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Recovery of iron from waste ferrous sulphate by co-precipitation and magnetic separation

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Abstract: Magnetite concentrate was recovered from ferrous sulphate by co-precipitation and magnetic separation. In co-precipitation process, the effects of reaction conditions on iron recovery were studied, and the optimal reaction parameters are proposed as follows: n(CaO)/n(Fe^{2+}) 1.4:1, reaction temperature 80 °C, ferrous ion concentration 0.4 mol/L, and the final mole ratio of Fe^{3+} to Fe^{2+} in the reaction solution 1.9−2.1. In magnetic separation process, the effects of milling time and magnetic induction intensity on iron recovery were investigated. Wet milling played an important part in breaking the encapsulated magnetic phases. The results showed that the mixed product was wet-milled for 20 min before magnetic separation, the grade and recovery rate of iron in magnetite concentrate were increased from 51.41% and 84.15% to 62.05% and 85.35%, respectively.

Key words: ferrous sulphate; titanium dioxide; magnetite concentrate; co-precipitation; wet milling; magnetic separation

1 Introduction

Titanium dioxide (TiO_2), the most widely used Ti products, can be used as pigment, as filler in paper, plastics and rubber industries and as flux in glass manufacture [1]. The commercial technologies for the manufacture of pigment grade titanium dioxide are the sulfate process and chloride process. In the sulfate process, a large amount of wastes or toxic by-products, such as spent sulfate acid and ferrous sulphate ($FeSO_4·7H_2O$), are produced [2,3]. The total ferrous sulphate production in China was more than $7×10^6$ t in 2013, and the annual growth rate of production exceeds 10% [4]. Unfortunately, this waste is less marketable and difficult to be utilized because of its high impurity content [5], which causes not only severe environmental problems but also the waste of iron resource. Consequently, the urgent need for proper utilization of $FeSO_4·7H_2O$ has attracted great attention of the researchers in the world.

At present, ferrous sulphate is principally used as raw material to manufacture iron oxide pigments or a coagulant for water treatment, new methods for utilization of ferrous sulphate are to prepare alkali ferrates, cation-substituted $LiFePO_4$ and iron(III) tanning salts, but all of these methods are restricted by insufficient market demand [6−14]. In the present study, a novel method to utilize $FeSO_4·7H_2O$ to prepare magnetite concentrate for steel-making was proposed. Many methods were developed to synthesize magnetic particles of magnetite such as co-precipitation, microemulsions, sol−gel syntheses, and hydrothermal or solvothermal reactions [15−18]. However, the most common method for producing synthetic magnetite particles is the co-precipitation of Fe^{2+}/Fe^{3+} ions (molar ratio 1:2) by sodium hydroxide or ammonia solution [19].

We focused on the preparation of magnetite concentrate from ferrous sulphate by co-precipitation and magnetic separation. Calcium hydroxide was selected as the precipitator and added to ferrous sulphate solution. Consequently, Fe^{2+} ions in the reaction solution were precipitated in the form of $Fe(OH)_2$, and then $Fe(OH)_2$ was converted into Fe_3O_4 by air oxidation and heating. Subsequently, the obtained mixture of magnetite and

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gypsum was wet-milled and then separated by magnetic separator, and magnetite concentrate was obtained. The technical parameters for synthesizing magnetite were optimized. Meanwhile, the effect of wet milling prior to magnetic separation on the iron grade in concentrate was studied. This process has the advantages of a lower cost than the traditional process and a simple processing flow.

2 Experimental

2.1 Materials

The dried ferrous sulphate sample used for this study was obtained from Guangdong Huiyun Titanium Industry Corporation Limited, China. Reagent-grade CaO (Guangdong Xilong Chemical Co., Ltd., China) was used directly without further purification.

2.2 Co-precipitation

Magnetite was prepared by the co-precipitation method. 400 mL of ferrous sulphate solution was added to a 500 mL four-necked flask fitted with a reflux condenser and electric heater, and the concentrations of ferrous ions in solution ranging from 0.2 to 0.6 mol/L were examined. To obtain lime milk, purified water was added to calcium oxide (CaO) with a mass ratio of liquid to solid 3:1 under vigorous stirring. The lime milk with a molar ratio of CaO to Fe^{2+} ranging from 0.8:1 to 1.6:1 was dropwise added into the solution under sufficient stirring. The reactor was heated to a certain temperature ranging from 60 to 90 °C at 10 °C increment, followed by an air flow (1 L/min) bubbled into the solution. The reaction time was maintained between 2 and 4 h at 0.5 h increment. After the reaction, a mixed precipitate of magnetite and gypsum was filtrated and then dried in a vacuum atmosphere at 80 °C.

2.3 Magnetic separation

The obtained mixed product was fully ground in a mortar, and magnetic separation was performed on the slurry of mixed product using a self-designed magnetic separator, as shown in Fig. 1. The magnetic separator is composed of stirring axis, cylinder, permanent magnets and stirring paddle. Stirring axis, cylinder and stirring paddle are made of stainless steel. The cylinder has dimensions of 27 mm in outer diameter, 21 mm in inner diameter and 115 mm in height. The upper end of the stirring axis can be fixed to an electric mixer which can adjust stirring rate, while the lower end is welded to the cylinder cover. The cylinder cover can be screwed to the cylinder surface, and a stirring paddle is welded to the cylinder bottom. The permanent magnets are composed of 4 identical magnet rings that superimpose together, and stuck into the cylinder with the help of cylinder cover. The magnet ring is made of N45H Ru−Fe−B magnet with dimensions of 20 mm in outer diameter, 12 mm in inner diameter and 25 mm in thickness, and radially magnetized with a maximum surface magnetic induction intensity of 0.509 T. 10 g of mixed product and 400 mL of purified water were added to a 500 mL high-type beaker for magnetic separation, and the stirring rate and time were held constant at 600 r/min and 1 h, respectively. Finally, the magnetic fractions were filtered, dried, weighed and subjected to chemical analysis.

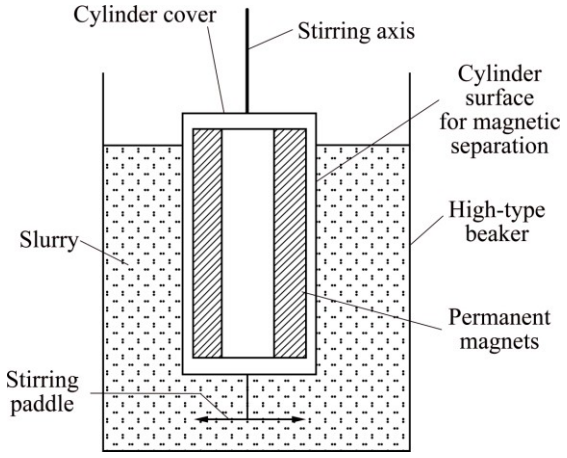

Fig. 1 Schematic diagram of self-designed magnetic separator

Based on the single factor experiments described above, the scale-up magnetite preparation procedure was carried out in a 5 L four-necked flask under the optimum experimental conditions.

4 L ferrous sulphate solution, with ferrous ion concentration of 0.4 mol/L and n(CaO)/n(Fe^{2+}) of 1.4:1, respectively, was placed in the flask under sufficient stirring and treated at 80 °C, followed by an air flow (0.6 m^3/h) bubbled into the solution. When the mole ratio of Fe^{3+} to Fe^{2+} in the reaction solution reached 1.9−2.1, the reaction was stopped. Finally, the obtained mixture of magnetite and gypsum was filtrated, dried and ground for the next experiments.

Magnetic separation was performed on a slurry of mixed product (5% in solid) using a low intensity magnetic separator (CRIMM DC CXGd50, Changsha Research Institute of Mining and Metallurgy Co., Ltd., China). A targeted magnetic induction intensity ranging from 0.05 to 0.25 T was used for 10 min magnetic separation. The field was then switched off and the magnetite fraction was washed, filtered, weighed and subjected to various analyses.

The wet milling pretreatment was conducted in a ball mill in a mixture with a mixed product-to-water mass ratio of 1:40 at room temperature and a rotation speed of 130 r/min. The milling time varied from 0 to 40 min, and the treated mixed products were used directly for magnetic separation under the previous best magnetic separation conditions.

The whole procedure used to prepare magnetite concentrate from ferrous sulphate is summarized in Fig. 2.

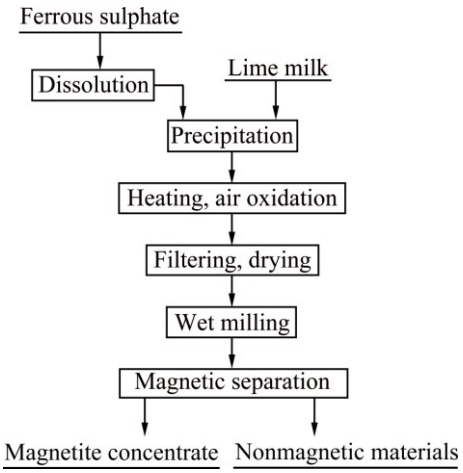

Fig. 2 Flow sheet of magnetite concentrate preparation from ferrous sulphate

2.4 Analysis

The samples were analyzed to examine the ferrous and ferric ions contents according to GB/T 1863−2008 [20]. The contents of trace elements in samples were determined by inductively coupled plasma optical emission spectrometry (ICP-OES, iCAP 7000 Series, Thermo Scientific) after the total dissolution of samples. Phase analysis of the samples was conducted by Rigaku D/max-TTR III X-ray diffractometer (XRD) with Cu K_α radiation (λ=1.54056 Å) at voltage of 40 kV, current of 250 mA and scanning rate of 10 (°)/min from 10° to 70°. The raw material sample was measured by X-ray fluorescence with a Bruker S4 Pioneer system equipped with two X-ray detectors. Surface morphology of the samples was observed by using an FEI Quanta 200 scanning electron microscope (SEM), coupled with an energy dispersive X-ray spectroscope (EDS). Laser particle size analyzer (LS-pop(6), Zhuhai OMEC instrument Co., Ltd.) was used to analyze the size distribution of samples.

After the experiment, the recovery rate of iron (η_1) in magnetite concentrate was calculated based on the mass of iron in raw material (m) and defined as follows:

$$\eta_1=(m_1/m)\times100\% \quad (1)$$

where m_1 is the mass of iron in magnetite concentrate. The grade of iron (η_2) in magnetite concentrate was calculated based on the mass of iron in magnetite concentrate (m_2) and defined as follows:

$$\eta_2=(m_1/m_2)\times100\% \quad (2)$$

3 Results and discussion

3.1 Characterization of dried ferrous sulphate

The XRD pattern of the dried ferrous sulphate is shown in Fig. 3. Rozenite ($FeSO_4\cdot4H_2O$) is identified to be the major component. The dried ferrous sulphate sample was dried in a vacuum atmosphere at 80 °C for 12 h, and then its chemical composition was analyzed by X-ray fluorescence (XRF) as shown in Table 1. It can be seen that iron content is 36.08% and the main impurities are Mg, Ti, Mn, Zn and Al.

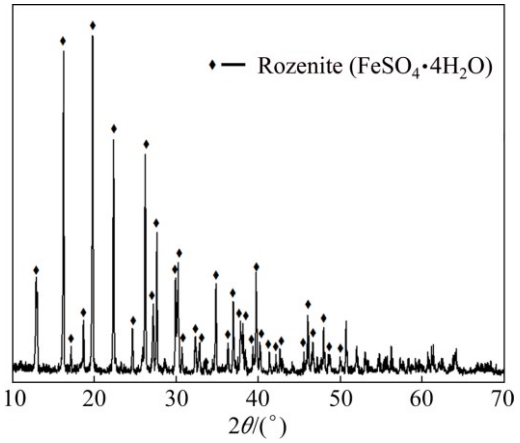

Fig. 3 XRD pattern of dried ferrous sulphate

Table 1 Chemical composition of dried ferrous sulphate (mass fraction, %)

O	Fe	S	Mg	Ti	Mn	Zn	Al
39.24	36.08	22.11	1.24	0.89	0.31	0.02	0.02

3.2 Co-precipitation

The factors affecting the grade and recovery rate of iron in magnetite concentrate were investigated. In this study, four important factors including $n(CaO)/n(Fe^{2+})$, reaction temperature, ferrous ion concentration and reaction time were investigated one by one by keeping the three other parameters constant, as shown in Fig. 4. It is clear that the optimum conditions are suggested as follows: $n(CaO)/n(Fe^{2+})$=1.4:1, reaction temperature 80 °C, ferrous ion concentration 0.4 mol/L and reaction time 3 h. Under such conditions, the grade and recovery rate of iron in magnetite concentrate are 45.36% and 94.74%, respectively.

In this study, magnetite can be formed from ferrous salts according to the following reactions [21]:

$$CaO+H_2O=Ca(OH)_2 \quad (3)$$

$$FeSO_4+Ca(OH)_2+2H_2O=Fe(OH)_2+CaSO_4\cdot2H_2O \quad (4)$$

$$4Fe(OH)_2+O_2+2H_2O=4Fe(OH)_3 \quad (5)$$

$$2Fe(OH)_3+Fe(OH)_2=Fe_3O_4+4H_2O \quad (6)$$

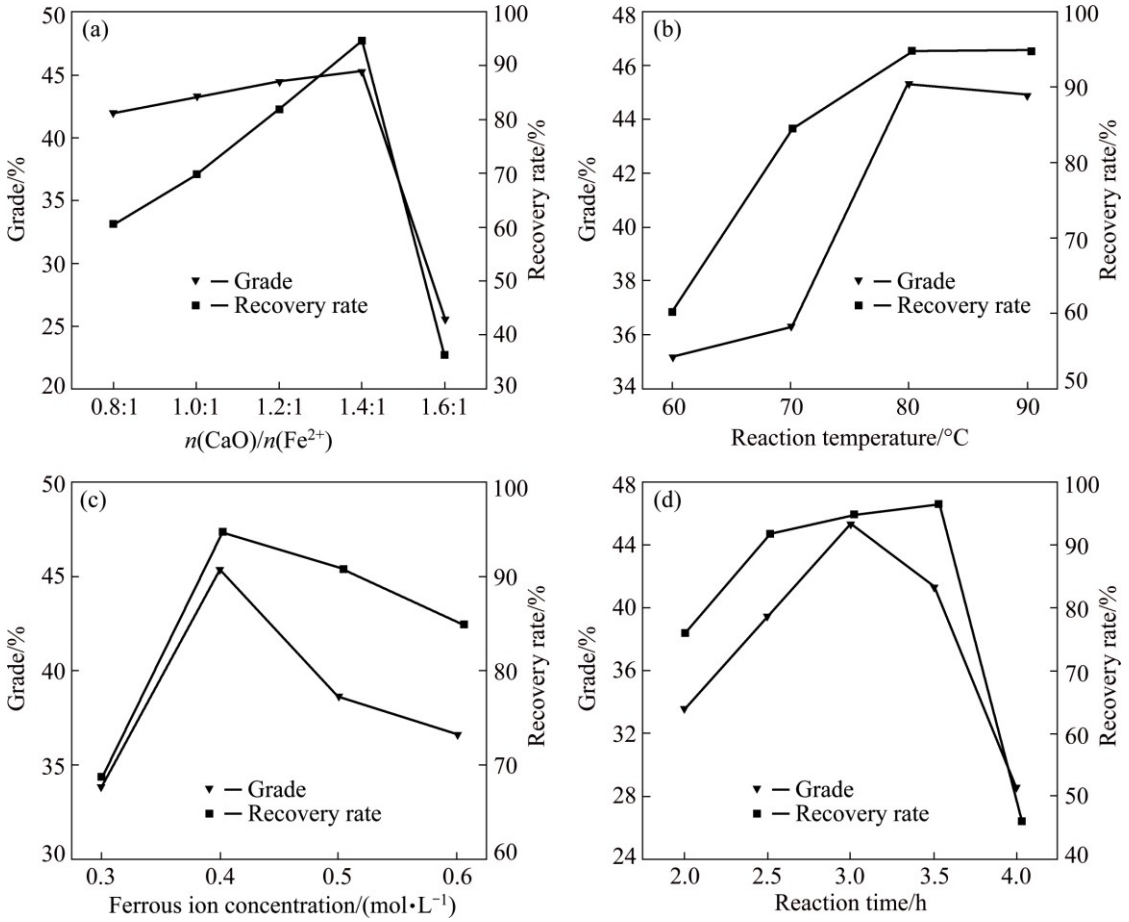

Fig. 4 Effects of n(CaO)/n(Fe^{2+}) (a), reaction temperature (b), ferrous ion concentration (c) and reaction time (d) on grade and recovery rate of iron in magnetite concentrate

Figure 4(a) shows that the grade and recovery rate of iron in magnetite concentrate both increase firstly and then decrease with the increase of n(CaO)/n(Fe^{2+}). It has been reported that $Fe(OH)_2$ is easily oxidized to FeOOH at a pH lower than 4.9 or more than 12 [22]. In order to get pure magnetite, it is necessary to keep the solution pH in an appropriate range by adding the right amount of CaO. Figure 4(b) illustrates that both the grade and recovery rate increase significantly with the reaction temperature increasing from 60 to 80 °C and achieve their maxima at 80 °C, then a constant recovery rate is observed and the grade weakens a little when the reaction temperature is increased to 90 °C. It can be inferred that high reaction temperature benefits to preparing Fe_3O_4. The results in Fig. 4(c) reveal that both the grade and recovery rate achieve their maxima at a ferrous ion concentration of 0.4 mol/L, and then decrease sharply with increasing the concentration from 0.4 to 0.6 mol/L. It is easy for rich air to enter reaction solution at lower ferrous ion concentrations, which leads to over-oxidation of magnetite due to the production of excess hematite (Fe_2O_3), while it is unfavorable for homogeneous distribution of air in reaction solution at higher ferrous ion concentrations, which induces heterogeneous nucleation of the precipitates due to partial over-oxidation or partial light oxidation of magnetite [23]. From Fig. 4(d), it is observed that the grade reaches its peak at a reaction time of 3 h, and the recovery rate reaches its peak at a reaction time of 3.5 h. Obviously, short oxidation time cannot make the mole ratio of Fe^{3+} to Fe^{2+} meet the requirement of Fe_3O_4 formula, while excessively long oxidation time can lead to the over-oxidation of Fe_3O_4.

3.3 Magnetic separation

3.3.1 Characterization of mixed product

Figure 5 shows the XRD pattern of the mixed product. XRD analysis indicates that magnetite (Fe_3O_4) and gypsum ($CaSO_4·2H_2O$) are the main crystalline phases. Figure 6(a) shows SEM image of mixed product. The corresponding EDS patterns are also presented in Figs. 6(b) and (c). From Fig. 6(a), two distinct phases (zones *A* and *B*) are observed; the phase in zone *A* is irregularly shaped plate while fine phase in zone *B* is apt to aggregate. The subsequent EDS analysis proves that the two phases are gypsum (zone *A*) and magnetite (zone *B*), which is in agreement with the XRD results. The line-by-line scanning images of Fe, Ca, S and O are

shown in Figs. 6(d)−(g), respectively. It is observed that Ca and S occupy almost the same partial area, whereas O is uniformly distributed in the whole area. This is because Ca and S are only the constituent elements of gypsum, while O is a common constituent element of gypsum and magnetite. In addition, by comparing the line-by-line scanning images of Fe, Ca and S, it can be seen that Fe phase is partly associated with Ca and S, which causes magnetite not to be separated from gypsum effectively. So, a wet milling pretreatment would be required to reduce the conglutination between magnetite and gypsum in order to obtain better separation of them.

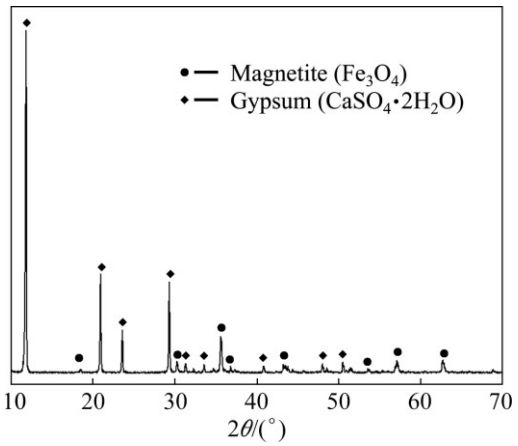

Fig. 5 XRD pattern of mixed product

3.3.2 Effect of magnetic induction intensity on magnetic separation

The effect of magnetic induction intensity on magnetic separation was investigated, and the results are shown in Fig. 7. It can be seen from Fig. 7 that magnetite can be separated from gypsum by the magnetic separator. When the magnetic induction intensity is over 0.05 T, the recovery rate of iron in magnetite concentrate increases remarkably with magnetic induction intensity increasing from 0.05 to 0.175 T, and then increases slowly with magnetic induction intensity increasing from 0.175 to 0.25 T. When magnetic induction intensity is about 0.175 T, the grade of iron in magnetite concentrate achieves a peak. It is probably because magnetic concentrate is hard to choose completely when the magnetic induction intensity is weaker. When the magnetic induction intensity is greater, impurity mineral mingles with the magnetic concentrate, producing magnetic reunion phenomenon and causing the yield of magnetic concentrate to increase, but the grade decreases due to the existence of nonmagnetic impurities mineral [24]. Based on the results of the experiment, the best magnetic induction intensity is 0.175 T. Under this condition, the grade and recovery rate of iron in magnetite concentrate are 51.41% and 84.15%, respectively, while the original grade of iron in mixed product is determined by titration to be only 20.55%.

3.3.3 Effect of wet milling on magnetic separation

The effect of milling time on magnetic separation was investigated under the best magnetic separation conditions, and the results are shown in Fig. 8. The complex dissemination characteristics of mixed product make it difficult in magnetic separation. It needed to be milled before magnetic separation [25]. If the mixed product samples are not milled (0 min), the grade of iron is just 51.41%. When the samples are milled for 20 min, the grade of iron is 62.05%. However, if the mixed product samples are milled to be too fine (40 min), the particles are easily agglomerated and difficult to separate in magnetic separator, so the grade of iron is only 58.64%. It is inferred that the optimum milling time is 20 min. Under this condition, the grade and recovery rate of iron in magnetite concentrate are 62.05% and 85.35%, respectively.

The SEM images and particle size distribution of magnetite concentrates obtained at different milling times are shown in Figs. 9 and 10, respectively. The comparison of Figs. 9(a) and (b) reveals that the physically combined particles are reduced after wet milling. This result means that wet milling can destroy the physical enfoldment of particles and cause the rise of iron recovery rate, as shown in Fig. 8. From Fig. 10, it is evident that the particle size of concentrates obtained after wet milling is smaller than that of concentrates obtained after direct magnetic separation, and their median particle sizes are 1.55 and 1.75 μm, respectively.

Figure 11 shows the XRD patterns of magnetite concentrates obtained at different milling times. As seen from Fig. 11, the diffraction peaks of gypsum disappear after wet milling, magnetite is the major mineral, and calcite is the minor one. This indicates that gypsum is separated out by the wet milling pretreatment, which makes Fe_3O_4 more available for magnetic separation, and the improvement of the grade and recovery rate of iron in magnetite concentrate [26]. This result is in accordance with the SEM images shown in Fig. 9. In addition, the diffraction peaks of magnetite concentrate obtained at the milling time of 20 min indicate that a small amount of calcite was removed incompletely, as shown in Fig. 9(b). This is the reason that the grade of iron after wet milling reaches only 62.05%, and is not very high. The reaction to form calcite can be expressed by the following reaction equation:

$$Ca(OH)_2+CO_2=CaCO_3+H_2O \quad (7)$$

Chemical compositions of magnetite concentrates obtained under different milling times were determined by titration and ICP-OES, and the results are shown in Table 2. From Table 2, the concentrate obtained after wet

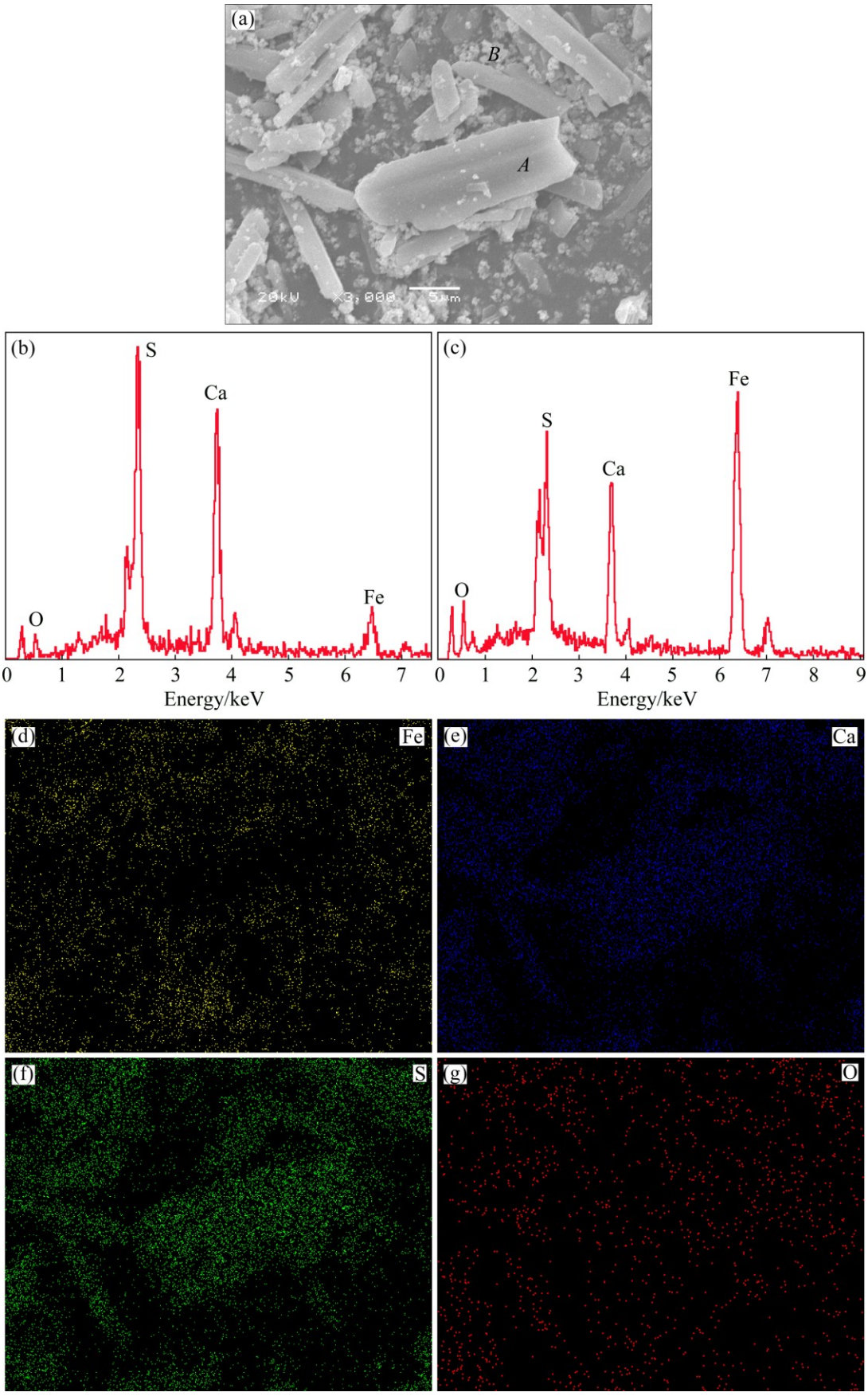

Fig. 6 SEM image (a) of mixed product, its corresponding EDS patterns of zones *A* (b) and *B* (c), and line-by-line scanning images of Fe (d), Ca (e), S (f) and O (g)

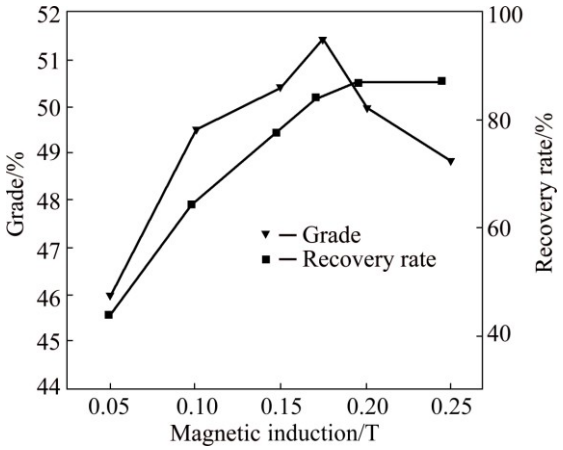

Fig. 7 Effects of magnetic intensity on grade and recovery rate of iron in magnetite concentrate

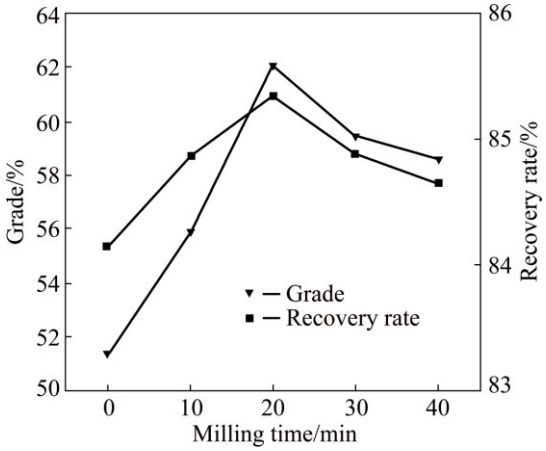

Fig. 8 Effects of milling time on grade and recovery rate of iron in magnetite concentrate

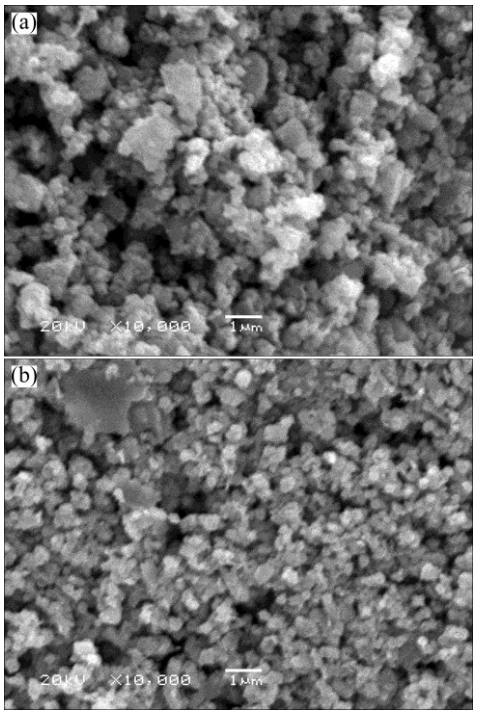

Fig. 9 SEM images of magnetite concentrates obtained at milling time of 0 min (a) and 20 min (b)

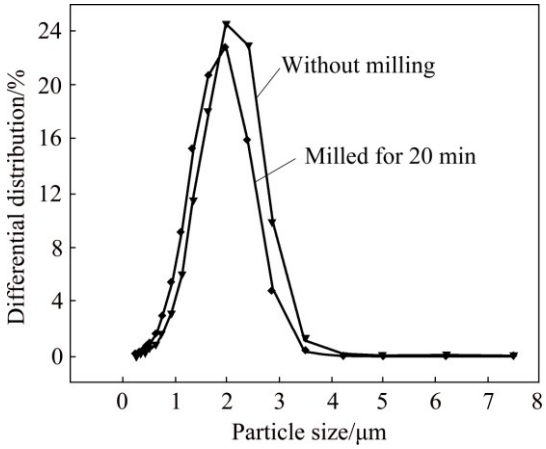

Fig. 10 Particle size distribution of magnetite concentrates obtained at different milling time

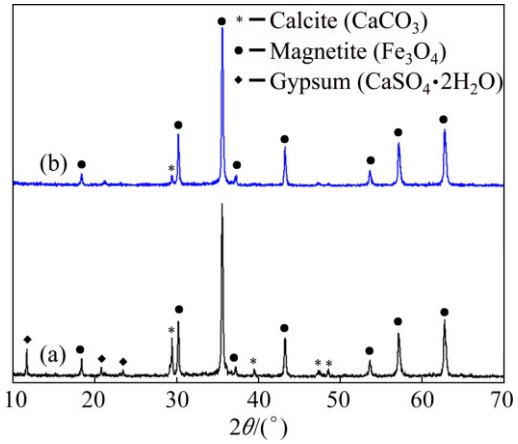

Fig. 11 XRD patterns of magnetite concentrates obtained at milling time of 0 min (a) and 20 min (b)

Table 2 Chemical compositions of magnetite concentrates obtained at different milling time

Milling time/min	Mass fraction/%							
	Fe	Ca	S	Mg	Ti	Mn	Al	Zn
0	51.41	7.89	2.01	0.36	1.18	0.30	0.08	0.02
20	62.05	2.91	1.05	0.20	1.59	0.45	0.09	0.03

milling presents higher contents in Fe, Ti, Mn, Al and Zn than the concentrate obtained after direct magnetic separation, while it exhibits less Ca, S and Mg. The content of Fe in magnetite concentrate obtained after wet milling increases from 51.41% to 62.05%, while the contents of Ca and S are reduced from 7.89% to 2.91% and from 2.01% to 1.05%, respectively. These results agree well with the XRD results in Fig. 11. Therefore, it can be concluded that effective separation of magnetite and gypsum could be realized by the wet milling pretreatment, and both the grade and recovery rate of iron in magnetite concentrate are improved.

4 Conclusions

1) Ferrous sulphate was used to prepare magnetite concentrate by co-precipitation and magnetic separation with calcium hydroxide as the precipitant.

2) The optimum technological parameters for synthesizing magnetite are as follows: $n(CaO)/n(Fe^{2+})$ of 1.4:1, reaction temperature of 80 °C, ferrous ion concentration of 0.4 mol/L, and when the mole ratio of Fe^{3+} to Fe^{2+} in the reaction solution reaches 1.9−2.1 by air oxidation, the reaction is stopped.

3) Wet milling prior to magnetic separation is an effective circuit for concentrating iron. When the mixed product of magnetite and gypsum was wet-milled for 20 min before magnetic separation, the grade and recovery rate of iron in magnetite concentrate were increased from 51.41% and 84.15% to 62.05% and 85.35%, respectively. The experimental results showed that wet milling could crush the physical inclusion of particles, which made Fe_3O_4 more available for magnetic separation.

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采用共沉淀法从绿矾中磁选回收铁

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摘 要：通过共沉淀和磁选从绿矾中回收磁铁矿。在共沉淀阶段，研究反应条件对铁回收的影响，确定最佳反应参数如下：n(CaO)/n(Fe^{2+})1.4:1、反应温度 80 °C、亚铁离子浓度 0.4 mol/L、反应终点溶液中 Fe^{3+}/Fe^{2+}摩尔比 1.9~2.1。在磁选阶段，研究球磨时间和磁感应强度对铁回收的影响。球磨可以破坏混合产物中磁铁矿的包裹和夹杂行为。结果发现，混合产物球磨 20 min 后，磁选精矿的铁品位和铁回收率分别从 51.41% 和 84.15%提高到 62.05%和 85.35%。

关键词：绿矾；二氧化钛；磁铁精矿；共沉淀；湿磨；磁选

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