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Atmospheric leaching characteristics of nickel and iron in limonitic laterite with sulfuric acid in the presence of sodium sulfite

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ABSTRACT

Atmospheric leaching of nickel from limonitic laterite ores is regarded as a promising approach for nickel production, despite its low nickel recovery and slower leaching rate than high pressure acid leaching. Sulfur dioxide can enhance the sulfuric acid leaching of laterite, but its behavior for enhancing atmospheric sulfuric acid leaching was uncertain due to SO_2 losses and emission. In this study, sodium sulfite was used as a substitute for SO_2 gas in the leaching and the sulfuric acid leaching characteristics of Ni and Fe from a limonitic laterite in the presence of sodium sulfite were investigated. A linear correlation exists between the extraction of Ni and Fe, indicating the difficulty in selective leaching of Ni over Fe. Most nickel is isomorphically substituted within the goethite and it is difficult to dissolve in a high oxidation–reduction potential solution environment, resulting in a low nickel recovery. SO_2(aq) generated from the reaction of sodium sulfite in sulfuric acid solution, lowers the potential for the reducing reaction of FeOOH to give Fe^{2+}, accelerating the iron extraction and nickel liberation from goethite.

1. Introduction

Due to the increasing world demand for nickel, it is imperative to utilize nickeliferous laterite ores which account for about 70% of the global nickel reserve (Rao et al., 2013). Limonitic laterites are therefore important nickel sources that are characterized by low nickel content and high total iron content.

A large number of studies on acid leaching of laterites have been reported. In general, high pressure acid leaching (HPAL) (Whittington and Muir, 2000; Dalvi et al., 2004; Rubisov et al., 2000) is known to be the most effective aqueous treatment process for extraction of valuable metals from laterite ores. The HPAL process has the advantage of high recovery of nickel and cobalt (above 90%). But the process requires high operating temperature (245–270 °C) and pressure (4–5 MPa) (Chou et al., 1977; Das et al., 1995; McDonald and Whittington, 2008a), and specialized equipment such as titanium-lined autoclaves is required (McDonald and Whittington, 2008a; Guo et al., 2011).

Meanwhile, atmospheric leaching (AL) has also been reported for the processing various limonitic and saprolitic laterite ores (McDonald and Whittington, 2008a,b; Büyükakinci and Topkaya, 2009). The AL process has low energy consumption and capital costs. It is broadly prospective for application in spite of low leaching selectivity of nickel over iron, high acid consumption, and long leaching times.

Many reducing reagents, such as sulfur dioxide (Senanayake and Das, 2004; Gbor et al., 2000; Das and de Lange, 2011; Senanayake et al., 2011), dithionite (Lee et al., 2005), thiosulfate (Li et al., 2011) and cuprous ions (Das and de Lange, 2011; Lu and Muir, 1988; Byerley et al., 1979) have been used to facilitate the nickel extraction in atmospheric acid leaching. Sulfur dioxide has been investigated extensively. From the study of Senanayake and Das (2004), the extraction rates of nickel and iron were increased from about 45% up to nearly 85% when leached with 0.72 M sulfuric acid liquor at 90 °C for 6 h in the presence of 0.3 M sulfur dioxide. However, in practice it is necessary to control SO_2 losses and emission in the experiments. Moreover, the leaching chambers have to be replenished with SO_2 gas continuously to keep the reaction going. These factors mean that it is difficult to ascertain the functional mechanism of sulfur dioxide in acid leaching, because the fixed initial solubility of SO_2(aq) is by no means guaranteed.

To recover valuable metals from limonitic laterite with minimum SO_2 losses and emission, various sulfur-bearing salts have been used as a substitute for SO_2 gas to enhance the AL process of nickel laterites. Dithionite was used in a recent study as an efficient intermediate reducing agent in the leaching of nickel from laterites (Lee et al., 2005). Nickel extractions of 50–80% were

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obtained over 90–120 min using the current density of 3.2–32 mA/cm^2. Furthermore, sulfuric acid with sodium thiosulfate was also used to selectively extract cobalt from limonitic laterite (Li et al., 2011). The metal extractions increase dramatically in sulfuric acid leaching with sodium thiosulfate. Thiosulfate is unstable in acidic solutions and readily decomposes to sulfur and sulfur dioxide, which both reduce goethite and manganese oxides. In this instance measures would be required to minimize the cost and environmental pollution due to the emission of sulfur dioxide. However, the intermediate agent sulfur interferes with the ascertainment of the mechanism for sulfur dioxide (Li et al., 2011).

To investigate the leaching behavior of Co and Ni during aqueous sulfur dioxide leaching of a nickel smelter slag, Gbor et al. (2000) prepared the aqueous sulfur dioxide firstly by pumping SO_2 gas into the deionized and deoxygenated water at fixed gas velocity. This operation was beneficial to investigation of the sulfur dioxide reduction mechanism, although it was not able to guarantee the homogeneous solubility of sulfur dioxide. For simplification of the experimental process and assurance of the same initial solubility of sulfur dioxide, sulfite can be used as an alternative to aqueous sulfur dioxide to promote the acid leaching of laterite ore. By adding a certain content of sodium sulfite, which reacts with H^+ ions from sulfuric acid, the reaction should generate a constant $SO_2(aq)$ reactant level under the control of the SO_2 solubility.

This paper is aimed at revealing the leaching characteristics of nickel and iron from limonitic laterite during atmospheric acid leaching. A limonitic laterite ore was leached to extract nickel and iron in the presence of sodium sulfite and the extraction mechanism was investigated. Based on the leaching results, the extraction correlation between nickel and iron an appropriate scope for selective leaching is discussed.

2. Experimental

2.1. Materials

2.1.1. Limonitic laterite ore

The laterite ore was obtained from Indonesia. Its chemical composition is shown in Table 1. The laterite is characterized by high iron content (Fe_{total} = 43.9 wt.%), low nickel content (1.03 wt.%) and high loss on ignition (LOI = 15.2 wt.%). According to the XRD results (seen in Fig. 1), the ore mainly consists of goethite, maghemite and gibbsite. The sample is a typical limonite-type nickeliferous laterite ore.

Previous ESEM studies (Li et al., 2011) of the sample shows that a majority of nickel occurs in iron-bearing mineral goethite (FeOOH). Chemical phase analysis (Zhang, 1992; Li et al., 2012) was used to further ascertain the phase distribution of nickel in the laterite ore, and the results shown in Table 2. Nearly 70 wt.% of nickel was determined as isomorphically substituted in goethite. In addition, 13.53 wt.% nickel is hosted in manganese oxides, and 7.52 wt.% and 3.75 wt.% of nickel are in the form of silicates and carbonate, respectively.

2.1.2. Reagents

Leaching reagents including sulfuric acid and sodium sulfite used in this work were of analytical grade.

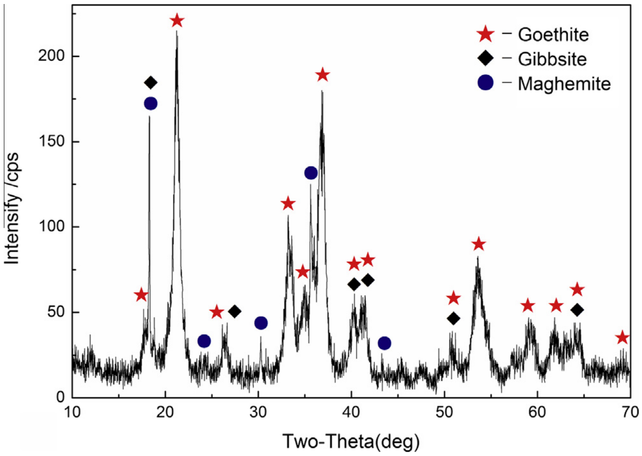

Fig. 1. XRD pattern of the laterite ore sample.

Table 2
Distribution of nickel in the laterite ore sample/wt.%.

Existential phase	Goethite	Manganese oxides	Silicates	Carbonate	Adsorbed nickel
Fraction	69.92	13.53	7.52	3.75	4.79

2.2. Methods

The laterite ore was dried at 110 °C for 6 h and then ground to 100% passing 74-μm standard sieve for sulfuric acid leaching. Leaching tests were conducted in a DY-8 autoclave equipped with eight 70 mL stainless steel pots rotating end to end in a glycerine bath. The protective lining of the pots is made from teflon. The bath was electrically heated and its temperature was controlled by a thermostat from room temperature to 150 °C. At the beginning of each trial, 5 g of the ground laterite ore sample was dissolved in 50 mL 8%(w/w) sulfuric acid or 8%(w/w) sulfuric acid containing 30 g/L sodium sulfite inside the stainless steel pots. The sealed pots were subsequently submerged and rotated at 30 rpm in the bath at a selected temperature and for a specified time. Filtration was performed immediately after leaching, followed by atomic absorption spectrophotometer (AAS, Shimadzu, AA-6800, Japan) analysis of the filtrate for determination of the nickel and iron contents. The residue was dried, and then a 0.1000 g sample was dissolved by mixed acid (sulfuric acid: phosphoric acid = 1:1), the iron content in the solution was determined by the titration method using $K_2Cr_2O_7$, and the nickel content was determined by AAS, the iron and nickel contents were calculated. The extractions of nickel and iron were taken as evaluation indexes and calculated by Eq. (1):

$$\gamma = \left[1 - \left(\frac{m_1 \times \beta}{m_0 \times \alpha}\right)\right] \times 100\% \tag{1}$$

where γ is the metal extraction, %; α is the metal content of dried laterite ore, wt.%; β is the metal content of dried residue; and m_0 is the mass of dried laterite ore; and m_1 is the mass of dried residue.

Table 1
Chemical composition of laterite ore sample/wt.%.

Composition	Fe_{total}	Ni	Co	SiO_2	Al_2O_3	CaO	MgO	MnO_2	LOI*
Content	43.95	1.03	0.13	4.25	9.72	3.16	0.98	1.25	15.2

* LOI is loss on ignition.