Amorphous iron phases in medium temperature leach residues and associated metal loss

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ABSTRACT

Leach residues, produced during pilot and demonstration scale medium temperature (150 °C) hydrometallurgical processing of sulfide ores contain amorphous/poorly crystalline and metastable nano-scale iron oxides/oxyhydroxide phases. These phases control the properties of the residue and contain a relatively high loading of the valuable (Cu, Ni) metals. Residue samples from CESL and Vale pilot and demonstration plant medium temperature processes were characterized using different techniques. Poor agreement between total iron analysis by inductively coupled plasma mass spectroscopy (ICP-MS) and quantitative X-ray powder diffraction QXRPD indicated the presence of amorphous/poorly crystalline iron oxide phases. QXRPD coupled with sequential extraction was used for quantification of the amorphous iron phases. Amorphous iron oxides/oxyhydroxides were found to be a major source of copper and nickel losses to the residue. The distribution of copper and nickel into the amorphous and crystalline iron oxide phases was determined by a two-stage sequential extraction process. Association of copper and nickel to the amorphous phases was found to be approximately 2–4 times higher than with the crystalline iron oxide phases.

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1. Introduction

Iron control in medium temperature hydrometallurgical processing of copper and nickel concentrates is a critical consideration. These processes generate residues which are usually a mixture of hematite, goethite, jarosite and other iron oxide/oxyhydroxide phases and which may contain an amorphous fraction. From an environmental point of view, jarosite and amorphous/poorly crystalline iron oxide phases are not considered good candidates for disposal. These phases transform with time, under certain conditions, and release acid and/or toxic elements to the surroundings (Dutrizac, 1987). Additionally, amorphous iron oxide/oxyhydroxide phases have a higher adsorption capacity compared with their counterpart crystalline phases and lead to higher valuable metal loss to the residue (Steel et al., 2010; Sahu and Asselin, 2011). Responsible and economical resource extraction necessitates minimum loss of valuable metals to the residues. Consequently, operators of medium temperature leach processes have an economic incentive to maximize copper and nickel recovery.

Cominco Engineering Services Limited (CESL — a subsidiary of Teck Corporation) and Vale have developed hydrometallurgical processes for the extraction and recovery of copper and nickel from base metal concentrates. CESL is a medium temperature (150 °C) and pressure

(1300 kPa) process that occurs in a mixed sulfate-chloride medium at about pH of 2–3, with retention time of 60 min (Defreyne et al., 2006; Defreyne and Cabra, 2009; Mayhew et al., 2010). Vale is in the process of commissioning a large medium temperature leach facility in Newfoundland and Labrador, Canada. The nickel process also operates under similar pressure oxidation conditions. The CESL and Vale processes can efficiently process low grade concentrates with widely varying Fe:Cu and Fe:Ni ratios (Defreyne et al., 2006). Typical copper and/or nickel recoveries from medium temperature leach processes are in the range of 92–98% (Defreyne et al., 2006), thus in some cases there is an opportunity to reduce losses of these metals by limiting their deportment to the process residues. During the processing of the ores it is preferred that iron be precipitated in the form of crystalline hematite because of its superior filtration and washing characteristics, its environmental stability and because it typically does not ad/absorb as much of the valuable metals (Ni and/or Cu) that these processes are trying to recover (Piret and Melin, 1993).

Residues from the hydrometallurgical processes usually contain elemental sulfur and iron oxide phases along with associated gangue minerals. The chemistry of iron precipitation in hydrometallurgical circuits is quite complex and it can precipitate in different oxide forms with variable crystallinity. Considering crystallinity of the precipitated phases, iron precipitates can be divided into three regimes (i) Crystalline (ii) Poorly crystalline and (iii) Amorphous iron oxides. Regime (i) normally contains hematite, goethite and jarosite. Possible phases

in regime (ii) can be hematite and goethite, as both of these phases have been shown to exhibit variable crystallinity (Machala et al., 2007; Schwertmann et al., 1985; Johnston and Glasby, 1978), and regime (iii) can contain phases such as ferrihydrite and schwertmannite. Ferrihydrite although often labelled as amorphous is not strictly amorphous (Jambor and Dutrizac, 1998; Janney et al., 2000a, 2000b, 2001) and commonly refers to a range of poorly crystalline iron oxide phases of which 2 line (exhibiting 2 broad XRD peaks) ferrihydrite and 6 line (exhibiting 6 broad XRD peaks) ferrihydrite are more common. It is also sometimes referred to as protoferrihydrite, amorphous iron hydroxide and colloidal or hydrous ferric hydroxide. It has been represented with the general formula $5Fe_2O_3 \cdot 9H_2O$ (Murad and Schwertmann, 1980). However, considerable debate as to its formula remains and no single formula has yet been agreed upon. A number of other formulae have also been suggested e.g. $Fe_5HO_8 \cdot 4H_2O$ (Towe and Bradley, 1967), $2FeOOH \cdot 2.6H_2O$ (Russel, 1979). Schwertmannite is represented by the ideal formula $Fe_8O_8(OH)_6SO_4$ and is a complex hydroxy ferric sulfate with poorly crystalline nature. Claassen et al. (2002) suggested that schwertmannite is nothing but ferrihydrite with high sulfate values. However, Loan et al. (2002a) stated that schwertmannite can be distinguished from ferrihydrite at least qualitatively on the basis of its morphology.

Several studies on hydrometallurgical residues have identified the presence of regime (iii) phases: Loan et al. (2006) identified approximately 40–50% 6 line ferrihydrite in the paragoethite process, which is used in zinc hydrometallurgy. Sahu and Asselin (2011) identified ferrihydrite in one of thirteen medium temperature sulfide leach residue samples. Steel et al. (2010) identified phases which were soluble in the reagents selective for amorphous iron oxides. However, true quantification of these phases, in hydrometallurgical residues, and associated valuable metal loss has always remained an issue for hydrometallurgists. Additionally in all the studies discussed above, the possible presence of regime (ii) phases was not addressed.

Amorphous/poorly crystalline phases do not respond to the X-ray diffraction as crystalline phases do. Therefore, the presence of regime (ii) and regime (iii) phases, if not taken into account properly, can result in inaccurate quantification of the crystalline phases determined by routine XRD. It should be noted that leach residues have heterogeneous mineralogy and gangue minerals can also contribute to regime (ii) and regime (iii) phases. We will only be focusing on iron oxide phases in regime (ii) and (iii). In this paper we used QXRPD coupled with ICP to determine the presence of regime (ii) and (iii) phases. Regime (iii) phases, and their associated metals, were further discriminated by sequential extraction (discussed later). The results were augmented by SEM and Mossbauer studies. As regime (ii) and (iii) both lead to X-ray amorphous content of the residue, these collectively will be referred to as X-ray amorphous phases. These phases are, in fact, the total amorphous content of the residue determined by QXRPD. A fraction of this X-ray amorphous content fell only under the category of regime (iii) i.e. the phases responsible for higher valuable metal loss to the residue, and this was determined by hydroxyl amine hydrochloride (HaHC) extraction. Therefore, it will be referred to as the HaHC phase (details of HaHC extraction are discussed later in this document).

2. Experimental

Sulfide concentrate leach residue samples (labeled as S1, S2 and S3) were supplied from CESL (S1 and S2) and Vale (S3) operations. The mineralogy of the concentrates used to generate the three samples is given in Table 1. The Munsell color of sample S1 was 7.5YR 5/6 (strong brown-dry), sample S2 was 10R 4/6 (red-dry) and sample S3 was 10R 3/6 (dark red-dry). The general conditions under which samples were generated are given in Table 2. The leach residues, produced from the leaching of sulfide concentrates, were washed, sampled, using coning and quartering, and dried in an oven at 60 °C overnight. Dried samples were lightly ground with the help of a mortar and pestle and a portion was analyzed

by ICP-MS after complete multi acid digestion. Quantitative phase analysis was performed using the Rietveld method and X-ray powder diffraction data. For this purpose, each sample was reduced into fine powder to the optimum grain-size range for X-ray analysis (<10 μm) by grinding under ethanol in a vibratory McCrone Micronising Mill for 7 min. Corundum was used as an internal standard for quantification of the relative amounts of crystalline and amorphous phases present. Continuous-scan X-ray powder-diffraction data were collected over a range 3–80° 2θ with CoKα radiation on a Bruker D8 Focus Bragg–Brentano diffractometer. The X-ray diffractograms were analyzed using the International Centre for Diffraction Database PDF-4 and Search-Match software DiffracPlus Evaluation 19.0.0.0 prior to the Rietveld analysis.

To determine the amounts of amorphous and crystalline iron oxides/ohyhydroxides in the leach residue samples and the distribution of copper/nickel into these phases, a two stage sequential extraction was employed. Comparisons between different sequential extraction methods (Kostka and Luther, 1994; Raiswell et al., 1994; Poulton and Canfield, 2005) have shown that HaHC is the most selective for dissolution of amorphous iron oxides/oxyhydroxides. The sequential extraction scheme is given in Fig. 1. Phases in regime (iii), together with water soluble phases were recovered in the first stage. Regime (i) and (ii) phases were recovered in the second stage. In the first stage extraction, about 5 g of the leach residue (R) was leached using 0.25 M HaHC and 0.25 M hydrochloric acid at 50 °C under atmospheric pressure for 30 min, keeping the solid to liquid mass ratio at 1:50. The reaction mixture was then filtered. The filtrate was analyzed for Cu, Fe, Ni, As, Si and Ca. The remaining residue (R_1) was dried in an oven at 60 °C, weighed and the percent weight loss was calculated. In the second stage, approximately ~1.5 g of R_1 was leached with 4 M hydrochloric acid at 95 °C and atmospheric pressure for 30 min keeping the solid to liquid mass ratio 1:40. The filtrates were analyzed for Cu, Fe, Ni, As, Si and Ca. The remaining residue (R_2) was dried in an oven at 60 °C, weighed and the percent weight loss was calculated. In some of the experiments where residue R_2 was less than a gram, experiments were repeated several times to make enough sample for characterization. After necessary correction for the water soluble phases from the weight loss in the first stage

Table 1
Concentrate mineralogy that was leached to generate samples S1, S2 and S3.

Phase name	Phase %		
	S1	S2	S3
Chalcopyrite	38	35	7
Cubanite		30	
Enargite	20	1	
Pyrite	18		
Bornite	7		
Covellite	5		
Tennantite	2		
Sphalerite	2		
Pentlandite		5	63
Pyrrhotite		7	29
Others	8	22	1

Table 2
Leaching conditions for sulfide concentrates.

Operating parameters	Unit	S1	S2	S3
Total pressure	kPa	1300	1264	1030
Temperature	°C	150	150	150
Retention time	min	91	58	80
Autoclave free acid concentration	g/L	10.7	0.0	10–12
Solids loading	%	10.2	23.2	5*
$[Cl^-]$	g/L	11.2	10.4	5

* Concentrate feed slurry is diluted with coolant and anolyte from electrowinning before entering the autoclave.