



# A novel hydrometallurgical approach to recover valuable metals from laterite ore



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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 mol·L<sup>-1</sup> HCl acid) to solid (saprolite and limonite laterite blends) ratio of 10:1 mL·g<sup>-1</sup>, and saprolite to limonite mass ratio ( $M_{\text{saprolite/limonite}}$ ) of 5:5. Under the optimum leaching conditions, the influence of  $M_{\text{saprolite/limonite}}$  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  $M_{\text{saprolite/limonite}}$  was controlled at 7:3, with the initial acid concentration of 2.75 and 3.0 mol·L<sup>-1</sup>, respectively.

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## 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<sup>3+</sup>, Mg<sup>2+</sup> and Mn<sup>2+</sup>, etc.) besides Ni<sup>2+</sup> are co-existing in the acid solution after leaching process, and importantly, the content of impurity ions is even higher than that of Ni<sup>2+</sup> 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<sub>2</sub>O<sub>4</sub> and MgFe<sub>2</sub>O<sub>4</sub> (formula of MFe<sub>2</sub>O<sub>4</sub>), 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 ( $R_{\text{Fe/M}}$ ) 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<sub>2</sub>O<sub>4</sub> 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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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 ( $M_{\text{saprolite/limonite}}$ ) 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·L<sup>-1</sup> HCl) in a 500 mL round bottom flask at a given liquid to solid ratio (6 to 11 mL·g<sup>-1</sup>) for a given time (20 to 120 min) and  $M_{\text{saprolite/limonite}}$  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·min<sup>-1</sup> 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

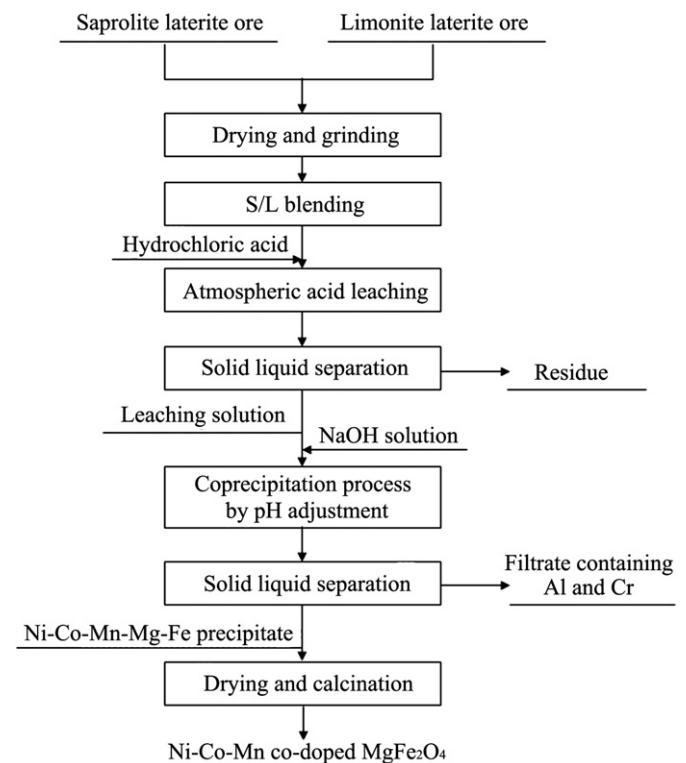
For the separation process, firstly, 100 mL of the leaching solutions was transferred into a teflon reactor, and then, the pH value of the leaching solutions was adjusted to about 13 by sodium hydroxide solution. The mixture was placed to react for 15 min on a magnetic stirrer at room temperature. After the coprecipitation process, the precipitate was filtered, washed several times with deionized water to remove Na<sup>+</sup> and Cl<sup>-</sup> 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<sup>2+</sup>, Fe<sup>3+</sup>, Co<sup>2+</sup>, Mn<sup>2+</sup>, and Mg<sup>2+</sup> 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  $\eta$  for each metal ion was calculated as follows:

$$\eta = \frac{V_c C_x}{M_1 W_{X1} + M_2 W_{X2}} \times 100\% \quad (1)$$

where  $C_x$  is the concentration of metal ions (Ni<sup>2+</sup>, Fe<sup>3+</sup>, etc.) in the leaching solution, g·mL<sup>-1</sup>;  $M_1$  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.

### 3. Results and discussion

#### 3.1. Atmospheric acid leaching

In order to synthesize metal co-doped magnesium ferrites, the  $R_{Fe/M}$  should be controlled at 2.0 according to the general molecular formula of  $MFe_2O_4$ . Based on the chemical composition analyses of raw saprolite and limonite laterite ores, the theoretical  $R_{Fe/M}$  in the laterite blends of different  $M_{\text{saprolite/limonite}}$  was calculated, and when the  $M_{\text{saprolite/limonite}}$  was 5:5, the  $R_{Fe/M}$  can be about 2.0. So, during the atmospheric acid leaching process, the  $M_{\text{saprolite/limonite}}$  was controlled at 5:5 to investigate the effects of initial acid concentration, liquid to solid ratio and leaching time on metal leaching efficiencies. Before the atmospheric acid leaching experiments, the thermodynamic calculation and analysis of mineral phases ( $Mg_3[Si_2O_5](OH)_4$ ,  $FeO(OH)$  and  $Fe_2O_3$ ) dissolved in acid solution was investigated in detail (see Table S1–S3 in Supplementary content). From the tables, it can be seen that pH (acid concentration) and leaching temperature play important roles in the metal leaching efficiency. So, by adjusting the leaching parameters (initial acid concentration, liquid to solid ratio, saprolite to limonite mass ratio, leaching time), the critical values of  $R_{Fe/M}$  can be obtained to synthesize the metal co-doped magnesium ferrites.

##### 3.1.1. Effect of initial acid concentration

A series of leaching experiments were carried out under the following conditions: leaching temperature at 100 °C, liquid to solid ratio of 10:1  $\text{mL}\cdot\text{g}^{-1}$ , and leaching time for 2 h. The effects of different initial acid concentrations (2.5, 2.75 and 3.0  $\text{mol}\cdot\text{L}^{-1}$ ) on metal efficiencies were investigated and the results are shown in Fig. 2.

It can be seen from Fig. 2 that with the acid concentrations increasing from 2.5 to 3.0  $\text{mol}\cdot\text{L}^{-1}$ , all metal leaching efficiencies including Ni, Mn, Co, Fe and Mg except Cr increased accordingly, indicating that higher acid concentration can lead to higher leaching efficiencies of metals from the laterite blends. Moreover, it can be observed that when the initial acid concentration increased from 2.75 to 3.0  $\text{mol}\cdot\text{L}^{-1}$ , the leaching efficiencies of Mn, Co and Mg increased from 87.0% to 97.7%, 84.8% to 97.7% and 72.6% to 80.5%, respectively, indicating that the initial acid concentration had greater effect on promoting the leaching efficiencies of Mn, Co and Mg compared with that of other metals. This can be explained that the metal efficiencies might be related to the elemental distributions in the ores and mineral dissolution behaviors (Li et al., 2012). However, it is worth noting that the content of Mn and Co in the laterite blends is about 0.75%, namely, it has little effects on the overall concentration of metal ion in the leaching solution. In

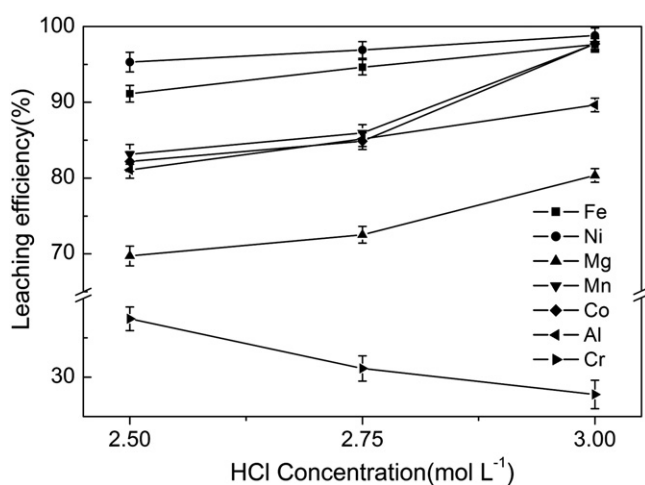


Fig. 2. Effect of initial acid concentration on metal leaching efficiencies. Leaching conditions: initial acid concentration of 2.5 to 3.0  $\text{mol}\cdot\text{L}^{-1}$ , leaching time of 2 h, liquid to solid ratio of 10  $\text{mL}\cdot\text{g}^{-1}$ , temperature of 100 °C and  $M_{\text{saprolite/limonite}}$  of 5:5.

addition, when the acid concentration was 2.75  $\text{mol}\cdot\text{L}^{-1}$ , the leaching efficiencies of Fe and Ni reached 94.6% and 96.9%, respectively. Considering the acid consumption and the pH adjustment during the coprecipitation process, the optimum concentration of the following leaching experiments was controlled at 2.75  $\text{mol}\cdot\text{L}^{-1}$ .

##### 3.1.2. Effect of liquid to solid ratio

In order to make sure that the metal phases in the laterite dissolved completely, experiments were carried out using different liquid to solid ratios in the range of 6 to 11  $\text{mL}\cdot\text{g}^{-1}$  (initial acid concentration of 2.75  $\text{mol}\cdot\text{L}^{-1}$ , leaching temperature at 100 °C and leaching time for 2 h) and the results are presented in Fig. 3. As shown in Fig. 3, when the liquid to solid ratio increased from 6 to 11  $\text{mL}\cdot\text{g}^{-1}$ , all the metal efficiencies increased correspondingly. This might be due to the increase of total acid content, which was good for the metal dissolution. Moreover, as for Fe and Ni, when the liquid to solid ratio was 10  $\text{mL}\cdot\text{g}^{-1}$ , the leaching efficiencies remained almost stable (about 95.0% and 97.0%, respectively). Considering the pH adjustment during the preparation of ferrites, 10  $\text{mL}\cdot\text{g}^{-1}$  was selected for further experiments.

##### 3.1.3. Effect of leaching time

Fig. 4 gives the influence of the leaching time on metal leaching efficiencies in the range of 20 to 120 min with initial acid concentration of 2.75  $\text{mol}\cdot\text{L}^{-1}$ , liquid to solid ratio of 10  $\text{mL}\cdot\text{g}^{-1}$  and leaching temperature at 100 °C. In general, the leaching time has a significant effect on metal leaching efficiency and the leaching process can be divided into three stages: fast dissolution period (stage I), slow reaction period (stage II) and, equilibrium period (stage III).

In stage I, it can be seen from Fig. 4 that all the metal leaching efficiencies increased rapidly in the initial 20 min, and especially, about 92.1% Fe and 94.1% Ni can be leached from the laterite blends within 20 min. While in stage II (20–60 min), all the rates of metal dissolution became slower because of the decreasing acid concentration. In stage III (60–120 min), all the metal leaching efficiencies were almost kept stable at 96.9%, 84.8%, 86.0%, 94.6% and 72.6% of Ni, Co, Mn, Fe and Mg, respectively. Namely, the metal dissolution reactions nearly reached equilibrium after leaching for 60 min. Furthermore, it can be also found that the leaching efficiencies of nickel and iron exhibited a correlation with the leaching time, implying that nickel and iron were dissolved simultaneously. This can be explained that in the limonite laterite ore, nickel was found to be uniformly distributed throughout the iron oxide crystal ( $FeO(OH)$ ), while nickel was mainly in the form of goethite ( $FeO(OH)$ ) and lizardite ( $Mg_3[Si_2O_5](OH)_4$ ) in the raw saprolite laterite ore (Guo et al., 2009; Tartaj et al., 2000).

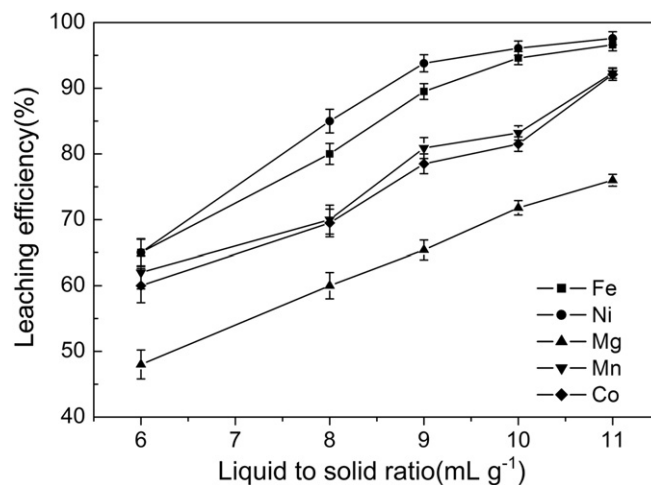


Fig. 3. Effect of liquid to solid ratio on metal leaching efficiencies. Leaching conditions: liquid to solid ratio of 6–11  $\text{mL}\cdot\text{g}^{-1}$ , initial acid concentration of 2.75  $\text{mol}\cdot\text{L}^{-1}$ , leaching time of 2 h, temperature of 100 °C and  $M_{\text{saprolite/limonite}}$  of 5:5.

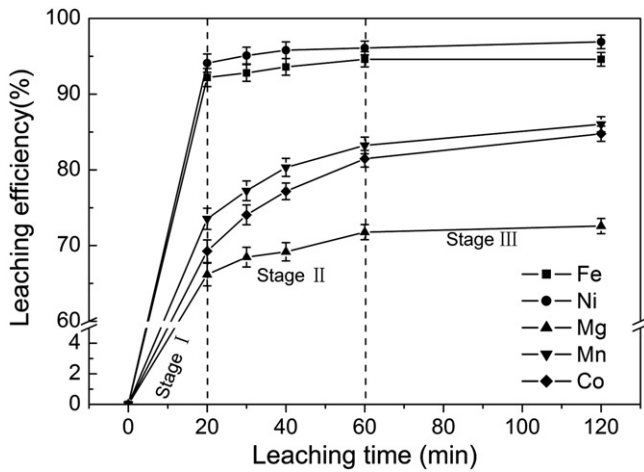


Fig. 4. Effect of leaching time on metal leaching efficiencies. Leaching conditions: leaching time of 20 to 120 min, initial acid concentration of  $2.75 \text{ mol}\cdot\text{L}^{-1}$ , liquid to solid ratio of  $10 \text{ mL}\cdot\text{g}^{-1}$ , temperature of  $100 \text{ }^\circ\text{C}$  and  $M_{\text{saprolite/limonite}}$  of 5:5.

Considering the energy consumption, the optimum leaching time was selected as 60 min.

### 3.2. Separation

According to the leaching experiments above, it can be concluded that the optimum leaching conditions were as follows: HCl acid concentration of  $2.75 \text{ mol}\cdot\text{L}^{-1}$ , liquid to solid ratio of  $10:1 \text{ mL}\cdot\text{g}^{-1}$ , leaching temperature at  $100 \text{ }^\circ\text{C}$  and leaching time of 60 min. Under this circumstance, the leaching solution was obtained and Table 2 illustrates the metal ion concentration of the leaching solution. From the table, it can be calculated that the  $R_{\text{Fe}/\text{M}}$  was about 2.5, and it was different from the theoretical  $R_{\text{Fe}/\text{M}}$  because of different leaching efficiencies of Fe and Mg (about 96.0% and 73.0%, respectively). In the meanwhile, Table 2 also gives solubility product constant and pH value of precipitate for metal hydroxides at  $25 \text{ }^\circ\text{C}$  (Hou, 1994). From the table, it can be concluded that the pH values of completely precipitated Fe, Ni, Co, Mn, Mg, Al and Cr are 3.5, 9.7, 9.2, 10.4, 12.4, 5.5 and 5.9, respectively. Consequently, the pH value of about 13.0 was chosen to realize the complete precipitation of Fe, Ni, Co, Mn and Mg etc.

In our study, the leaching solutions were used to prepare soft magnetic material metal co-doped magnesium ferrites. However, Al and Cr in the leaching solutions are nonmagnetic elements, which can lead to the weakening of magnetic properties. Consequently, for preparation of ferrites with good magnetic properties from laterite leaching solutions, it is critical to separate Al and Cr from Fe, Ni, Co, Mn and Mg. As we all know, the compounds of aluminum and chromium are amphoteric compounds, suggesting that it is feasible to separate Al and Cr from the precipitate by adjusting the pH value of the solution during the coprecipitation process. Fig. 5 exhibits the total aluminum

Table 2

Chemical composition of laterite leaching solution C, solubility product constant and pH value of precipitate for metal hydroxides at  $25 \text{ }^\circ\text{C}$ . Experimental conditions: HCl concentrations of  $2.75 \text{ mol}\cdot\text{L}^{-1}$ , liquid to solid ratio of  $10 \text{ mL}\cdot\text{g}^{-1}$ , leaching time of 60 min,  $M_{\text{saprolite/limonite}}$  of 5:5.

Element	Concentration ( $\text{g}\cdot\text{L}^{-1}$ )	Solubility product constant	pH <sub>1</sub>	pH <sub>2</sub>
Fe	21.49	$4 \times 10^{-38}$	1.67	3.5
Ni	0.96	$2 \times 10^{-15}$	7.54	9.7
Co	0.05	$2.3 \times 10^{-15}$	7.6	9.2
Mn	0.35	$1.5 \times 10^{-15}$	7.68	10.4
Mg	3.10	$1.8 \times 10^{-11}$	9.07	12.4
Al	1.52	$3.0 \times 10^{-34}$	3.24	5.5
Cr	0.18	$6.3 \times 10^{-31}$	4.75	5.9

pH<sub>1</sub>, pH value of beginning to precipitate in the solutions; pH<sub>2</sub>, pH value of completely precipitated ( $[M] = 10^{-6} \text{ mol}\cdot\text{L}^{-1}$ ).

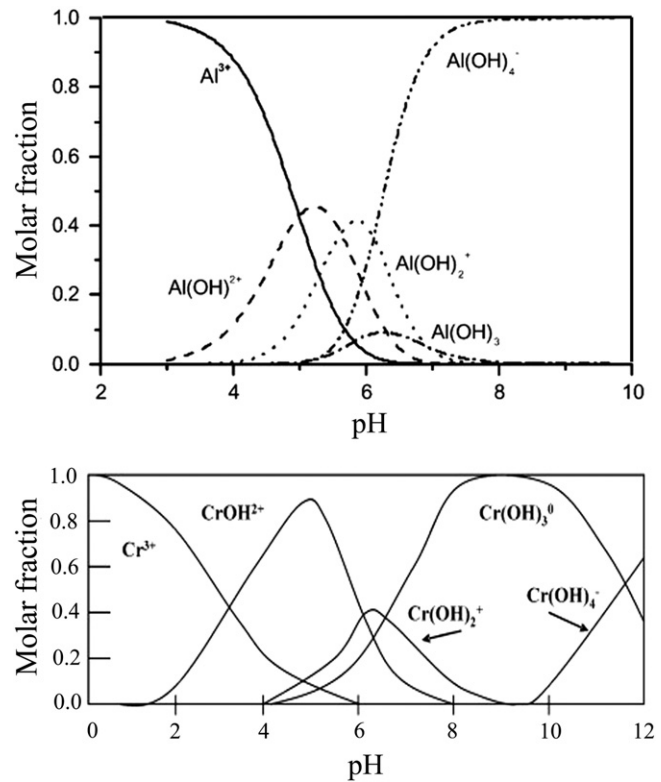


Fig. 5. The total aluminum and chromium present in the solution at a given pH value.

and chromium present in the solution at a given pH value (Bradly, 2004; Duan and Gregory, 2003). This distribution diagram showed the extent of hydrolysis, which depended on the total metal concentration and pH value. With the increasing pH value, the dominant species changed, in this case from  $\text{Al}^{3+}$  to  $\text{Al}(\text{OH})_4^-$  ion and  $\text{Cr}^{3+}$  to  $\text{Cr}(\text{OH})_4^-$  ion, which tended to remain in the solution. Moreover, the pH values of  $\text{Al}(\text{OH})_3$  and  $\text{Cr}(\text{OH})_3$  present as precipitate were among 3.5 to 11, and with the pH value of the solution increasing over 12.0,  $\text{Al}(\text{OH})_3$  and  $\text{Cr}(\text{OH})_3$  precipitates decreased sharply and completely changed into  $\text{Al}(\text{OH})_4^-$  and  $\text{Cr}(\text{OH})_4^-$  ions in the solution, namely, separation of Al and Cr from the precipitate can be realized by adjusting the pH value of the solution during coprecipitation process.

After the coprecipitation process, the precipitate was measured by XRF as shown in Table 3. It can be seen that there were less Al and Cr in the precipitate, which might be ascribed to the absorption of the precipitate. However, compared with the content of Al and Cr in the leaching solutions, the content in the precipitate decreased from 5.5% to 0.8% and 0.65% to 0.3%, respectively, indicating that Ni, Co, Mn, Mg and Fe could be effectively separated from Al and Cr in the leaching solutions by adjusting the pH value during coprecipitation method. According to the literatures (Mohamed and Wahba, 2014), Al and Cr ions absorbed on the precipitate could be substituted for Fe ions in the prepared ferrites after calcination. As a result, Ni–Co–Mn–Al–Cr co-doped magnesium ferrites could be synthesized from the precipitate.

### 3.3. Metal recovery

In recent years, many efforts have been taken on the preparation of all kinds of ferrites due to their novel properties and great applications

Table 3

Chemical composition of the precipitate after co-precipitation process (wt.%).

Constituent	Fe <sub>2</sub> O <sub>3</sub>	NiO	Co <sub>2</sub> O <sub>3</sub>	MnO	MgO	Al <sub>2</sub> O <sub>3</sub>	Cr <sub>2</sub> O <sub>3</sub>
Precipitate	80.9	3.75	0.39	1.56	11.5	0.8	0.3



in various fields. Generally, analytical chemical reagents (e.g. ferric salts and nickel salts) with controlled  $R_{Fe/M}$  (Ni, Co, Mn or Mg etc.) were used to prepare ferrites (Salavati-Niasari et al., 2009; Sivakumar et al., 2011). In this paper, synthesis of metal co-doped magnesium ferrites from the acid leaching solutions was investigated. Based on the leaching experiments above, different leaching solutions were prepared from laterite blends of different  $M_{\text{saprolite/limonite}}$  with the initial acid concentration of  $2.75 \text{ mol}\cdot\text{L}^{-1}$ , liquid to solid ratio of  $10 \text{ mL}\cdot\text{g}^{-1}$  and leaching time of 60 min as shown in Table 4. From the table, it can be seen that with  $M_{\text{saprolite/limonite}}$  increasing from 5:5 to 7:3, the  $R_{Fe/M}$  decreased from 2.52 to 1.55. As mentioned in the introduction, the most important thing to prepare pure spinel ferrite is controlling the  $R_{Fe/M}$  to about 2.0, and it is believed that pure metal co-doped magnesium ferrite could be prepared from the leaching solutions. In our study, coprecipitation method was adopted to obtain the precursors for preparation of metal co-doped magnesium ferrites and the formation equation was as follows:

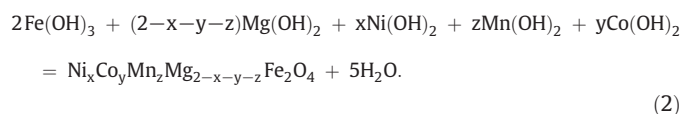
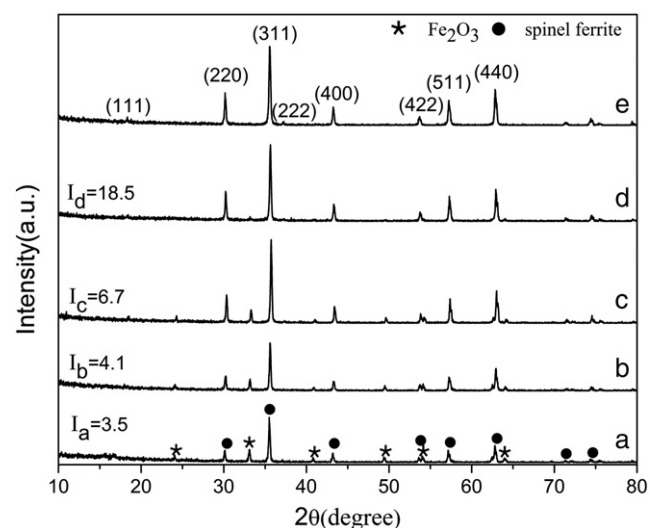


Fig. 6 illustrates the XRD patterns of the samples prepared from different leaching solutions of the  $M_{\text{saprolite/limonite}}$  of 5:5, 5.5:4.5, 6:4, 6.5:3.5 and 7:3 with HCl acid concentration of  $2.75 \text{ mol}\cdot\text{L}^{-1}$ . From Fig. 6, it can be seen that some diffraction peaks ((110), (220), (311), (222), (400), (422), (511) and (440), JCPDS 073-1720) of spinel ferrite existed in all of the XRD patterns, and in the meantime, the diffraction peaks of  $\text{Fe}_2\text{O}_3$  ((012), (104), (113), (024), (116) and (300), JCPDS 086-0550) were also found in the XRD patterns of sample a to d. With the  $M_{\text{saprolite/limonite}}$  increasing from 5:5 to 7:3, the diffraction peak intensity of impurity  $\text{Fe}_2\text{O}_3$  decreased gradually, indicating that the amount of impurity  $\text{Fe}_2\text{O}_3$  reduced accordingly in the as-prepared samples. In order to clearly describe the changing trend of phase variation, I was defined as the intensity ratio of the strongest diffraction peak of spinel ferrite (311) to that of  $\text{Fe}_2\text{O}_3$  (104) in Fig. 6. It is shown that with  $M_{\text{saprolite/limonite}}$  from 5:5 to 7:3, the values of I in sample a–d were 3.5, 4.1, 6.7 and 18.5, respectively. The diffraction peaks of  $\text{Fe}_2\text{O}_3$  in sample e were hardly detected, suggesting that metal co-doped magnesium ferrite could be synthesized when the  $M_{\text{saprolite/limonite}}$  was 7:3. That is to say, the leaching solution with relatively lower  $R_{Fe/M}$  (1.55) may be suitable for synthesis of pure metal co-doped magnesium ferrites other than that with higher  $R_{Fe/M}$  (1.73–2.52), and this phenomenon can be found in the previous reports (Naeem et al., 2009). According to the leaching experiments, it is well known that the  $R_{Fe/M}$  of the leaching solution was closely linked to both the  $M_{\text{saprolite/limonite}}$  and leaching conditions. As shown in Fig. 2, when the HCl solution concentration was  $2.75 \text{ mol}\cdot\text{L}^{-1}$ , the leaching efficiencies of Fe and Mg were different about 94.6% and 72.6%, respectively. Considering that the  $M_{\text{saprolite/limonite}}$  was about 5:5, the actual  $R_{Fe/M}$  in the leaching solution was calculated to be 2.52, which was larger than the stoichiometric ratio of 2.0 for synthesis of metal co-doped magnesium ferrite. In other words, as for preparation of ferrites, the amount of Fe is excess, and thus  $\text{Fe}_2\text{O}_3$  phase could be generated. With  $M_{\text{saprolite/limonite}}$  increasing from 5:5 to

**Table 4**

The molar ratio of Fe, Ni, Co, Mn and Mg, and  $R_{Fe/M}$  of the leaching solutions. Experimental conditions:  $2.75 \text{ mol}\cdot\text{L}^{-1}$  HCl solution, leaching time of 60 min, leaching temperature of  $100^\circ\text{C}$ , liquid to solid ratio of  $10 \text{ mL}\cdot\text{g}^{-1}$ .

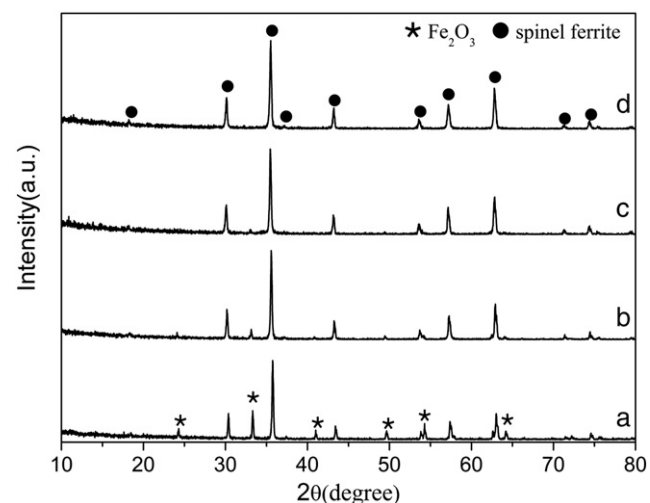
$M_{\text{saprolite/limonite}}$	Fe	Ni	Co	Mn	Mg	$R_{Fe/M}$
5:5	100	4.28	0.24	1.72	33.50	2.52
5.5:4.5	100	4.60	0.23	1.68	38.56	2.22
6:4	100	4.95	0.23	1.64	44.43	1.95
6.5:3.5	100	5.32	0.22	1.60	50.67	1.73
7:3	100	5.73	0.22	1.55	57.62	1.55



**Fig. 6.** XRD patterns of the samples prepared from leaching solutions with  $M_{\text{saprolite/limonite}}$  of (a) 5:5, (b) 5.5:4.5, (c) 6:4, (d) 6.5:3.5 and (e) 7:3. Leaching conditions: initial acid concentration of  $2.75 \text{ mol}\cdot\text{L}^{-1}$ , liquid to solid ratio of  $10 \text{ mL}\cdot\text{g}^{-1}$ , leaching time of 60 min and temperature of  $100^\circ\text{C}$ .

7:3, the actual  $R_{Fe/M}$  in the leaching solution decreased, leading to that the content of impurity  $\text{Fe}_2\text{O}_3$  decreased and pure metal co-doped magnesium ferrite ( $\text{Ni}_{0.13}\text{Co}_{0.005}\text{Mn}_{0.035}\text{Mg}_{0.83}\text{Fe}_{1.95}(\text{Al,Cr})_{0.05}\text{O}_4$ ) was obtained.

Based on the experimental study and detailed analysis of synthesizing metal co-doped magnesium ferrites from different leaching solutions with the initial acid concentration of  $2.75 \text{ mol}\cdot\text{L}^{-1}$ , it can be concluded that the key parameter to prepare pure ferrites is to control the  $R_{Fe/M}$  in the leaching solution. In our study, the important influencing factors to affect the metal ion concentrations in the leaching solution included initial acid concentration, liquid to solid ratio and leaching time etc. Moreover, as described in Fig. 2, the initial acid concentration played a key role in the different metal leaching efficiencies, indicating that ferrites with different amounts of Ni, Co, Mn and Mg can be prepared from the leaching solutions which were obtained by using different acid concentrations. Therefore, in this paper, synthesis of metal co-doped magnesium ferrites from the leaching solutions obtained from different laterite blends ( $M_{\text{saprolite/limonite}}$  of 5:5, 6:4, 6.5:3.5 and 7:3) with the initial acid concentration of  $3.0 \text{ mol}\cdot\text{L}^{-1}$  was also investigated



**Fig. 7.** XRD patterns of the samples prepared from leaching solutions with  $M_{\text{saprolite/limonite}}$  of (a) 5:5, (b) 6:4, (c) 6.5:3.5 (d) 7:3. Leaching conditions: initial acid concentration of  $3.0 \text{ mol}\cdot\text{L}^{-1}$ , liquid to solid ratio of  $10 \text{ mL}\cdot\text{g}^{-1}$ , leaching time of 60 min and temperature of  $100^\circ\text{C}$ .

**Table 5**  
Each metal element recovery and overall metal recovery of Ni, Fe, Co, Mn and Mg from laterite blends.  
Leaching conditions: initial acid concentration of 2.75 mol·L<sup>-1</sup>, liquid to solid ratio of 10 mL·g<sup>-1</sup>, leaching time of 60 min, leaching temperature of 100 °C and M<sub>saprolite/limonite</sub> of 7:3.

Elements	Ni	Fe	Co	Mn	Mg
Saprolite (wt.%)	1.99	21.74	0.37		11.92
Limonite (wt.%)	1.02	46.42	1.09		1.04
Blends (M <sub>saprolite/limonite</sub> = 7:3) (wt.%)	1.70	29.14	0.59		8.66
Metal element recovery <sup>a</sup> (%)	90.00	95.00	80.00		70.00
Metal element recovery <sup>b</sup> (wt%)	1.53	27.69	0.47		6.06
Overall metal recovery (%)	(1.53 + 27.69 + 0.47 + 6.06) / (1.70 + 29.14 + 0.59 + 8.66) = 89.20%				

Metal element recovery<sup>a</sup> presents the mass ratio between each metal element in ferrite and in the laterite blends; metal element recovery<sup>b</sup> presents the mass percent of each metal element in the laterite blends; overall metal recovery presents the mass ratio between all the metal elements in ferrite and in the laterite blends.

as shown in Fig. 7. From the figure, it can be seen that when the M<sub>saprolite/limonite</sub> was 7:3, pure metal co-doped magnesium ferrite can be also obtained.

### 3.4. Overall metal recovery

According to the experiments, the optimum leaching conditions for synthesis of single phase metal co-doped magnesium ferrite were as follows: HCl concentration, 2.75 mol·L<sup>-1</sup>, liquid to solid ratio 10:1 mL·g<sup>-1</sup>, leaching time of 60 min, leaching temperature at 100 °C and M<sub>saprolite/limonite</sub> of 7:3. Under these conditions, 20.00 g laterite blends could produce 13.50 g mixed metal hydroxide precipitate. After calcination, 13.50 g mixed metal hydroxide precipitate could produce about 11.20 g ferrites. And the metal element recoveries of Ni, Fe, Co, Mn and Mg were calculated to be about 90.00%, 95.00%, 80.00%, 80.00% and 70.00%, respectively. So, the overall metal recovery from the laterite blends was about 89.20% as summarized in Table 5.

## 4. Conclusions

A novel hydrometallurgical process was reported to produce single phase metal co-doped magnesium ferrites from laterite blends by using an atmospheric acid leaching and coprecipitation methods. The initial HCl concentration of 2.75 mol·L<sup>-1</sup> has been proven to be good to treat laterite ore with liquid to solid ratio of 10 mL·g<sup>-1</sup>, leaching temperature at 100 °C and leaching time of 60 min. Under the optimum conditions, leaching efficiencies of Fe, Ni, Co, Mn and Mg were 94.5%, 96.7%, 84.5%, 85.5% and 72.5%, respectively. Moreover, while coprecipitation of Ni, Co, Mn, Mg and Fe, most of Al and Cr in the leaching solution can be separated from the precipitate due to their different behaviors at the pH value of 13.0 in the solution. Moreover, single phase metal co-doped magnesium ferrites were successfully prepared from the leaching solutions when the M<sub>saprolite/limonite</sub> was controlled at 7:3 with the initial acid concentration of 2.75 and 3.0 mol·L<sup>-1</sup>, respectively. And under the optimum leaching conditions, the overall metal recovery could be about 89.20%. The novel process can explore a pathway for efficient and comprehensive utilization of laterite ore.

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## Appendix A. Supplementary data

Supplementary data to this article can be found online at <http://dx.doi.org/10.1016/j.hydromet.2014.10.010>.

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