5 with 300 g L^{-1} H_2SO_4. The acid consumption was calculated as follows:

$$\text{Acid consumption (kg acid/t ore)} = (V_{acid} * c_{acid})/m_{ore}$$

where V_{acid} = volume of acid used (mL), c_{acid} = acid concentration $\left(\text{g L}^{-1}\right)$, m_{ore} = mass of ore used (g).

2.2. Biological generation of ferric iron

Two iron-oxidising bioreactors were operated to generate ferric iron for the subsequent oxidation of pyrite in upflow columns. The bioreactors were inoculated with a mixture of four enrichment cultures: three mixed cultures obtained from different sites within Collie coal mine, WA, and one mixed culture of iron-oxidising microorganisms obtained from CSIRO Land and Water culture collection. The first bioreactor was a saturated downflow packed bed reactor (total liquid volume 5.8 L) and the second one an upflow packed bed reactor (total liquid volume 1 L). Both bioreactors were filled with plastic bioballs (Resun) which had a diameter of 2.6 cm and a nominal surface area of 84 cm^2. The downflow and upflow bioreactors contained 565 and 117 bioballs, respectively with total bioball surface areas of approximately 4.7 m^2 and 0.98 m^2, respectively.

The bioreactors were fed with the medium (pH 1.0) containing (g L^{-1}): 0.1 $MgSO_4 \cdot 7H_2O$, 0.1 KH_2PO_4, 0.4 $(NH_4)_2SO_4$, 130 $FeSO_4 \cdot 7H_2O$ (fertiliser grade) and 1 mL L^{-1} trace element solution (pH 1.8) containing (mg L^{-1}): 62 $MnCl_2 \cdot 2H_2O$, 68 $ZnSO_4 \cdot 7H_2O$, 64 $CoCl_2 \cdot 6H_2O$, 30 H_3BO_3, 10 Na_2MoO_4, 66 $CuCl_2 \cdot 2H_2O$ and 33 $NaVO_3$. No liquid recycling was used in the bioreactors. The bioreactors were aerated (2.5–5 L min^{-1}) from the bottom of the reactors. Attempts were made to stepwise decrease the hydraulic retention time (HRT) of the bioreactors to assess the minimum HRT required to completely oxidise 26 g Fe^{2+} L^{-1} in the influent. The bioreactors were initially operated at room temperature (21 °C). After 32 days of operation a heating tape was wrapped around the small upflow bioreactor and the temperature of the reactor was increased to 28–30 °C to test if higher temperature could increase the iron oxidation rate and allow a lower HRT.

The iron-oxidising bioreactors were monitored for flow rate, pH and redox potential. Influent and effluent pH were measured in unfiltered samples using a TPS general purpose pH probe, and redox potential using an Ionode ORP Comb Electrode, Model PRFO, with Ag/AgCl reference electrode. The redox potential values reported in this paper are against Ag/AgCl reference. The dissolved Fe^{2+} concentration was calculated based on redox potential and a calibration curve prepared by titrating the ferrous iron media with potassium dichromate.

2.3. Oxidation of pyrite with biologically generated ferric iron

2.3.1. Column setup

Four upflow columns (columns 1–4) were assembled for the ferric oxidation of pyrite-containing gold ore. Each column contained 1.6 kg of 1–4 mm size fractioned ore. The ore placed in the columns was first washed for 7 days with tap water (pH 1 adjusted with H_2SO_4) at 30 L h^{-1} m^{-2} corresponding to 3.7 mL min^{-1} to solubilise acid soluble minerals, until the pH of the effluent was approximately 1.5. Thereafter, the columns were inoculated by pumping 50 mL culture of native *Acidithiobacillus ferrooxidans* strain Straits #2 into the columns. The inoculum was a mixture of *At. ferrooxidans* strains grown under aerobic and anaerobic conditions at 30 °C. The aerobic culture was grown with the growth medium containing 0.4 g L^{-1} of each $(NH_4)_2SO_4$, $MgSO_4.7H_2O$ and KH_2PO_4, 1 mL L^{-1} trace element solution (see above) and 20 g L^{-1} $FeSO_4.7H_2O$. The anaerobic culture was grown in a medium which was prepared by filtering the ferric iron solution