Application of a selective dissolution protocol to quantify the terminal dissolution extents of pyrrhotite and pentlandite from pyrrhotite tailings

Srinath Garg [a], Vladimiros Papangelakis [a,*], Elizabeth Edwards [a], Radhakrishnan Mahadevan [a,b]

[a] Department of Chemical Engineering and Applied Chemistry, University of Toronto, 200 College Street, Toronto, ON M5S 3E5, Canada
[b] Institute of Biomaterials and Biomedical Engineering, University of Toronto, 164 College Street, Toronto, ON M5S3E1, Canada

ARTICLE INFO

ABSTRACT

The recovery of valuable base metals from mining rejects presents an economical alternative to conventional hydrometallurgical processes. The reject of interest investigated in the present work is a nickeliferous, upgraded pyrrhotite tailings produced by Vale Base Metals in the Sudbury Basin of Ontario. A QEMSCAN™ analysis of the tailings showed a total Ni content of 1 wt%, with 59% of the total Ni deported to pyrrhotite and 40% associated with pentlandite. The initial part of this study involved the development of a selective dissolution protocol to quantify the differential dissolution extents of the two Ni-bearing minerals. Application of this protocol to the pyrrhotite tailings sample showed that an acidity of 15 wt% HCl, and a temperature of 80 °C was adequate to selectively dissolve 96% of pyrrhotite from the tailings. Subsequently, an anoxic acidic leach of the tailings at pH 1.5, and at 5% (w/v) solids loading showed minimal dissolution of Fe and Ni from pentlandite in tests with and without pH control. The extent of Ni dissolution was next evaluated as a function of pH during an oxic acid leach. The testing protocol involved leaching the tailings under two pH regimes: fixed and uncontrolled pH. The results showed that operation at a fixed pH increases the extent of Ni dissolution due to the higher concentration of the oxidant Fe(III) in solution. Finally, an oxic ferric leach showed that the terminal dissolution extents of pyrrhotite and pentlandite were comparable at 46% total Ni extraction.

© 2016 Elsevier B.V. All rights reserved.

1. Introduction and background

With stricter environmental regulations necessitating investment in emissions reduction technology, the mining industry is moving towards more cost-effective and environmentally friendly methods of extracting metals from minerals. The microbial-mediated recovery of valuable base metals from mining rejects presents an economical alternative to conventional hydrometallurgical processes (Cameron et al., 2009; Garg et al., 2012; Garg et al., 2015). The last decade has seen the development, and expansion of the heap bioleaching technology to primary Cu sulfide and Ni sulfide ores (Hunter, 2002; Riekkola-Vanhanen, 2007; Wen et al., 2006). Base metals could also be potentially recovered from waste streams that result from the milling of Ni sulfide-containing ores (Peek et al., 2011). Currently, sulfide ores contribute to 60% of the primary Ni production, with pentlandite being the primary mineral of interest (USGS Minerals Information, 2012). Pyrrhotite, chalcopyrite, and pyrite are minerals that are typically found to be associated with

pentlandite and are separated from floatation processes. Nickeliferous pyrrhotite is known to be the most abundant phase to be separated and rejected from Ni sulfide ores, and contains up to 0.8% Ni in solid solution (Habashi, 1997, Peek et al., 2011). Kerfoot et al. (1997) showed that Ni sulfide ores may contain Cu, Co, and numerous platinum group elements, all of which represent significant market value. Due to incomplete mineral separation, these metals report to the tailings at various, yet minor concentration levels.

Previous estimations have shown that a conservative estimate would assign Sudbury with 50–100 million metric tonnes of recoverable tailings (Peek et al., 2011). Thus, the nickeliferous pyrrhotite tailings are regarded as an alternative Ni source, with the added advantage of being easily reclaimed through surface mining.

Pyrrhotite is known to occur naturally in two forms: monoclinic (Fe_7S_8), and hexagonal (Fe_9S_{10}) (Carpenter and Desborough, 1964; Arnold, 1967; Yund and Hall, 1969; Bennett et al., 1972). Previous studies have shown that both forms are acid-soluble, reacting rapidly with heated aqueous HCl (Ingraham et al., 1972; Parsons and Ingraham, 1970; Pilgrim and Ingraham, 1970) as shown below:

$$Fe_7S_8 + 14HCl \rightarrow 7FeCl_2 + 7H_2S + S^0 \tag{1}$$

$$Fe_9S_{10} + 18HCl \rightarrow 9FeCl_2 + 9H_2S + S^0 \tag{2}$$
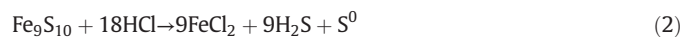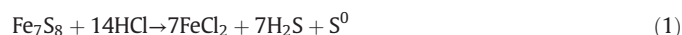
* Corresponding author.
  E-mail addresses: srinath.garg@mail.utoronto.ca (S. Garg),
vladimiros.papangelakis@utoronto.ca (V. Papangelakis), elizabeth.edwards@utoronto.ca
(E. Edwards), krishna.mahadevan@utoronto.ca (R. Mahadevan).

Parsons and Ingraham (1970) investigated the extent of pyrrhotite dissolution in HCl, and showed that this method allows the recovery of S^0 from H_2S by reaction with air or SO_2 according to reactions 3 and 4.

$$2H_2S + O_2 \rightarrow 2H_2O + 2S^0 \qquad (3)$$

$$2H_2S + SO_2 \rightarrow 2H_2O + 3S^0 \qquad (4)$$

On the other hand, Corrans and Scholtz (1976) showed that the effect of acidity on pentlandite dissolution was negligible. The material investigated in this study is a nickeliferous pyrrhotite tailings reject stream produced by Vale Base Metals in the Sudbury Basin of Ontario. The primary Ni-bearing minerals in the tailings are pyrrhotite and pentlandite. To evaluate the viability of extracting Ni by a bioleaching operation, it is necessary to develop a pyrrhotite-pentlandite mineral separation protocol that will enable the measurement of the differential rates of dissolution of these minerals. Separation can be achieved if a selective chemical dissolution protocol could be developed. Such separation protocol that involved the sequential and selective dissolution of mineral phases was recently used to characterize leach residues generated during the leaching of a chalcopyrite concentrate in the CESL process (Sahu and Asselin, 2011).

The initial part of the study is focused on the mineralogical characterization of the tailings sample using QEMSCAN™ methodology. Next, a testing protocol was developed to establish conditions of acidity, temperature, and agitation speed to selectively dissolve pyrrhotite from the tailings, without dissolving pentlandite. The resistance of pentlandite to acidic dissolution was determined by quantifying the extent of Ni dissolution from a chalcopyrite-pentlandite mineral specimen that contained no pyrrhotite. Finally, the developed selective dissolution protocol was used to determine the terminal unreacted fractions of the two Ni-bearing minerals under two leaching regimes: an anoxic acidic leach, and an oxic ferric sulfate leach.

2. Experimental

2.1. Pyrrhotite tailings

Upgraded pyrrhotite tailings were used in this study, and were obtained from Vale's facilities in Sudbury, Ontario. The upgraded tailings were shipped to the University of Toronto in two 10 L buckets that were hermetically sealed to prevent the influx of oxygen. Upon receipt of the shipment, the slurry contents were homogenized using a heavy-duty impeller driven by a hand drill. The slurry was filtered under vacuum, bagged, and stored in a freezer at −20 °C to prevent any further surface oxidation.

2.2. Chalcopyrite-pentlandite specimen

A chalcopyrite-pentlandite mineral specimen was obtained from Xstrata's strathcona mill in Sudbury, Ontario. The specimen was initially pulverized in a jaw crusher, and subsequently ground in a ball mill. Its chemical composition was determined using an aqua regia digestion protocol. Major sulfide and gangue phases were qualitatively determined using XRD, and then confirmed using an SEM-EDX analysis. The fraction of Ni assigned to pentlandite was calculated from the mass fraction of this phase, and the average elemental wt% of Ni in pentlandite.

2.3. XRD analysis

Samples were analyzed at the Department of Geology, University of Toronto using a BRUKER AXS D8 Advance Diffractometer. The accelerating voltage and the beam current were maintained at 40 kV and 35 mA, respectively. A step time of 0.2 s, together with a step increment of 0.02° and a 2θ range of 3–70° was used to map the relative intensities of the phases as functions of the diffraction angle. The relative peak intensities

were then qualitatively matched with the corresponding mineral of interest using the PDF2/PDF4 powder diffraction databases provided by the International Center for Diffraction Data (ICDD). The detection limit was between 0.5 and 2 wt%, depending on the crystallinity of the material.

2.4. Mineralogical characterization of pyrrhotite tailings

About 200 g of a representative subsample was submitted to the mineralogy department at SGS Canada Inc. for an exhaustive mineralogical characterization using QEMSCAN™. For the purpose of this analysis, a micro-riffled subsample of the head sample was used for XRD, and also for calibrating the QEMSCAN™ methodology. The head sample was further separated into two size fractions: +25 μm and −25 μm. A subsample of each size fraction was analyzed by XRF to determine the elemental compositions, and from that the mass distribution of minerals in the tailings based on the stoichiometric mineral compositions as identified by XRD. A total of four graphite-impregnated, polished, epoxy mounts were prepared from each fraction, which were then analyzed for their mineralogical variability on the micrometer scale using QEMSCAN™. A Bulk Mineral Analysis (BMA) was performed using the linear intercept method by rastering an electron beam at a pre-defined point spacing, and covering the entire polished section at any given magnification (Grammatikopoulous et al., 2011; Ayling et al., 2012). The bulk-phase chemical composition of the tailings was independently determined by digesting a representative subsample in aqua regia, and analyzing for base metals using an Optima 7300 dual view ICP-OES. The chemical composition was then compared with the QEMSCAN™ data for validation purposes.

2.5. SEM analysis for S^0 in leach residues

The preparation of polished cross sections involved dispersing 1 g of the sub-sample on an epoxy resin (EpoThin 2 low viscosity epoxy, agar scientific), and curing it for 24 h. Prior to grinding, any surface dust on the sample was removed using compressed air. Subsequently, the sample was sonicated, and ground for 10 min using a 600 grit silicon carbide paper, and then for 5 min each using a combination of 1500 grit and 2000 grit paper. After grinding, the sample was carbon-coated to enhance conductivity, and allow the electron beam to raster the surface without deflection. Sample preparation did not involve the use of the diamond suspension, or any organic solvents (i.e., polyvinyl alcohol/acetone) during the polishing stage, as S^0 is known to be soluble in an organic phase. Polished cross sections of the tailings were viewed using a JEOL JSM-6610LV Scanning Electron Microscope operated under the back-scattered electron mode (BSE). For the entire duration of this analysis, an operating voltage of 15 kV and a specimen current of 3 nA was used. Mineral phases and any reaction products such as S^0 were identified semi-quantitatively using the Kα characteristic EDX spectra obtained using an X-max energy dispersive, silicon drift X-ray detector (Oxford instruments).

2.6. Deportment of Ni

An electron microprobe analysis (EMPA) was used to determine the Ni content in the Ni-bearing minerals, via a wavelength-dispersive X-ray spectroscopy (WDS) using a Cameca SX-50 Microprobe Analyzer. The analysis was carried out at an accelerating voltage of 20 kV and a probe current of 20 nA. The Kα characteristic X-ray spectrum was used to identify the elements associated with the Ni-bearing minerals (Fe, S, and Ni).

2.7. Chemical analysis

The concentrations of base metals in solution were determined using an Optima 7300 dual view ICP-OES. The tailings and leach residue