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Characterisation of iron-rich precipitates from synthetic atmospheric nickel laterite leach solutions

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ABSTRACT

Iron-rich precipitates from atmospheric nickel laterite leach solutions normally contain large amounts of poorly defined phases such as schwertmannite and ferrihydrite. This complicates mineralogical identification using routine X-ray Diffraction (XRD) technique. In the present study, the iron-rich precipitates from synthetic nickel laterite leach solutions were characterised by a combination of several techniques that include selective Acidified Ammonium Oxalate (AAO) dissolution, Differential X-ray Diffraction (DXRD), Scanning Electron Microscopy (SEM) and Fourier Transform Infra-Red (FTIR) spectroscopy. These techniques in combination allowed reliable mineralogical identification for samples containing high proportions of schwertmannite and ferrihydrite. The effects of foreign metallic cations on the crystallization, dissolution behaviour and surface sulphate coordination were investigated. The results suggest that selective AAO dissolution is a good method to distinguish between poorly and highly structurally-ordered phases in a mixed assemblage. The presence of goethite in the iron-rich precipitates was only determined after removing the schwertmannite and/or ferrihydrite. Nickel, aluminium and chromium retarded the transformations of schwertmannite and/or ferrihydrite to goethite, but aluminium and chromium supressed the formation of 6-line ferrihydrite. Also, aluminium and chromium influenced the absorbed sulphate symmetry of iron-rich precipitates. The structural order of the phases became less pronounced with the presence of foreign metallic cations, particularly aluminium and chromium. Aluminium and chromium can strongly stabilize iron-rich precipitates making these resistant to leaching by AAO solution. FTIR analysis confirmed the presence of goethite in the bi-metallic precipitates and suggested that the sulphate is present to a greater extent in lower symmetry environments.

1. Introduction

Atmospheric acid leaching (AL) to process nickel laterite ores has attracted increasing attention in recent years due to its lower capital cost compared to high pressure acid leaching (HPAL) (McDonald and Whittington, 2008). Unlike HPAL, in which iron, aluminium and chromium are precipitated as oxide, hydroxide or basic sulphate during the leaching process (Whittington and Muir, 2000), the pregnant leach solution (PLS) from AL usually contains significant amounts of trivalent iron, aluminium and chromium ions. For example, typical concentration values for these impurities in the PLS from heap leaching of Greek nickeliferrous laterite with sulphuric acid have been reported as 23 g/L Fe^{3+}, 6.0 g/L Al^{3+} and 1.0 g/L Cr^{3+} (Agatzini-Leonardou et al., 2009).

During the downstream hydrometallurgical processing of AL laterite leach liquors, the effective removal of impurities is required to produce pure nickel and cobalt compounds and/or metals. This is usually achieved by precipitation and often involves co-precipitation and/or incorporation of nickel and cobalt. In our earlier work (Wang et al., 2011), the effects of the factors governing nickel loss during iron removal from synthetic AL liquors containing just nickel and iron were examined by statistical methods. The precipitates obtained under various experimental conditions were dominated by ferrihydrite and/or schwertmannite. These iron-bearing oxyhydroxide and oxyhydroxysulphate minerals are thermodynamically unstable, and tend to transform over time to more stable iron oxides such as goethite and/or hematite (Cornell and Schwertmann, 2003). Moreover, the data on the thermodynamic properties and precise crystal structures of schwertmannite and ferrihydrite are still under debate (Jambor and Dutrizac, 1998; Majzlan et al., 2004). The disordered nature of these structures often leads to difficulty in mineralogical identification using routine X-ray Diffraction (XRD) techniques. Furthermore, the mutual poor structural order of schwertmannite and ferrihydrite complicates their identification in a mixed assemblage. In particular, schwertmannite and ferrihydrite can become nearly undetectable by XRD when significant amounts of minerals with high structural order are also present in the mixed

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precipitate (Campbell and Schwertmann, 1984; Schwertmann et al., 1982). On the other hand, trace to minor amounts of minerals with good structural order can be overlooked due to their XRD peaks being masked by those of poorly defined minerals (Caraballo et al., 2009; Schulze, 1981). In such cases, a correct mineralogical analysis can only be made using a combination of several techniques that include selective dissolution using Acidified Ammonium Oxalate (AAO), Differential X-ray Diffraction (DXRD), Scanning Electron Microscopy (SEM), Fourier Transform Infra-Red (FTIR) spectroscopy.

Metallic cations that include aluminium, chromium and nickel have been found to influence both the formation and transformation of iron oxides. These either change the composition and properties of the end products or slow the transformation rates of their intermediates (Cornell and Schwertmann, 2003). Much research has been directed toward understanding the association of aluminium, chromium and nickel with goethite and ferrihydrite: see, for example, Al, Cr and Ni-goethite (Schwertmann et al., 1989; Singh and Gilkes, 1992; Singh et al., 2002) and Al, Cr and Ni-ferrihydrite (Giovanoli and Cornell, 1992; Lewis and Schwertmann, 1979; Schwertmann, 1991). These studies have established the mechanism of cation substitution for iron in goethite. However so far, no direct evidence of structural incorporation has been provided for the co-precipitation of ferrihydrite with various cations, probably due to the small particle size and poor crystallinity of ferrihydrite which makes the distinction between surface and adsorption and structural incorporation difficult to determine (Cornell and Schwertmann, 2003). Furthermore, very few studies have examined the mixtures of iron oxides, oxyhydroxide and oxyhydroxysulphate with other metallic cations that commonly occur in the hydrometallurgical processing of AL liquors. Acero et al. (2006) studied the behaviour of trace metallic cations during schwertmannite precipitation and subsequent transformation into goethite and jarosite. However, this study as well as others (Caraballo et al., 2009; Dold, 2003b) all focused on natural precipitates from acidic mine water and under conditions that differ from hydrometallurgical precipitation processes.

The present study, which is an extension of our earlier work (Wang et al., 2011), aims to apply selective AAO dissolution and characterisation techniques that include DXRD, SEM and FTIR spectroscopy to obtain an accurate and detailed mineralogical identification of complicated iron-rich precipitates from synthetic atmospheric nickel laterite leach solutions, which contain both poorly and highly structurally-ordered phases formed in the presence of foreign metallic cations. Emphasis is directed toward the effects of the foreign metallic cations on crystallization, dissolution behaviour and mineralogical properties of the precipitates.

2. Experimental and analytical methods

All precipitation experiments were conducted using a semi-batch reaction vessel. The experimental set-up and procedure has been detailed in our earlier work (Wang et al., 2011). For each test a volume of 500 mL of synthetic PLS containing 30 g/L Fe^{3+} [as $Fe_2(SO_4)_3 \cdot xH_2O$], 0 to 5 g/L Ni^{2+} [as $NiSO_4 \cdot 6H_2O$], 0 to 6.5 g/L Al^{3+} [as $Al_2(SO_4)_3 \cdot 18H_2O$], and 0 to 2 g/L Cr^{3+} [as $Cr_2(SO_4)_3 \cdot xH_2O$] was pumped into a baffled reaction vessel containing a pre-determined amount of de-ionised water over a period of 2.5 h. A $CaCO_3$ (25% w/w) suspension in de-ionised water was simultaneously pumped into the reaction vessel to maintain the pH at 4. The temperature was controlled using an oil bath and the precipitation reactions conducted at both 25 and 85 °C. At the completion of the reaction, the resulting slurry was vacuum filtered through a 0.45 μm Gelman Supor® membrane. The metal concentrations in the filtrate were analysed by ICP-OES, and the filter cake was carefully washed with large amounts of hot de-ionised water until the conductivity of the filtrate was constant (<100 μS) and then dried overnight at 60 °C. The chemical composition of the dried solid products was determined by ICP-OES after aqua regia digestion.

To obtain standards for comparison, schwertmannite was synthesized by the method of Loan et al. (2004) and 6-line ferrihydrite according to the method of Schwertmann and Cornell (2000). Briefly, schwertmannite was prepared by placing 1 L of 0.7 g/L ferric solution (as $Fe_2(SO_4)_3 \cdot xH_2O$) in a Nalgene® bottle and agitated using a mechanical bottle-roller water bath at 85 °C for 1 h. The solution was filtered through a 0.45 μm Gelman Supor® membrane, washed with Milli-Q water and dried overnight at 60 °C. The 6-line ferrihydrite was prepared by adding 20 g of $Fe(NO_3)_3 \cdot 9H_2O$ into preheated 75 °C Milli-Q water for 10 min, quenching in an ice bath and transferring the product to dialysis tubing for at least 3 weeks to remove the NO_3^- ions. The colloidal 6-line ferrihydrite formed was collected by freeze drying.

Selective dissolution experiments were conducted by dissolving the dried precipitates in 0.2 M ammonium oxalate solution acidified to pH 3.0 with 0.2 M oxalic acid at room temperature in the absence of visible light, as described by Schwertmann et al. (1982). The dissolution kinetics was studied by shaking approximately 2 g of sample in 1 L of acidified ammonium oxalate solution and extracting 10 mL samples at specific time intervals. The samples were immediately filtered and the ion concentration in the filtrate analysed by ICP-OES.

Dried solid samples were analysed by X-ray Diffraction (XRD) using a Philips X'pert diffractometer with Co Kα radiation operated at 45 kV and 40 mA with a step scan of 0.02°. Fourier Transform Infra-Red (FTIR) spectroscopy measurements were made with a Bruker infrared spectrometer from 4000 to 400 cm^{-1} at room temperature using the KBr pellet technique. Some samples were carbon-coated and examined at high magnification with a Zeiss Neon 40EsB Focussed Ion Beam-Scanning Electron Microscope (FIB–SEM).

3. Results and discussion

3.1. Chemical compositions and mineralogical properties of the iron precipitates

The first two experiments shown in Table 1, labelled as EM-1 and EM-2 refer to the precipitates obtained from the PLS containing only ferric iron, which serve as "baselines" for other experiments. EM-3 and EM-4 are the bi-metallic samples precipitated from PLS containing iron and nickel, while EM-5 and EM-6 represent the multi-metallic samples obtained from PLS containing iron, aluminium, chromium and nickel. Notably, from Table 2, increasing temperature resulted in more aluminium, chromium, and nickel, but less sulphur in the iron-rich solid precipitates.

Fig. 1 shows the XRD patterns of the synthetic 6-line ferrihydrite, synthetic schwertmannite, single-, bi- and multi-metallic samples. Schwertmannite and ferrihydrite have poor structural order, and usually precipitate as a mixture from acid sulphate solutions. Furthermore, ferrihydrite can adsorb sufficient sulphate to approximate the composition of schwertmannite, making it difficult to distinguish between ferrihydrite and schwertmannite (Bigham and Nordstrom, 2000). The XRD patterns of both schwertmannite and 6-line ferrihydrite exhibit a strong peak at around 41° 2θ and two weaker peaks between 70° and 80° 2θ, although the intensities are reversed for these two peaks. Schwertmannite displays two better defined peaks at around 21° and 31° 2θ, while 6-line ferrihydrite shows a characteristically sharper peak at around 47° 2θ. Despite the differences, it is difficult to unambiguously identify these phases in a mixed assemblage of hydrated iron oxides, particularly when admixed with other minerals.

The XRD patterns of single-metallic sample EM-1 and bi-metallic sample EM-3 appear to be dominated by schwertmannite,