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A novel hydrometallurgical approach to recover valuable metals from laterite ore

Jian-ming Gao, Zhi-kai Yan, Jing Liu, Mei Zhang, Min Guo *

Beijing key Lab. of Green Recycling and Extraction of Metals, School of Metallurgical and Ecological Engineering, University of Science and Technology Beijing, Beijing 100083, PR China

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ABSTRACT

A novel hydrometallurgical process was developed to produce metal co-doped magnesium ferrites from saprolite and limonite laterite blends by using an atmospheric acid leaching–coprecipitation method. The effects of initial acid concentration, liquid to solid ratio and leaching time on the metal leaching efficiencies were investigated systematically. It is shown that extraction efficiencies of Fe, Ni, Mn, Co and Mg can reach 94.6%, 96.9%, 86.0%, 84.8% and 72.6%, respectively, after leaching for 60 min at 100 °C with the liquid (2.75 $\mathrm{mol\cdot L^{-1}}$ HCl acid) to solid (saprolite and limonite laterite blends) ratio of 10:1 $\mathrm{mL\cdot g^{-1}}$, and saprolite to limonite mass ratio ($M_{\mathrm{saprolite/limonite}}$) of 5:5. Under the optimum leaching conditions, the influence of $M_{\mathrm{saprolite/limonite}}$ on the synthesis of metal co-doped magnesium ferrites from leaching solutions was also discussed. X-ray Diffraction (XRD) results showed that pure metal co-doped magnesium ferrites could be obtained when the $M_{\mathrm{saprolite/limonite}}$ was controlled at 7:3, with the initial acid concentration of 2.75 and 3.0 $\mathrm{mol\cdot L^{-1}}$, respectively.

1. Introduction

At present, with the reduction of the world's nickel sulfide ore and rising demand for nickel, more and more attention has been paid on the nickeliferous laterite ore, which is an important nickel oxide ore that amounts to about 70% of global land-based nickel resources although it has lower grade and is difficult to treat (Dalvi et al., 2004; Mudd, 2010). According to the chemical analysis, the laterite ore contains many valuable metals (such as Fe, Co, Mn and Mg etc.) besides Ni, and the laterite ore can be classified into three different kinds including limonite, transition and saprolite laterite ore due to its different element composition contents. For example, the limonite laterite ore has the characteristic of high iron and low magnesium contents, while the saprolite laterite ore has low iron and high magnesium contents, which would lead to different treating methods.

Generally, traditional hydrometallurgical processes of the laterite ore including pressure acid leaching and atmospheric acid leaching have attracted considerable interests because low Ni grades make pyrometallurgical processes uneconomical. For pressure acid leaching process, the most important characteristic is selective extraction of Ni and Fe (Georgiou and Papangelakis, 1998; Rubisov et al., 2000). Even so, the process has been limited in the industrial production because of the harsh leaching conditions (250–270 °C, 4–5 MPa) and numerous engineering problems. Compared with pressure acid leaching process, atmospheric acid leaching process has the advantages of high extraction efficiency, low energy consumption and low equipment cost etc. (Li et al., 2012; Luo et al., 2009; McDonald and Whittington, 2008a, 2008b). However, as for acid leaching process, it is worth noting that many impurity ions (for example, Fe^{3+}, Mg^{2+} and Mn^{2+}, etc.) besides Ni^{2+} are co-existing in the acid solution after leaching process, and importantly, the content of impurity ions is even higher than that of Ni^{2+} in the leaching solution, which might lead to nickel loss and difficult separation (Chang et al., 2010; Liu et al., 2010; Luo et al., 2010; Wang et al., 2011; Zhu et al., 2010). Therefore, how to increase nickel separation efficiency from acid leaching solution, and in the meantime make full use of valuable metals are still big challenges for effective utilization of laterite ore.

Spinel ferrites such as $NiFe_2O_4$, and $MgFe_2O_4$ (formula of MFe_2O_4), have attracted considerable interests and efforts due to their novel magnetic and electric 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. Generally, ferrites or metal-doped ferrites were synthesized from pure chemical reagents with controlled Fe to M (Ni, Co, Mn and Mg etc.) mole ratio ($R_{\mathrm{Fe/M}}$) of 2.0. So far, none of the effort has been taken on the synthesis of ferrites from laterite ore, especially producing metal co-doped magnesium ferrites directly from the laterite ore. Recently, by using a pressure acid leaching–hydrothermal coprecipitation–calcination method (Gao et al., 2014), we synthesized Co–Mn–Mg–Al co-doped nickel ferrites only from saprolite laterite ore. We found that the acid leaching solution with controlled mole ratio of Fe to Ni for preparation of metal-doped $NiFe_2O_4$ can be realized by selective extraction of Fe and Ni from the ore. However, this method requires two hydrothermal processes comprising leaching and hydrothermal coprecipitation, which may limit its application in the practical utilization. As mentioned above, it

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* Corresponding author. Tel./fax: +86 10 62334926.
E-mail address: guomin@ustb.edu.cn (M. Guo).

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is well-known that relatively higher metal extraction efficiency from laterite ore can be realized by atmospheric acid leaching process, and the process is good for industrialized production. In addition, the limonite and saprolite laterite ores have the opposite characteristic of Fe and Mg contents. Considering the chemical composition contents of saprolite and limonite laterite blends (saprolite to limonite mass ratio 1:1), it is reasonable to assume that the leaching solutions with controllable $R_{Fe/M}$ of about 2.0 can be obtained by atmospheric acid leaching of laterite blends and M is the sum of the molar concentrations of the metal ions.

In this paper, synthesis of metal co-doped magnesium ferrites from laterite blends was investigated by using an atmospheric acid leaching–coprecipitation method. During the leaching process, the effects of the critical factors including the initial acid concentration, liquid to solid ratio and leaching time on metal leaching efficiencies were studied. Then coprecipitation method was adopted to separate Ni, Co, Fe, Mn and Mg from Al and Cr in the leaching solution by adjusting the pH value due to their different precipitate behaviors. After the coprecipitation process, metal co-doped magnesium ferrites were successfully synthesized from the precipitate. This paper may explore a novel pathway for efficient and comprehensive utilization of laterite ore.

2. Experimental

2.1. Materials

The saprolite and limonite laterite ores used in this study were supplied by Beijing Research Institute of Mining and Metallurgy. These raw ores were firstly dried overnight at 105 °C, and then grinded into powders with particle size smaller than 150 μm. The typical chemical analysis of the laterite ores is presented in Table 1.

From the table, it can be found that the saprolite laterite ore is rich in Mg and low in Fe, while the limonite laterite ore is rich in Fe and low in Mg. According to the calculation, when the saprolite to limonite mass ratio ($M_{saprolite/limonite}$) is 1:1, the theoretical $R_{Fe/M}$ is 1.97, indicating that the blends may be suitable for preparation of metal co-doped magnesium ferrites. Analytical reagent (AR) grade sodium hydroxide and hydrochloric acid (36–38%) were purchased from the Beijing Reagent Factory of China.

2.2. Methods

2.2.1. Leaching process

Leaching experiments were performed by taking initial concentrations of acid (2.5 to 3.0 $mol \cdot L^{-1}$ HCl) in a 500 mL round bottom flask at a given liquid to solid ratio (6 to 11 $mL \cdot g^{-1}$) for a given time (20 to 120 min) and $M_{saprolite/limonite}$ of laterite blends were from 5:5 to 7:3. The mixture reacted at 100 °C without stirring. After the leaching process, the solid–liquid separation was conducted in the RJ-TDL-50 A centrifuge with the speed of 4500 $r \cdot min^{-1}$ for 10 min. Then, leaching solutions containing Ni, Mn, Mg and Fe etc. were obtained. The leaching residue was washed to neutral and dried at 105 °C. All the experiments were conducted three times to assure the repeatability.

Table 1
The chemical composition of raw saprolite and limonite laterite ores (wt.%).

Constituent	Ni	Co	Mn	Mg	Fe	Cr	Al	Ti	Zn	Si
Saprolite laterite ore	1.99	0.05	0.32	11.92	21.74	0.56	1.79	0.30	0.05	13.04
Limonite laterite ore	1.02	0.14	0.95	1.04	46.42	1.24	3.57	0.20	0.04	2.03

2.2.2. Separation and preparation of metal co-doped magnesium ferrites

For the separation process, firstly, 100 mL of the leaching solutions was transferred into a teflon reactor, and then, the pH value of the leaching solutions was adjusted to about 13 by sodium hydroxide solution. The mixture was placed to react for 15 min on a magnetic stirrer at room temperature. After the coprecipitation process, the precipitate was filtered, washed several times with deionized water to remove Na^+ and Cl^- completely and dried in an oven at 90 °C for 10 h, and the precursor for preparation of metal co-doped magnesium ferrites was obtained. Finally, the precipitate was grinded into powder and calcinated at 1000 °C for 2 h, and metal co-doped magnesium ferrite was generated. Fig. 1 shows the general flow sheet of producing metal co-doped magnesium ferrites from saprolite and limonite laterite blends.

2.3. Analysis and characterization

Concentration of Ni^{2+}, Fe^{3+}, Co^{2+}, Mn^{2+}, and Mg^{2+} etc. in the leaching solutions was determined by Inductively Coupled Plasma Atomic Emission Spectrometer (ICP-AES, America, Varian). The phase structure and chemical composition of the laterite ore were investigated by X-ray Diffraction (XRD, Japan, Rigaku) and X-Ray Fluorescence (XRF-1800, Japan), respectively. During the leaching process, the leaching efficiency η for each metal ion was calculated as follows:

$$\eta = \frac{V_C C_X}{M_1 W_{X1} + M_2 W_{X2}} \times 100\% \tag{1}$$

where C_X is the concentration of metal ions (Ni^{2+}, Fe^{3+}, etc.) in the leaching solution, $g \cdot mL^{-1}$; M_1 and M_2 are the initial mass of dried saprolite and limonite laterite ores added into the reactor, respectively, g; V_c is the volume of leaching solution, mL; and W_{X1} and W_{X2} are the mass percentage of X (Ni, Fe, etc.) in dried saprolite and limonite laterite ores, wt.%.

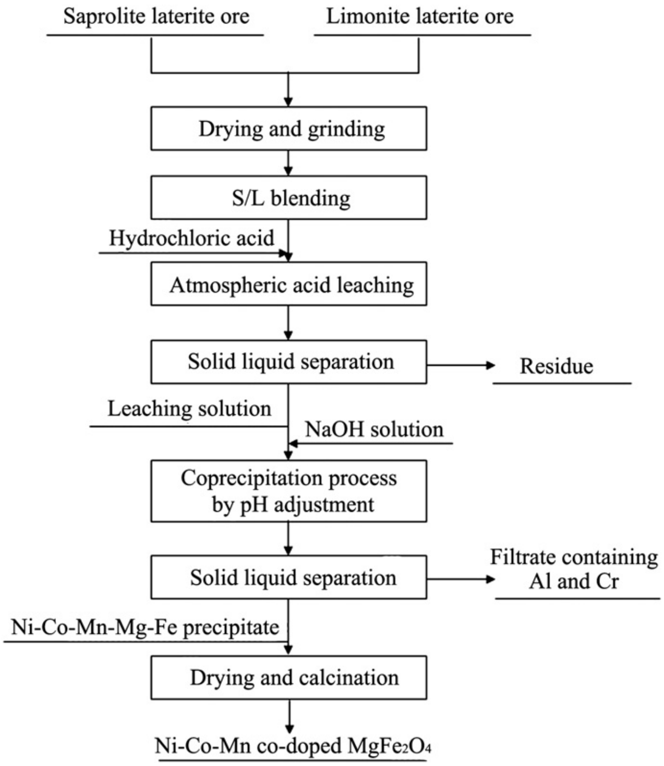

Fig. 1. General flow sheet of producing metal co-doped magnesium ferrites from saprolite and limonite laterite blends.