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Magnetite precipitation for iron removal from nickel-rich solutions in hydrometallurgy process

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ABSTRACT

In nickel hydrometallurgical operations, the removal of iron from process liquors was critical, with the method of choice commonly being crystallization (precipitation). In this paper special attention was given to the magnetite precipitate. Potential/pH diagram for Fe–H_2O system was derived at 100 °C, and indicated that the iron ion may precipitate as magnetite at the lower oxidation potential. And the crystallization experiments proved that the iron ion partly precipitate as magnetite by slow oxidation at pH 2.0–2.2 and temperature 90–100 °C. The precipitates could be efficiently separated from the solutions by magnetic flocculation and separation. Further, analyses with Environmental scanning electron microscopy (ESEM) and X-ray Diffraction (XRD) provided a fundamental understanding of the magnetite precipitation process.

1. Introduction

Since the early 1970s, various hydrolysis–precipitation methods have been developed for iron removal from hydrometallurgical solutions. The widely used techniques, for examples, include the Hematite Process (Ismael and Carvalho, 2003), the Jarosite Process (Swarnkar et al., 1996; Claassen et al., 2002), and the Goethite Process (Davey and Scott, 1976; Pradel et al., 1993). The Goethite Process has the advantages of lower CAPEX over the Hematite Process and producing eco-friendly products relative to the Jarosite Process. The essential feature of the Goethite Process is that the concentration of ferric iron should be maintained at less than 1 g/L during precipitation (Dutrizac, 1987). This requirement can be met by either reducing all ferric ions to the ferrous state (V.M. method) (Bodson, 1972) or by adding the concentrated PLS into a large precipitation vessel at the same rate as goethite precipitation (E.Z. method) (Loan et al., 2006). The E.Z. method led to the development of another two iron removal processes: the Paragoethite Process and Zincor Process (Cubeddu et al., 1996; Meyer et al., 1996). Unlike the Hematite, Jarosite and Goethite Processes, the Paragoethite and Zincor Processes are much less common, in operation at only three commercial zinc processing sites (Wang et al., 2011). Very little information was available on the exact nature of the Paragoethite and Zincor residues, until recent studies of (Loan et al. (2002a)) and Claassen et al. Loan et al. (2002b) indentified 6-line ferrihydrite and schwertmannite to be the major iron precipitation products.

While the iron removal processes are widely used for solution purification in the zinc industry, their application to nickel sulfate projects has also been explored. Generally, the rejection of iron by precipitation in the hydrometallurgical processing of nickel follows the same routes used in the zinc industry, and an understanding of these processes therefore comes from the studies centered on the processing of zinc. Research has focused on the removal of iron by goethite precipitation from iron-containing nickel sulfate solutions (Wang et al., 2011; Allan, 1973; Chang et al., 2010). However, in the case of goethite process, the precipitates were “amorphous iron phases”, likely to be nanoscale minerals ferrihydrite or schwertmannite (Loan et al., 2006). The finely grained, poorly crystalline residues generally resulted to the bad filterability (Claassen et al., 2002).

This study conducted goethite process at a lower pH value by V.M method, and found that the iron could partly precipitate in the form of magnetite. The magnetite particles would offset the bad settleability and filterability of the precipitates by magnetic flocculation or magnetic separation. Further Environmental scanning electron microscopy (ESEM) and X-ray Diffraction (XRD) analysis provided a fundamental understanding of the characteristics of the precipitates. And the Eh–pH diagram of iron was plotted for providing persuasive evidence.

2. Experimental

2.1. Materials and preparation

Concentrated acidic $NiSO_4/Fe^{2+}$ feed liquor that contained 0.1 g L^{-1} H_2SO_4 (pH $\approx$ 1), 107.99 g $L^{-1}Ni^{2+}$ and 6.54 g L^{-1} Fe^{2+} was obtained from the 4th Nickel Smelter of Jinchuan Group ltd in Gansu province, China. The nickel smelter adopted the pressure oxidative leaching process. As shown in Table 1, the nickel sulfate leaching solution contained a large amount of ferrous ion, as well as a variety of analytes, such as Cd, As, Pb, Cu, Ni, and Mn, accounting for the complication of the nickel-rich solution.

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Table 1
The properties of nickel sulfate leaching solution.

Analyte	Fe^{2+}	Fe^{3+}	Ni	Cu	Co	S	Na	Pb	Si	As
Content/(g/L)	6.54	0.09	107.99	0.39	1.38	70.23	10.61	0.11	0.060	0.068

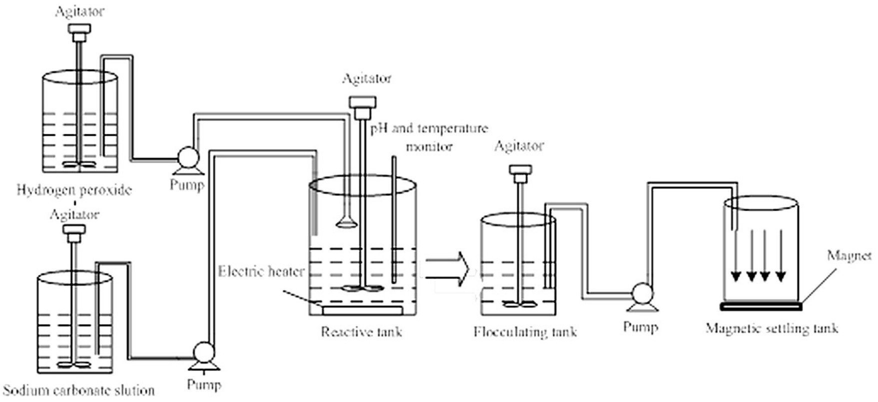

Fig. 1. Diagram of the experimental process, including iron precipitation and removal in the magnetic flocculation process.

2.2. Experimental procedure

The experiments were carried out in a 2 L water-heating reaction kettle by the V.M. process as Fig. 1. The temperature was maintained at 95 °C. The oxidizing agent, hydrogen peroxide, was pumped at a constant rate to keep the low levels of Ferric (<1 g/L) in the reactor. Meanwhile, the neutralizer, sodium carbonate, was pumped at a flow rate designed to control the pH set point (2.0–2.2) and allow the precipitation to proceed. After the precipitation, the polyacrylamide (0.1%) was added to favor the flocculation process and the slurry was pumped to the magnetic settling device for magnetic flocculation and rapid solid–liquid separation. The residues were immediately filtered and the filter cakes were washed with hot sulfuric acid solution (pH 2.0) and dried at 80 °C for 2–3 h. After drying, the samples were divided into several portions for a series of analyses.

2.3. Analytical techniques

Different materials were subjected to chemical analysis and Inductively Coupled Plasma Atomic Emission Spectrometer (ICP-AES) analyses for mass balance purposes, and X-ray Diffraction (XRD) analysis for characterization of the crystalline phase. Qualitative and semi-quantitative data from Environmental Scanning Electron Microscopy (ESEM) analyses were indicative of the phases and genesis of precipitated particles, thus were used to support the XRD, XRF and chemical analysis findings.

Table 2
A_T values at different temperatures.

T/K	298	333	373	423	473	573
A_T	0.511	0.545	0.595	0.689	0.809	1.983

Table 3
Theϕ^{θ} values of various reactions in Fe–H_2O system at different temperatures.

Reaction no.	Reaction	$\phi^{\theta}{}_T$/V	
		25 °C	100 °C
A	$O_2+4H^++4e=2H_2O$	1.228	1.225
B	$2H^++2e=H_2$	0	0.0578
1	$Fe^{2+}+2e=Fe$	−0.442	−0.373
2	$Fe^{3+}+e=Fe^{2+}$	0.736	0.881
3	$Fe_2O_3+H_2O+2e=2HFeO_2^-$	−1.182	−1.230
4	$Fe_3O_4+8H^++8e=3Fe+4H_2O$	−0.120	−0.0925
5	$3Fe_2O_3+2H^++2e=2Fe_3O_4+H_2O$	0.178	0.229
6	$HFeO_2^-+3H^++2e=Fe+2H_2O$	0.461	0.530
7	$Fe_3O_4+8H^++2e=3Fe^{2+}+4H_2O$	0.847	0.750
8	$Fe_3O_4+2H_2O+2e=2HFeO_2^-+H^+$	−1.862	−1.960
9	$Fe_2O_3+6H^++2e=2Fe^{2+}+3H_2O$	0.624	0.576

2.4. The ϕ-pH diagram of Fe–H_2O system

A brief method for construction of ϕ-pH diagram, which could be constructed from the stoichiometry of reactions and free energy data for the species involved. Either the van't Hoff isotherm or Nernst equation was utilized for the determination of the equilibrium lines of reactions.

The calculation required to obtain the ϕ-pH diagram was based upon the general equilibrium equations for an aqueous system containing ferric and ferrous ions. The basic equation of reactions was shown as formula (1), ϕ_T and pH for this equation could be calculated as formulas (2) and (3):

$$aA_b + nH^+ + ze = bB_a + cH_2O \tag{1}$$

$$\phi_T = \phi_T^{\theta} - 2.303[RTn/(ZF)]pH - 2.303[RTn/(ZF)]\lg\left(a_{B_a}^{b}/a_{A_b}^{b}\right) \tag{2}$$

$$pH_T = pH_T^{\theta} - 1/n\ln\left(a_{B_a}^{b}/a_{A_b}^{a}\right). \tag{3}$$

Values of ϕ_T^{θ} were determined according to Nernst equation, ϕ-pH diagram was obtained based on formulas (2) and (3) sequently, and free energy data of high temperature were required by formula

Table 4
The $pH^{\ominus}$ values of various reactions in Fe–H_2O system at different temperatures.

Reaction no.	Reaction	$pH^{\theta}{}_T$/V	
		25 °C	100 °C
10	$Fe_2O_3+6H^+=2Fe^{3+}+3H_2O$	1.730	1.174

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