



## Leaching characteristics of ion-adsorption type rare earths ore with magnesium sulfate

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**Abstract:** Magnesium sulfate was proposed to be leaching agent to deal with the ion-adsorption type rare earths ore to reduce or even eliminate ammonia–nitrogen emissions. The effects of temperature, particle size and stirring speed on rare earth leaching process and the leaching behaviors of the single rare earth element were investigated in order to reveal the rare earth leaching characteristics. Besides, the comparison of leaching effects between magnesium sulfate and ammonium sulfate was also studied. The results showed that the rare earth leaching process could be well described with inner diffusion control model and the apparent activation energy was 9.48 kJ/mol. The leaching behaviors of the single rare earth element were brought into correspondence with rare earths. Moreover, when the concentration of leaching agent was 0.20 mol/L, the rare earth leaching efficiency could all reach above 95% and the leaching efficiency of aluminum impurities could be restrained by 10% using magnesium sulfate compared with ammonium sulfate.

**Key words:** rare earth; leaching agent; kinetics; magnesium sulfate; ion-adsorption type rare earths ore

### 1 Introduction

The rare earth (RE) elements, especially the mid and heavy rare earths, are extensively used in several areas such as new materials, energy conservation and environmental protection [1,2]. The ion-adsorption type rare earths ores are the main resources of mid and heavy rare earths in the world [3]. They are sparsely distributed throughout seven adjacent provinces of southern China [4]. The main form of rare earth elements (REEs) is the ion-exchangeable phase adsorbed on clay minerals, which can be leached when encountering the cations ( $\text{Na}^+$ ,  $\text{NH}_4^+$ ,  $\text{H}^+$ , and  $\text{Mg}^{2+}$ ) [5].

Since the ion-adsorption type rare earths ores in China were discovered in 1969, a series of hydrometallurgy methods for the special ores have been developed by scientists and engineers of China [6–8]. Nowadays, rare earth is recovered from the ion-adsorption type rare earths ore with ammonium sulfate in the industry. But ammonium sulfate as leaching

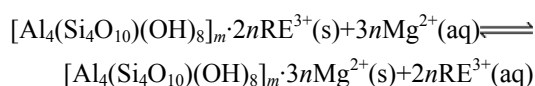
agent would lead to serious environmental problems, such as ammonia-nitrogen pollution in water body which could be difficult to handle to reach the standard, and plant growth difficulties because of the lose of calcium, magnesium and other nutrients in the leaching process [9,10]. So, new studies in laboratory recently have been focused on the development of new non-ammonium leaching agent [11–13], such as iron sulfate, aluminum sulfate and citrate. But these new leaching agents were expensive and would introduce aluminum and iron ions into leaching liquid, which would lead to numbers of problems [14]. HUANG et al [15] proposed a new technology to recover rare earths from ion-adsorption type rare earths ore with magnesium sulfate. With this technology, ammonia-nitrogen emissions could be reduced or even eliminated. And it might be environment-friendly to mine and water [16]. However, at present, there are few basic research reports on the recovery of rare earth from the ion-adsorption type rare earths ore with magnesium sulfate.

In this work, the effect of temperature, particle size and stirring speed on leaching rare earth from the ion-adsorption type rare earths ore with magnesium sulfate in agitation leaching process was investigated in order to know the leaching characteristics. Moreover, the comparison studies between magnesium sulfate and ammonium sulfate were listed. It would be useful to provide a scientific approach and a theoretic basis for leaching rare earth with magnesium sulfate from this kind of ores. It could also be applied to optimizing the rare earth leaching conditions and to taking mathematics simulation on the leaching process.

## 2 Experimental

### 2.1 Leaching mechanism of rare earth

The leaching process of the ion-adsorption type rare earths ore is a kind of ion-exchangeable process between the magnesium ions in the leaching agent and the clay minerals [17]. The chemical reaction equation is as follows:



where s and aq represent solid phase and aqueous phase, respectively. It was reported that the leaching process can be described by the shrinking-core model, and subdivided into five steps [18], as shown in Fig. 1. The leaching rate of rare earths ore with  $\text{MgSO}_4$  solution may be controlled by one of the following steps: outer diffusion through the fluid film, inner diffusion through the product layer or the chemical reaction on the surface. And the leaching equations of the kinetics can be expressed as [19]

Chemical reaction controlling type:

$$1 - (1 - \eta)^{1/3} = k_1 t \quad (1)$$

Outer diffusion controlling type:

$$1 - (1 - \eta)^{1/3} = k_2 t \quad (2)$$

Inner diffusion controlling type:

$$1 - 2/3\eta - (1 - \eta)^{2/3} = k_3 t \quad (3)$$

Mixed controlling type:

$$1 - (1 - \eta)^{1/3} = k_4 \frac{c_0 M}{r_0 \rho} t \quad (4)$$

where  $\eta$  is the rare earth leaching efficiency,  $t$  is the leaching time,  $c_0$  is the initial concentration of leaching reagent,  $M$  is the molar mass of ore sample particle,  $r_0$  is the average initial radius of ore sample particle,  $\rho$  is the mole density of ore sample particle,  $k_1$ ,  $k_2$ ,  $k_3$  and  $k_4$  are apparent reaction rate constants.

### 2.2 Characterization of experimental rare earths ore

The samples of ion-adsorption type rare earths ore were collected from Liutang Rare Earth Mine area located in the Chongzuo City (CZ rare earths ore), Guangxi Province, China. The chemical compositions of ion-exchangeable phases of rare earth and non-rare earth impurities in CZ rare earths ores and the rare earth partitioning of the ion-exchangeable phase were analyzed by National Tungsten & Rare-earth Product Quality Supervision Testing Center, Ganzhou, China, with ICP-AES (VARIAN, 720-ES), which are shown in Tables 1 and 2, respectively. It was evident that the CZ ore was the rare earth mineral with middle Y and rich Eu.

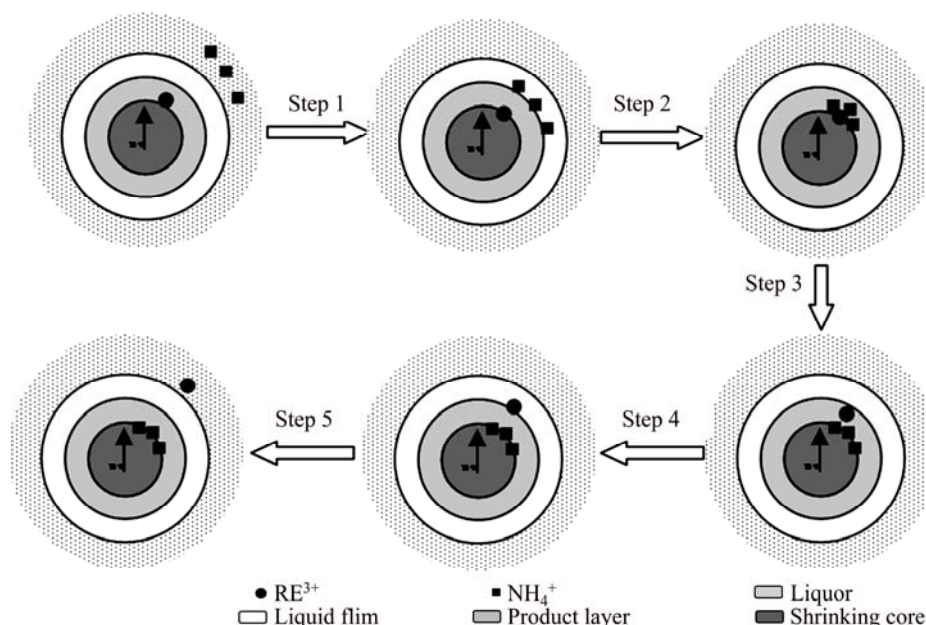


Fig. 1 Shrinking core model of ore particle

**Table 1** Main chemical composition of ion-exchangeable phase of CZ rare earths ore sample (mass fraction,  $10^{-3}$ )

| RE <sub>2</sub> O <sub>3</sub> | Mg   | Ca   | Al   | Fe    |
|--------------------------------|------|------|------|-------|
| 1.50                           | 0.05 | 0.25 | 0.03 | <0.01 |

**Table 2** Rare earth partitioning of ion-exchangeable phase in CZ rare earths ore (mass fraction, %)

| La <sub>2</sub> O <sub>3</sub> | CeO <sub>2</sub>               | Pr <sub>6</sub> O <sub>11</sub> | Nd <sub>2</sub> O <sub>3</sub> | Sm <sub>2</sub> O <sub>3</sub> |
|--------------------------------|--------------------------------|---------------------------------|--------------------------------|--------------------------------|
| 21.87                          | 2.99                           | 5.32                            | 18.68                          | 3.98                           |
| Eu <sub>2</sub> O <sub>3</sub> | Gd <sub>2</sub> O <sub>3</sub> | Tb <sub>4</sub> O <sub>7</sub>  | Dy <sub>2</sub> O <sub>3</sub> | Ho <sub>2</sub> O <sub>3</sub> |
| 0.68                           | 4.57                           | 0.78                            | 4.43                           | 0.88                           |
| Er <sub>2</sub> O <sub>3</sub> | Tm <sub>2</sub> O <sub>3</sub> | Yb <sub>2</sub> O <sub>3</sub>  | Lu <sub>2</sub> O <sub>3</sub> | Y <sub>2</sub> O <sub>3</sub>  |
| 2.36                           | 0.29                           | 1.51                            | 0.20                           | 31.46                          |

### 2.3 Batch leaching tests

All chemicals, such as MgSO<sub>4</sub> (AR, Sinopharm Chemical Reagent Co., Ltd.) used in the study, were of analytic reagent grade.

The tests were conducted in a 500 mL three-necked flask which was partially immersed in a heated water bath to control the leaching temperature in the range of 10 °C to 55 °C. And the three-necked flask was fitted with a thermometer, stirrer paddle and bottle stopper. A total of 200 mL of a certain concentration of leaching agent solution was put in the reactor and preheated to desired leaching temperature. 40 g dried rare earths ore in a specific particle size was placed into the reactor, and then stirrer was rapidly stirred with a certain speed. After completion of each given time experiment, the samples were collected with 5 mL by a pipette, and rapidly transferred to centrifuge tube with 40 mL deionized distilled water. After that, a centrifuge (Eppendorf Centrifuge 5804(R)/5810(R)) was employed to solid-liquid separation. The liquid was diluted to 50 mL with deionized distilled water and analyzed by ICP-AES (PerkinElmer, Co., Ltd., Optima 8300).

From the analysis results, the leaching efficiency of rare earth could be defined as

$$\eta = \varepsilon_t / \varepsilon_0 \quad (5)$$

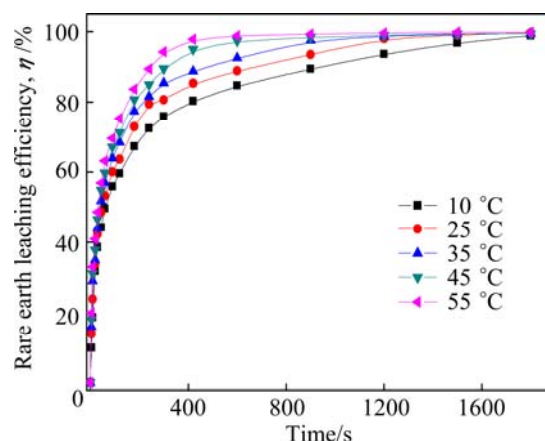
where  $\varepsilon_t$  is the total amount of rare earth in leaching solution before the leaching time was  $t$ ,  $\varepsilon_0$  is the total amount of rare earth in original ore sample.

## 3 Results and discussion

### 3.1 Effect of leaching temperature on rare earth leaching

To investigate the leaching process and leaching characteristics of rare earth from CZ rare earths ore with magnesium sulfate solution, the effect of temperature on

the leaching efficiency was examined in the range of 10–55 °C. The results are shown in Fig. 2. As shown in Fig. 2, the leaching efficiency of rare earth increased rapidly in the first 250 s and then slowed down with the passage of time at all temperatures. The higher the temperature was, the severer the thermal motion of ions was, so the leaching rate of rare earth increased with the increase of leaching temperature. The efficiency would be more than 95% finally when the leaching time was long enough in any temperature.



**Fig. 2** Effect of leaching temperature on rare earth leaching of CZ ore ( $r_0=0.60\text{--}0.90$  mm,  $c(\text{MgSO}_4)=0.20$  mol/L,  $\omega=400$  r/min,  $L/S=5:1$ )

The data of the rare earth leaching efficiency were substituted into the kinetic control model of the shrinking-core model. For the kinetics type of outer diffusion or chemical reaction controlling, the plot of  $1-(1-\eta)^{1/3}$  vs time ( $t$ ) was a straight line. For the kinetics type of inner diffusion controlling, the plot of  $1-2/3\eta-(1-\eta)^{2/3}$  vs time ( $t$ ) was a straight line. For the kinetics type of mixed controlling, both the plots of  $1-(1-\eta)^{1/3}$  and  $1-2/3\eta-(1-\eta)^{2/3}$  vs time ( $t$ ) were not straight lines [20]. The kinetics equation was obtained by applying trial or error method from the experiment data in Fig. 2. The results showed that the data satisfied Eq. (3), which was shown in Fig. 3. This suggested that the leaching rate was controlled by inner diffusion of reactants and leaching products through mineral porous layer during the kinetics district. As shown in Fig. 3, the leaching apparent reaction rate constants increased with the rise of temperature, whose values were  $6.29 \times 10^{-4}$  (10 °C),  $7.44 \times 10^{-4}$  (25 °C),  $8.55 \times 10^{-4}$  (35 °C),  $9.63 \times 10^{-4}$  (45 °C) and  $1.09 \times 10^{-3}$  (55 °C), respectively. The Arrhenius equation could then be expanded and represented as follows:

$$k_3 = Ar_0^n \exp\left(-\frac{E}{RT}\right) \text{ or } \ln k_3 = \ln A + n \ln r_0 - \frac{E}{RT} \quad (6)$$

where  $A$  is the apparent pre-exponential factor,  $E$  is the activation energy,  $R$  is the mole gas constant.

The kinetic information could be obtained by plotting  $\ln k_3$  vs  $1/T$  for the five temperatures, as shown in Fig. 4. The apparent activation energy  $E$  of the leaching process calculated from the slope of the straight line was 9.48 kJ/mol. This value fell within the activation energy conventionally found for inner diffusion-controlled leaching processes, which was in the range of 4–12 kJ/mol [21].

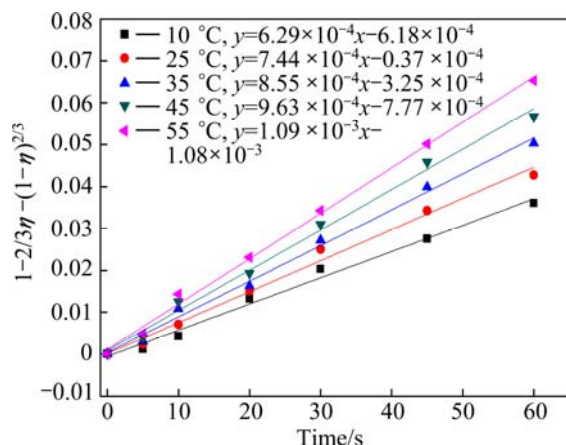


Fig. 3 Plots of  $1-2/3\eta-(1-\eta)^{2/3}$  vs time at different temperatures of rare earth leaching

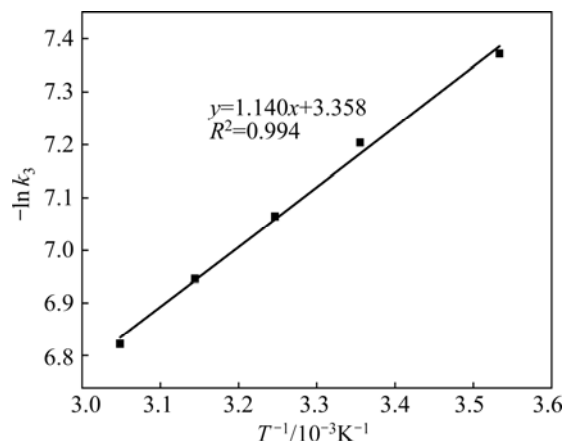


Fig. 4 Arrhenius plot of leaching rare earth from CZ rare earths ore

### 3.2 Effect of particle size of CZ rare earths ore on rare earth leaching

In order to further confirm that the leaching process was inner diffusion controlled and also to establish mechanism of leaching rare earth, the influence of particle size on the leaching efficiency was investigated, and the results were presented in Fig. 5. The smaller the radius was, the smaller the thickness of product layer was, and the shorter the diffusion distance of cations would be. It showed that the rare-earth leaching rate with a smaller ore particle size was greater. From the

experimental data in Fig. 5, a set of linear regressions were obtained by plotting  $1-2/3\eta-(1-\eta)^{2/3}$  vs  $t$ , as shown in Fig. 6. It was evident that the rare earth leaching process could be well described with inner diffusion control model. Furthermore, a good linearity existed between  $\ln k_3$  and  $\ln r_0$ , as shown in Fig. 7, from which the  $n$  and  $A$  values in the Arrhenius equation in Eq. (6) could be calculated to be  $-1.217$  and  $0.011$ . Then, the  $k_3$  values could be obtained as the following equation:

$$k_3 = 0.011r_0^{-1.217} \exp\left(-\frac{9.48 \times 10^3}{8.314T}\right) \quad (7)$$

After the evaluation of activation energy and pre-exponential factor, the kinetic model for the ion-adsorption type rare earths ore may be expressed as

$$1 - \frac{2}{3}\eta - (1-\eta)^{2/3} = 0.011r_0^{-1.217} \exp\left(-\frac{9.48 \times 10^3}{8.314T}\right) \quad (8)$$

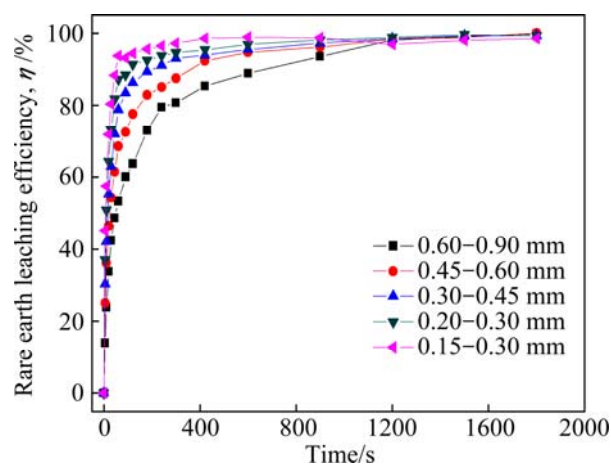


Fig. 5 Effect of particle size of CZ rare earths ore on rare earth leaching (Temperature 25 °C,  $c(\text{MgSO}_4)=0.20$  mol/L,  $\omega=400$  r/min, L/S=5:1)

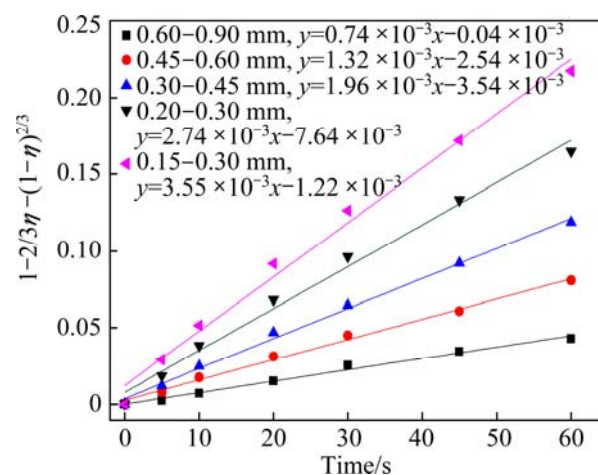


Fig. 6 Plots of  $1-2/3\eta-(1-\eta)^{2/3}$  vs time for different particle sizes of CZ ore

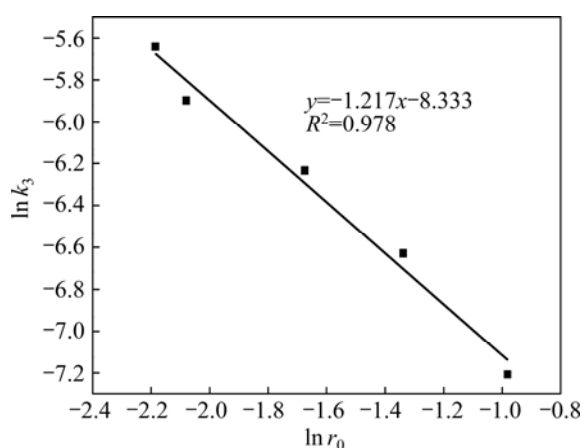


Fig. 7 Relationship between  $\ln k_3$  and  $\ln r_0$  at 25 °C of CZ ore

To enhance the leaching process, it was desirable to create suitable environment to accelerate the inner diffusion rate of leaching agent, such as raising the reaction temperature, reducing the mineral particle size, increasing the concentration of leaching agent and using heat ball mill leaching technology to reduce the product layer thickness.

### 3.3 Effect of stirring speed of CZ rare earths ore on rare earth leaching

The influence of stirring speed was studied to further confirm that the leaching process was inner diffusion controlled. The results were shown in Table 3. The rare earth efficiencies were almost the same at different stirring speeds anytime. It means that stirring speed had no effect on rare earth leaching, which proved from a different angle that the leaching rate was controlled by inner diffusion [21].

**Table 3** Effect of stirring speed on rare earth leaching of CZ ore (Temperature 25 °C,  $r_0=0.60\text{--}0.90$  mm,  $c(\text{MgSO}_4)=0.20$  mol/L, L/S=5:1)

| Leaching time/s | Leaching rate/% |           |           |
|-----------------|-----------------|-----------|-----------|
|                 | 200 r/min       | 300 r/min | 400 r/min |
| 60              | 53.96           | 54.20     | 53.32     |
| 120             | 63.60           | 62.68     | 63.72     |
| 600             | 89.20           | 89.04     | 88.92     |
| 1200            | 98.40           | 98.61     | 98.13     |

### 3.4 Leaching behaviors of single rare earth element under different conditions

To describe the leaching behaviors of the single rare earth element, the main rare earth partitioning in the leaching solution under different conditions was calculated and listed in Table 4. It was obvious that the rare earth partitioning in the leaching solution under

different conditions was substantially constant over time, which was basically consistent with the rare earth partitioning of the ion-exchangeable phase in the CZ rare earths ore. In the leaching system, an L/S of 5:1 was big enough, and the magnesium sulfate concentration of 0.20 mol/L was sufficiently high, so the weak differences in leaching characteristics between rare earth elements would be concealed. Thus, it could be seen that the leaching behavior of the single rare earth element was brought into correspondence with rare earths, and their leaching process should be described with inner diffusion control model too.

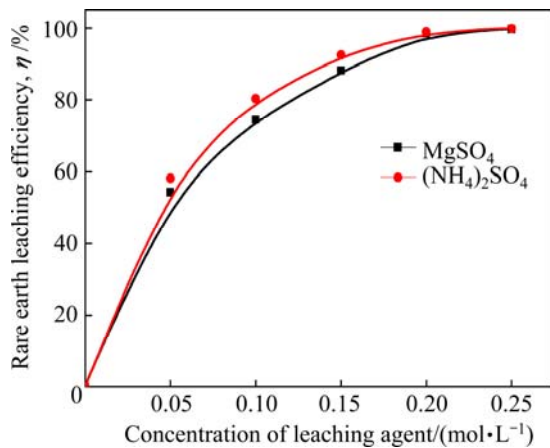
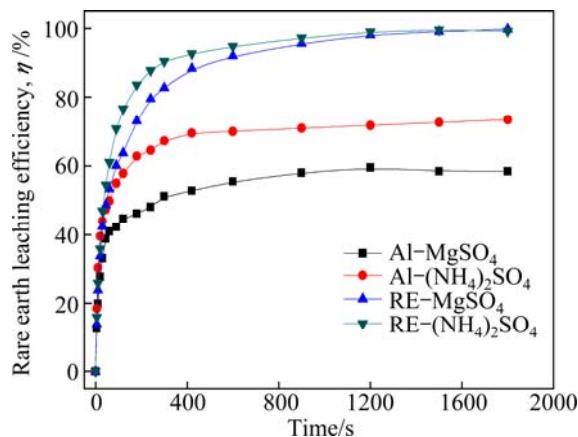
### 3.5 Comparison of leaching effects between $\text{MgSO}_4$ and $(\text{NH}_4)_2\text{SO}_4$

The comparison of leaching effects between two kinds of leaching agents was investigated. Firstly, the comparison of rare earth efficiency in different concentrations is shown in Fig. 8. The rare earth efficiency increased rapidly with the rising of concentration, and it was a little bit lower when leached with  $\text{MgSO}_4$  than  $(\text{NH}_4)_2\text{SO}_4$ . But they all could be above 95% when the concentration of leaching agent was added to 0.20 mol/L, and basically remained stable later. Furthermore, the comparison of rare earth and aluminum leaching efficiency was shown in Fig. 9. When the ion-adsorption type rare earths ore was leached by  $(\text{NH}_4)_2\text{SO}_4$ , the rare earth leaching efficiency and rare earth efficiency were a little higher than those leached by  $\text{MgSO}_4$ . This may be caused by the weak hydration effects and the larger number of cations in the  $(\text{NH}_4)_2\text{SO}_4$  solution [22]. Furthermore, aluminum in the leaching liquor would cause numbers of unwanted influences, such as low product purity, low rare earth yield and high consumption of precipitant [23]. And the aluminum impurities in rare earth carbonate precipitation would increase operating loads of the follow-up separation process, so the aluminum leaching efficiency was studied in the experiment. The result in Fig. 9 showed that the aluminum leaching efficiency was only 58% by  $\text{MgSO}_4$  and 73% by  $(\text{NH}_4)_2\text{SO}_4$ . The aluminum leaching efficiency was much lower than that of rare earth because leaching reaction and hydrolysis reaction of aluminum was in competition in the system when the pH of solution was around 5.8 [24,25]. The aluminum leaching efficiency was higher in the leaching system with  $(\text{NH}_4)_2\text{SO}_4$ , which might be because there was a coordination effect between ammonium and aluminum ions. Therefore, the leaching efficiency of aluminum could be reduced and leaching efficiency of rare earth would be almost the same by using  $\text{MgSO}_4$  as leaching agent instead of  $(\text{NH}_4)_2\text{SO}_4$ .



**Table 4** Main rare earth partitioning in leaching solution under different conditions

| Time/s | Condition                             | Mass fraction/%                |                                 |                                |                                |                                |                                |                               |
|--------|---------------------------------------|--------------------------------|---------------------------------|--------------------------------|--------------------------------|--------------------------------|--------------------------------|-------------------------------|
|        |                                       | La <sub>2</sub> O <sub>3</sub> | Pr <sub>6</sub> O <sub>11</sub> | Nd <sub>2</sub> O <sub>3</sub> | Sm <sub>2</sub> O <sub>3</sub> | Gd <sub>2</sub> O <sub>3</sub> | Dy <sub>2</sub> O <sub>3</sub> | Y <sub>2</sub> O <sub>3</sub> |
| 10     | Temperature 10 °C, $r_0=0.60-0.90$ mm | 21.87                          | 5.27                            | 18.61                          | 3.95                           | 4.53                           | 4.39                           | 31.62                         |
| 60     | Temperature 10 °C, $r_0=0.60-0.90$ mm | 21.98                          | 5.27                            | 18.69                          | 3.96                           | 4.51                           | 4.36                           | 31.41                         |
| 600    | Temperature 10 °C, $r_0=0.60-0.90$ mm | 21.65                          | 5.21                            | 18.69                          | 3.97                           | 4.69                           | 4.39                           | 31.53                         |
| 1800   | Temperature 10 °C, $r_0=0.60-0.90$ mm | 21.79                          | 5.24                            | 18.58                          | 3.94                           | 4.73                           | 4.45                           | 31.22                         |
| 10     | Temperature 35 °C, $r_0=0.60-0.90$ mm | 21.83                          | 5.29                            | 18.44                          | 4.00                           | 4.66                           | 4.48                           | 31.59                         |
| 60     | Temperature 35 °C, $r_0=0.60-0.90$ mm | 21.72                          | 5.26                            | 18.42                          | 4.01                           | 4.58                           | 4.48                           | 31.82                         |
| 600    | Temperature 35 °C, $r_0=0.60-0.90$ mm | 21.73                          | 5.31                            | 18.43                          | 4.01                           | 4.82                           | 4.48                           | 31.61                         |
| 1800   | Temperature 35 °C, $r_0=0.60-0.90$ mm | 21.82                          | 5.27                            | 18.50                          | 4.02                           | 4.73                           | 4.49                           | 31.58                         |
| 10     | Temperature 25 °C, $r_0=0.20-0.30$ mm | 21.99                          | 5.28                            | 18.51                          | 4.03                           | 4.59                           | 4.47                           | 31.37                         |
| 60     | Temperature 25 °C, $r_0=0.20-0.30$ mm | 21.79                          | 5.18                            | 18.42                          | 4.06                           | 4.62                           | 4.41                           | 31.75                         |
| 600    | Temperature 25 °C, $r_0=0.20-0.30$ mm | 21.91                          | 5.24                            | 18.55                          | 4.04                           | 4.53                           | 4.42                           | 31.20                         |
| 1800   | Temperature 25 °C, $r_0=0.20-0.30$ mm | 21.79                          | 5.35                            | 18.59                          | 4.08                           | 4.59                           | 4.47                           | 31.30                         |

**Fig. 8** Comparison of rare earth efficiency at different concentrations of leaching agents (temperature 25 °C,  $r_0=0.60-0.90$  mm,  $\omega=400$  r/min,  $L/S=5:1$ ,  $t=1800$  s)**Fig. 9** Comparison of rare earth and aluminum leaching efficiency between two kinds of leaching agents (temperature 25 °C,  $r_0=0.60-0.90$  mm,  $\omega=400$  r/min,  $L/S=5:1$ ,  $c(\text{MgSO}_4)=c((\text{NH}_4)_2\text{SO}_4)=0.20$  mol/L)

## 4 Conclusions

1) Magnesium sulfate instead of ammonium sulfate was presented to be leaching agent to deal with the ion-adsorption type rare earths ore to reduce or even eliminate ammonia–nitrogen emissions.

2) The rare earth leaching efficiency increased with the increase of leaching temperature and the decrease of particle size. The leaching behaviors of the single rare earth element were brought into correspondence with rare earths, and the leaching equation of the kinetics could be expressed as

$$1 - \frac{2}{3}\eta - (1 - \eta)^{2/3} = 0.011r_0^{-1.217} \exp\left(-\frac{9.48 \times 10^3}{8.314T}\right).$$

3) When the concentration of leaching agent was 0.20 mol/L, the rare earth leaching efficiency could all reach above 95% and the aluminum leaching efficiency was only 58% by  $\text{MgSO}_4$  and 73% by  $(\text{NH}_4)_2\text{SO}_4$ , so the leaching efficiency of aluminum could be reduced and rare earth efficiency would be almost the same by using  $\text{MgSO}_4$  as leaching agent instead of  $(\text{NH}_4)_2\text{SO}_4$ .

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## 硫酸镁浸取离子吸附型稀土矿的浸取特性

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**摘 要:** 为了减少甚至消除氨氮污染, 提出采用硫酸镁作为浸取剂浸取离子吸附型稀土矿的方法。研究反应温度、矿物粒度和搅拌速度对浸取过程的影响以及单一稀土元素的浸出行为, 以此获得稀土浸取机理; 另外, 还对对比分析硫酸镁和硫酸铵两种浸取剂的浸取效果。研究结果表明: 稀土的浸取过程可以采用内扩散控制模型描述, 其表观活化能为 9.48 kg/mol, 而单一稀土元素与稀土总量的浸出行为一致。另外, 当硫酸镁或硫酸铵浸取剂的浓度为 0.2 mol/L 时, 稀土浸出率都能达 95%以上, 但是使用硫酸镁浸出剂能使铝的浸出率较硫酸铵的降低 10%以上。

**关键词:** 稀土; 浸取剂; 动力学; 硫酸镁; 离子吸附型稀土矿

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