Innovative methodology for comprehensive utilization of saprolite laterite ore: Recovery of metal-doped nickel ferrite and magnesium hydroxide

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ABSTRACT

A new hydrometallurgical process was developed to synthesize metal-doped nickel ferrite ($NiFe_2O_4$) and magnesium hydroxide ($Mg(OH)_2$) from saprolite laterite ore. Selective extraction of Ni and Fe with a controlled Fe-to-Ni mole ratio ($R_{Fe/Ni}$) from saprolite laterite ore was investigated. It is shown that the leaching efficiencies of Ni and Fe were approximately 85.0% and 17.0% with an $R_{Fe/Ni}$ of 2.6 after hydrothermal leaching at 200 °C with a liquid-to-solid ratio of 6:1 mL·g^{-1} and HCl solution concentration of 2 mol·L^{-1}. After the leaching process, the hydrothermal coprecipitation method (200 °C, 2 h) was adopted to separate Ni, Co, Fe, Mn and Al from Mg ions in the leaching solution by controlling the initial pH value of 7.0. Under optimal conditions, metal-doped $NiFe_2O_4$ magnetic material with a cubic spinel structure was successfully synthesized directly from the precipitate; meanwhile, $Mg(OH)_2$ (96.8 wt.%) was obtained from the filtrate. Moreover, it is estimated that 96.95 g of metal-doped $NiFe_2O_4$ and 278.6 g of $Mg(OH)_2$ could be produced from 1000 g of processed saprolite laterite ore.

1. Introduction

Nickel is widely used in batteries, catalysts, and the preparation of stainless steel and nonferrous alloys to increase impact strength, corrosion resistance and ductility (Chang et al., 2008; Sudol, 2005; McDonald and Whittington, 2008a; Lokhande et al., 2011). At present, with the depletion of the world's nickel sulfide ore and the rising demand for nickel, laterite ore is becoming the primary resource for extraction of nickel; however, it has a lower grade (0.75–1%) and is more difficult to treat compared to nickel sulfide ore (Pickles, 2004; Dalvi et al., 2004). Until now, much effort has been devoted to the recovery of nickel from laterite ore by hydrometallurgical processes such as reduction roasting–ammonia leaching (RRAL) (Chen et al., 2010), high-pressure acid leaching (HPAL) (Georgiou and Papangelakis, 1998; Rubisov et al., 2000) and atmospheric acid leaching (AL) (McDonald & Whittington, 2008b). Among these processes, acid leaching is an attractive and promising technology for low-grade laterite ore, however, the recovery of valuable metals is low due to the complex separation and purification processes (Long, 2009; Luo et al., 2010; Liu et al., 2010; Zhu et al., 2010). Wang et al. (2011) studied the effect of iron precipitation on nickel losses and indicated that a greater mole ratio of Fe to Ni in the leaching solution may lead to greater nickel loss in the final products. The higher the removal efficiency of iron was, the greater the nickel loss was. Chang et al. (2010) also discussed the removal of iron from the acidic leaching solution by

the formation of a goethite precipitate. They found that the pH value had a significant effect on the ferrous ion oxidation degree and the loss of nickel. Increasing the pH value enhanced the oxidation rate of ferrous ion but resulted in greater nickel loss. In short, many studies have focused only on extracting Ni from the laterite ore regardless of the unavoidable nickel loss and neglected the utilization of coexisting valuable metal ions such as Fe, Co, Mn, and Mg, leading to waste of resources and potential pollution to the environment. The effective way to solve the problem is to increase the nickel separation efficiency from the leaching solution, and meanwhile make full use of valuable resources in the laterite ore.

Spinel ferrites with the common formula MFe_2O_4 (M = Ni, Mn, Co, Mg, etc.) have attracted considerable interest because of their novel properties and great applications in the fields of ferrofluids (Pileni, 2001), catalysts (Lin et al., 2011), magnetic high-density storage (Srinivasan et al., 2009), etc. More importantly, Co, Mn or Mg co-doped nickel ferrite ($NiFe_2O_4$) can lead to enhanced magnetic performance (Xiang et al., 2012; Koseoglu, 2013; Deraz, 2012). Generally, $NiFe_2O_4$ or metal-doped $NiFe_2O_4$ was prepared by using pure chemical reagents (Salavati-Niasari et al., 2009; Sivakumar et al., 2011). No effort has been made to synthesize $NiFe_2O_4$, especially metal-doped $NiFe_2O_4$, directly from saprolite laterite ore.

In this paper, a novel hydrometallurgical process was proposed to recover valuable metals from saprolite laterite ore by using a selective acid leaching-hydrothermal coprecipitation method. The effects of the critical factors, including the leaching temperature and HCl solution concentration, on the metal leaching efficiency and the mole ratio of

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Table 1
Chemical composition of the raw saprolite laterite ore.

Constituent	NiO	CoO	Fe$_2$O$_3$	MgO	MnO	Cr$_2$O$_3$	Al$_2$O$_3$	SiO$_2$
Content (wt.%)	2.7	0.1	34.9	21.0	0.5	1.0	2.9	35.4

Fe to Ni in the leaching solution ($R_{Fe/Ni}$) were studied. The hydrothermal coprecipitation method was then adopted to separate Ni, Co, Fe, Mn and Al from Mg ions in the leaching solution. After coprecipitation, metal-doped NiFe$_2$O$_4$ was successfully synthesized from the precipitate, and magnesium hydroxide (Mg(OH)$_2$) was prepared from the filtrate. Finally, the general flow sheet for the recovery of metal-doped NiFe$_2$O$_4$ and Mg(OH)$_2$ from saprolite laterite ore was quantitatively summarized. This paper presents a novel pathway for comprehensive utilization of saprolite laterite ore.

2. Experimental

2.1. Materials

The saprolite laterite ore used in this study originated from Jinchuan Group Ltd., China. The raw ore was first dried overnight at 105 °C, and then ground to particles of sizes smaller than 150 μm. Analytical reagent (AR) grade sodium hydroxide and hydrochloric acid (36–38%) were purchased from the Beijing Reagent Factory of China.

The typical chemical composition of the saprolite laterite ore was determined by X-ray fluorescence (XRF) and inductively coupled plasma (ICP), and the results are given in Table 1. The mineralogical phases of raw saprolite laterite ore were characterized by X-ray diffraction (XRD), as shown in Fig. 1(a). The main mineralogical phases were goethite (FeO·OH), hematite (Fe$_2$O$_3$), lizardite (Mg$_3$Si$_2$O$_5$(OH)$_4$) and quartz (SiO$_2$). However, the nickel-containing phases cannot be found because the content is low, as indicated in Table 1. Based on the mineralogical research on saprolite laterite ore, the majority of Ni was found in the lizardite and goethite by substituting Mg and Fe elements with Ni element (Tartaj et al., 2000).

Fig. 1(b) shows the thermogravimetry-differential scanning calorimetry (TG-DSC) plots of the raw saprolite laterite ore. The DSC pattern features four peaks at 85.0 °C, 264.6 °C, 590.7 °C and 826.5 °C with temperatures increasing from 25 °C to 1000 °C. The first peak at 85.0 °C can be ascribed to the evaporation of the absorbed water. The next two peaks at approximately 264.6 °C and 590.7 °C may correspond to the endothermic reactions described as reactions (1) and (2), respectively. The fourth peak at 826.5 °C might be due to the recrystallization of magnesium olivine (Mg$_2$SiO$_4$).
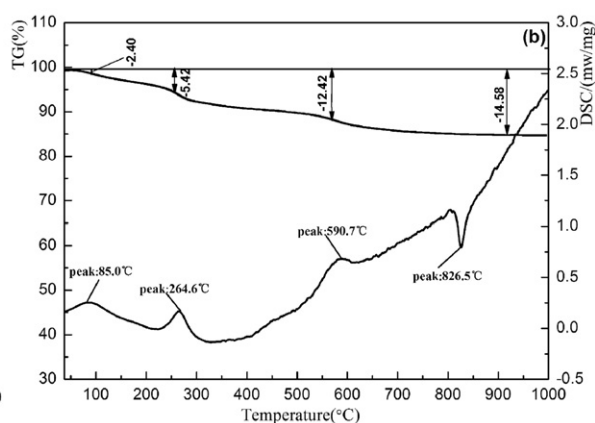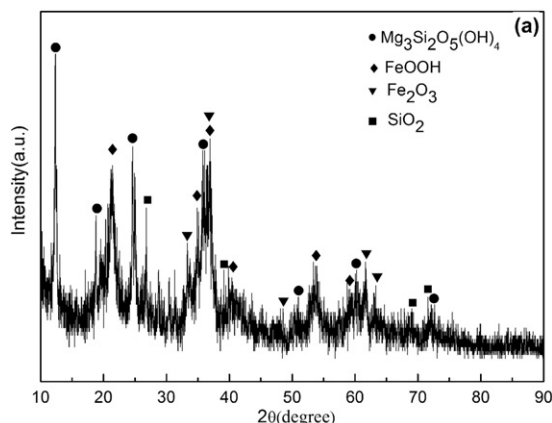
$$2FeO \cdot OH \rightarrow Fe_2O_3 + H_2O\uparrow \tag{1}$$

Table 2
pH values for the existence of free Fe^{3+} and Ni^{2+} in the acid solution at different temperatures.

Temperature (°C)	pH (Fe^{3+})	pH (Ni^{2+})
25	<2.0	<6.0
100	<1.5	<4.4
150	<1.0	<3.7
200	<0.5	<3.0

pH values were summarized from the E-pH diagrams presented in Ref. Yang and Yang (1991), which were measured or calculated from equilibrium thermodynamics.

$$Mg_3Si_2O_5(OH)_4 \rightarrow Mg_2SiO_4 + MgSiO_3 + 2H_2O\uparrow \tag{2}$$

Fig. 1(b) shows that the mass losses of the first three peaks were 2.4%, 5.4% and 12.4%, respectively. Considering reactions (1) and (2), the weight losses originating from reactions (1) and (2) were about 3.0% (5.4%–2.4%) and 7.0% (12.4%–5.4%); thus, the mass fraction of goethite and lizardite in the raw saprolite laterite ore can be calculated to be approximately 33.4% and 53.7% according to the principle of chemical equilibrium. This suggests that goethite and lizardite were the main mineralogical phases of the raw saprolite laterite ore, as shown in Fig. 1(a).

2.2. Experimental procedure

2.2.1. Selective extraction of Ni and Fe from saprolite laterite ore

The saprolite laterite ore (10 g, 150 μm) was added to 2.0 mol·L^{-1}, 2.5 mol·L^{-1} and 3.0 mol·L^{-1} hydrochloric acid with a liquid-to-solid ratio of 6:1 (mL·g^{-1}). The mixture was transferred to a 100-mL Teflon-lined stainless steel autoclave, which was sealed and placed in a drying oven with a temperature precision of ±1 °C to complete the selective extraction process without agitation. The leaching temperature varied from 100 to 200 °C at intervals of 25 °C, and the leaching time was 10 h. After the leaching process, the solid–liquid separation was conducted in an RJ-TDL-50 A centrifuge with a speed of 4800 r·min^{-1} for 15 min. The leaching solution was then used for preparation of metal-doped NiFe$_2$O$_4$ and Mg(OH)$_2$. The leaching residue was washed with deionized water several times and dried at 105 °C. All the experiments were conducted in duplicate to ensure repeatability.

2.2.2. Preparation of metal-doped NiFe$_2$O$_4$ and Mg(OH)$_2$

For the preparation of metal-doped NiFe$_2$O$_4$, first, the pH value of the obtained leaching solution was adjusted to be approximately 7.0 using an NaOH solution at room temperature; then, the mixture was placed in a 100-mL Teflon-lined stainless steel autoclave to perform the hydrothermal coprecipitation process for 2 h without agitation while the temperature was controlled at 200 °C. After the solid–liquid separation, the precipitate was dried at 80 °C for 10 h and then ground into a fine

Fig. 1. XRD pattern (a) and TG-DSC plots (b) of the raw saprolite laterite ore.