



Effect of activation pretreatment of limonitic laterite ores using sodium fluoride and sulfuric acid on water leaching of nickel and cobalt



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ABSTRACT

This study investigated the effect of activation pretreatment of limonitic laterite ores using sodium fluoride and sulfuric acid on water leaching of nickel (Ni) and cobalt (Co) over iron at atmospheric pressure. X-ray diffraction, thermogravimetric and differential scanning calorimetry, scanning electron microscopy/energy-dispersive spectroscopy, and optical microscopy were used to characterize ore samples before and after activation. Results showed that iron oxides are the major minerals of the original ore, as well as the major Ni- and Co-bearing minerals. Activation pretreatment can break these mineral lattices and expose their Ni and Co to the reaction interface, thereby facilitating easy and selective extraction of both metals over iron under mild leaching conditions. Ni and Co leaching reached 85.3% and 93.9%, respectively, and the Fe dissolution was <8% under optimal conditions. Furthermore, behaviors of Fe, Ni, and Co in the activation process were illustrated. The effects of such behaviors on their leaching were also discussed.

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1. Introduction

Owing to its distinct physical and chemical properties, nickel has been widely used in military and civilian applications, such as electroplating and production of stainless steel and other corrosion-resistant metal materials, petrochemical catalysts, electronic and electrode materials, as well as hydrogen storage and ceramic materials (Jackson, 2005; Li, 2011). Nickel laterite ores account for over 70% of the total nickel reserves worldwide; nevertheless, only approximately 40% of the current nickel production worldwide is derived from these ores (Luo et al., 2010; INSC, 2012). Recent years, sufficient consideration has been given toward the extraction of nickel (and cobalt) from laterite ores because of the competitive advantages of oxide reserves, such as easier mining and high cobalt content, as well as the sustained depletion of sulfide reserves (Agatzini-Leonardou et al., 2009; McDonald and Whittington, 2008a).

Laterite ores are generally divided into limonitic, saprolitic, and garnieritic layers. Limonitic laterite exists in the top layer, which mainly consists of iron oxide/oxyhydroxide with iron content higher than 40%.

Moreover, limonitic laterite ores account for a large proportion, which is almost twice that of the other two layers (saprolite and garnierite) (Dalvi et al., 2004; Kempthorne and Myers, 2007). However, the mineral composition in different layers is complex and the metal content (especially nickel, iron, and magnesium) greatly varies; thus, the methodologies of mineral processing being diverse and complicated. Several investigations have been performed to promote the recoveries of valuable metals (Kim et al., 2010; Liu et al., 2010; Guo et al., 2011; Senanayake et al., 2011; Zhu et al., 2012; Ma et al., 2013a, 2013b; Terekhov and Emmanuel, 2013; Gao et al., 2014; Pickles et al., 2014; Ma et al., 2015; Park et al., 2015). Hydrometallurgical processes are generally adopted to treat limonitic laterite ores (McDonald and Whittington, 2008b). The other types of laterite ores are amenable to pyrometallurgical treatment to produce ferronickel or matte by considering the high acid consumption and great economical throughput attributed to the higher magnesium content (Dalvi et al., 2004; Ma et al., 2013c).

High-pressure acid leaching (HPAL) is a representative hydrometallurgical technology with high recoveries of nickel and cobalt over iron. However, the high operating cost and safety risk of the autoclaves could not be disregarded (Rubisov et al., 2000; Büyükkinci and Topkaya, 2009). Atmospheric acid leaching can be well controlled and maintained at a lower cost, but the process generates leach liquor with significant concentrations of iron and aluminum, which complicates downstream processing (McDonald and Whittington, 2008a; Chander, 1982; Thubakgale et al., 2013). Apart from the two aforementioned

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industrialized processes, other approaches have been applied, including an upgraded chlorination–water leaching process to selectively extract nickel and cobalt from reduced limonitic laterite (Fan et al., 2010), a sulfation roasting–leaching process to treat low Ni-grade limonitic ores at a high temperature approximately 700 °C (Guo et al., 2009; Harris et al., 2011), and a chloridization and reduction roasting–magnetic separation process to produce ferronickel (Zhou et al., 2016). These treatments enable recoveries of nickel and cobalt with low cost for equipment and operation, whereas relatively high energy consumption of higher roasting temperature will increase the production cost.

Given the current issues, activation pretreatment of limonitic laterite ores with sodium fluoride–sulfuric acid at lower temperature followed by water leaching to extract nickel and cobalt has been developed as an improved technology. Based on thermodynamic analysis, a series of tests were completed in this research. Basic parameters, including the sulfuric acid and sodium fluoride dosage, temperature, and the activation duration, were optimized to selectively extract nickel and cobalt over iron. The phase transformation behavior of the main minerals in the limonitic laterite ore before and after activation was studied to explain the experimental results.

2. Experimental

2.1. Materials and apparatus

The limonitic laterite ore used in this study was from the Philippines, as provided by Jiangsu Huahai Material Science and Technology Company Ltd. (China). A representative sample was obtained by coning and quartering. The sample was ground with a XZM-100 laboratory cylinder ball mill until the average size of the sample was <74 μm. The chemical components and mineral compositions of the selected representative sample were determined.

The chemical components of each sample were analyzed by inductively-coupled plasma–atomic emission spectroscopy (ICP–AES) with an Optima 5300 Dual View spectrometer. X-ray diffraction (XRD) data collection was performed with a Rigaku D/MAX-rA diffractometer (Cu Kα radiation; 40 mA, 50 kV; from 10° to 90° with 0.02° increments). Phase identification was performed with the PANalytical X'Pert HighScore Plus by searching the ICDD-PDF2 database (International Center for Diffraction Data, 2003). The elemental composition of the particular regions of significantly different mineral phases was analyzed by scanning electron microscopy (SEM, HITACHI S-3500 N) combined with energy-dispersive spectroscopy (EDS, INCA Oxford). Simultaneous differential scanning calorimetry and thermogravimetry (TG–DSC) analyses were performed on a NETZSCH STA 449F3 unit under a nitrogen atmosphere at a linear heating rate of 10 °C/min.

2.2. Experimental set-up and procedures

A muffle furnace was used during the activation process. The temperature of ore samples was monitored by a sheathed thermocouple inserted into the muffle furnace and controlled by a programmable temperature controller with a precision of ±1 °C. All activation tests were conducted based on the conditions in Table 1. First, a 30 g ore sample and a known amount of sodium fluoride were homogeneously mixed

in a laboratory rotary mixing drum. The mixture was transferred into a wide-mouth corundum crucible to ensure that the layer was very thin. Approximately 5 g of deionized water was sprayed into the ore with a self-designed apparatus. A certain amount of sulfuric acid was also sprayed into the mixture via the same apparatus. A stirring glass rod was used to ensure homogenous mixing between samples and sprayed liquids. After mixing, the crucible was placed inside a muffle furnace that had been pre-heated to the required temperature, and the activation reaction (defined as zero time) was started. After a specified reaction time, the crucible was removed and cooled in air followed by dry grinding until all particles of the activation product were smaller than 150 μm.

The activation product was transferred into a 250 mL round-bottom flask with three ports; the flask contained a known amount of deionized water to extract nickel and cobalt. Subsequently, liquid/solid separation was performed with a Buchner funnel and the products were washed thrice with deionized water. For accurate evaluation, the following leaching conditions were used: liquid-to-solid ratio, 5:1 mL/g; leaching duration, 3 h; leaching temperature, 90 °C; stirring speed, 300 rpm.

The activation products were characterized by XRD and SEM/EDS for the elemental determination of critical regions of the significantly different mineral phases. The leach residue was dried at 50 °C, melted by mixed fluxes of sodium borate and sodium carbonate at 950 °C, and dissolved in diluted HCl solution at 80 °C for chemical analysis by ICP–AES. The extraction of nickel and cobalt was calculated by the following formula:

$$X\% = 100 - (C_i/C\% \times m_i/m) \times 100 \quad (1)$$

where X% is the leaching yield of nickel or cobalt; C_i% and C% are the mass fraction of metals in the leach residues and the original laterite, respectively; m_i and m are the mass of the leach residues and the original laterite, respectively.

3. Results and discussion

3.1. Chemical analysis and characterization

The chemical analysis of the limonitic laterite ore sample is summarized in Table 2. The ore contains a significant amount of iron, but only a small proportion of which is divalent. Based on the results of optical microscopy, semi-quantitative analysis of XRD, electron probe micro-analysis, and chemical analysis, the limonite-rich laterite ore mainly consisted of goethite, hematite with a small amount of magnetite, serpentine, quartz, chromite, clays, and other gangue phases. The details are shown in Table 3. The distribution of nickel, cobalt, and iron is also listed in this table. The major minerals of the ore, iron oxides, are the major Ni- and Co-bearing minerals. Iron oxides account for nearly 80% of all minerals; approximately 91% of nickel and 56% of cobalt was present in these oxides. The remaining cobalt (nearly 44%) was distributed in fine gangues and clay particles. The detailed investigation results were reported in our previous publication (Ma et al., 2013c).

The XRD pattern of the original ore is shown in Fig. 1. The laterite is poorly crystalline but is typical limonitic laterite (Dalvi et al., 2004; Ma et al., 2013c). No isolated crystalline structures containing Ni or Co were observed. Some isolated Ni- or Co-bearing minerals exist; however, these compounds are amorphous or below the detection limit. The reflective light microscopy showed that limonitic minerals usually exhibit colloidal and concretionary textures, which indicate the formation

Table 1
List of process parameters studied during experiments.

Studied parameters	Range	Fixed parameters
Temperature (°C)	200, 250, 300, 350, 400, 450	300 kg/t-ore, 120 min, 3 wt%
Duration (min)	5, 15, 30, 60, 90, 120, 150	350 °C, 300 kg/t-ore, 3 wt%
Sulfuric acid dosage (kg/t-ore)	150, 200, 250, 300, 350, 400, 450, 500, 550, 600	350 °C, 120 min, 3 wt%
NaF dosage (wt%)	0, 1, 2, 3, 4, 5, 6, 7	350 °C, 300 kg H ₂ SO ₄ /t-ore, 120 min

Table 2
Main chemical compositions of the as-received laterite ore sample.

Component	Fe _{total}	Fe(II)	Ni	Co	Cr	Al	Mn	Mg	SiO ₂	LOI
Percentage (wt%)	48.3	1.3	1.1	0.10	2.6	1.9	0.8	1.0	3.2	10.7

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