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Leaching behaviour of rare earth elements from low-grade weathered crust elution-deposited rare earth ore using magnesium sulfate

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ABSTRACT: The present study investigates the use of magnesium sulfate ($MgSO_4$) instead of $(NH_4)_2SO_4$ as a lixiviant in the recovery of rare earth elements (*REE*s) from clays. Experiments were carried out to investigate the influence of leaching conditions such as leaching time, lixiviant concentration and liquid:solid ratio on the leaching efficiency. The optimum leaching conditions, leading to 75.48% of total *REE* leaching efficiency, required a stirring speed of 500 rpm, a leaching time of 30 min, a lixiviant concentration of 3 wt.% and a liquid:solid ratio of 3:1. After extension of the leaching process by a second stage, the leaching efficiency may reach up to 96.19%, which is slightly higher than that obtained by $(NH_4)_2SO_4$. Leaching varies from element to element, with Ce presenting the lowest leaching efficiency, and the partition in leaching solution is in agreement with that in raw ore other than for Ce. Based on these findings, $MgSO_4$ lixiviant is an excellent alternative leaching agent for a sustainable *REE* industry because it reduces or eliminates NH_4^+–N pollution.

KEYWORDS: rare earth elements, leaching efficiency, lixiviant, $MgSO_4$, ammonia–nitrogen.

China's rare earth element (*REE*) reserves that are of industrial grade are mainly classified into three categories: mixed bastnäsite and monazite (accounting for 83.7% of China's total *REE* reserves, located in Bayan Obo, Inner Mongolia), bastnäsite (10.6%, in Sichuan and Shandong provinces) and *REE* ions adsorbed on clays (2.9%, in seven provinces of southern China) (Dołęgowska & Migaszewski, 2013; Yang *et al*., 2013; Weng *et al*., 2016). The demand for *REE*s and their compounds in the high-tech industry and the ongoing development of advanced technologies has increased considerably over recent years (Morais & Ciminelli, 2004; Binnemans *et al*., 2013; Liu *et al*., 2016; Schaeffer *et al*., 2016; Song *et al*., 2016). Medium and heavy *REE*s (*MREE*s and *HREE*s) find more applications and are of greater value than light *REE*s. Bayan Obo *REE* deposits are rich in light *REE*s (accounting for 97% of the total rare earths of the deposit), whereas the deposits of *REE* ions adsorbed on clays are rich in *MREE*s and *HREE*s (accounting for >80% of world's total *MREE*s and *HREE*s) (Kanazawa & Kamitani, 2006; Chi & Tian,

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2008; Castor, 2008). *REE*s in weathered rare earth ores exist in four phases (Chi *et al*., 2005): (1) the water-soluble phase, which refers to the *REE*s dissolved in water, accounting for <1 in 10,000 total *REE*s and should be considered negligible; (2) the ion-exchangeable phase, which refers to the *REE*s adsorbed on clay minerals by electrostatic interaction, accounting for >80% of total *REE*s. It may be released easily into leaching liquor upon ion exchange with NH^{4+}, Mg^{2+}, Fe^{2+} and Fe^{3+}; (3) the colloidal sediment phase, which refers to the *REE*s adsorbed on iron manganese colloids by coordination and to the *REE* oxides or hydroxides bonded with or deposited on minerals, mainly CeO_2/$Ce(OH)_4$; and (4) the mineral phase, which includes the *REE* minerals with ionic compounds as well as diffusion of *REE* ions to displace mineral crystals in the ores, such as bastnäsite, apatite and so on. Utilizing physical processing methods such as flotation, magnetic, gravity and electrostatic separation may improve the grade of rare earth oxide (REO), and ion exchange is indispensable for extracting *REE*s from the concentrate (Kul *et al*., 2008).

The leaching methods employed in the extraction of ion-adsorption clays have been greatly improved based on three different leaching processes, including the first-generation leaching process with NaCl solution, the second-generation leaching process with $(NH_4)_2SO_4$ solution and the third-generation *in situ* leaching process with $(NH_4)_2SO_4$ solution (Huang *et al*., 2005). Among the chemical leaching approaches, the *in situ* leaching technology is advantageous in terms of protection of surface vegetation because it reduces the need for soil excavation. However, it has also caused serious environmental problems, such as underground water contamination, mine collapse, landslides and plant-growth difficulties, because the ammonium salt is still the major leaching agent in this process (Huang *et al*., 2005; Yang *et al*., 2013). Therefore, China needs to implement an integrated rare earth resource management approach to meet global demands, preserve resources for future generations and protect the environment by adopting a more environmentally friendly leaching agent.

Much effort is being expended in the research and development of hydrometallurgical leaching processes for the specially weathered crust elution-deposited rare earth ores to improve the intensification of the leaching process or reduce the consumption of leaching agents by introducing magnetochemistry, sesbania gum, compound leaching agents and impurity-inhibited leaching (Qiu *et al*., 2002, 2014; Tian *et al*., 2013; Yang & Zhang, 2015). However, the major leaching agent in these processes is still ammonium salt, which fails to tackle the ammonia–nitrogen pollution problem. Chinese scientists and engineers have been engaged in the research and development of many lixiviants without ammonia–nitrogen such as $CaCl_2$, $MgCl_2$, $Fe_2(SO_4)_3$, $Al_2(SO_4)_3$, citrates and so on, to replace the $(NH_4)_2SO_4$ lixiviant. To date, all of the lixiviants introduced would not only increase processing costs, but also bring about new environmental issues with respect to Al/Fe poisoning of plants and high Ca and Na contents in soil (Huang *et al*., 2008, 2013). Magnesium fertilizer is lacking in the soil of southern China due to the lack of ion-exchangeable magnesium (Bai *et al*., 2004). Based on China's water-quality standard, the Mg ion content in the underground and surface water is relatively low; using magnesium sulfate as the lixiviant in the *in situ* leaching could, therefore, act as a source of magnesium fertilizer for the soil.

In the present study, magnesium sulfate ($MgSO_4$) was chosen as a leaching agent to remove *REE*s from a weathered crust elution-deposited *REE* ore to reduce or even eliminate ammonia–nitrogen pollution. Experimental work was conducted to investigate the influence of $MgSO_4$ concentration, leaching time and liquid:solid ratio (L:S) on REE-leaching efficiency. The results provide a theoretical basis for and scientific approach to achieving high-efficiency and optimized leaching conditions in industrial practice and to obtaining more evidence and a better understanding of $MgSO_4$ as a productive leaching agent.

METHODS

Rare earth ore sample and experimental reagents

The experimental weathered crust elution-deposited REE ore sample was kindly supplied by Chalco Guangxi Nonferrous Chongzuo Rare-Earth Development Ltd Co. The chemical composition of the sample was determined by inductively coupled plasma atomic emission spectrometry (ICP-AES; VARIAN, 720-ES) and X-ray fluorescence spectrometry (SHIMADZU Co., Ltd, Japan). The sample contained only 0.11% total *REE* (~0.072 mmol REE/100 g clay; *i.e.* its grade is very low) (Table 1).

The chemical composition of the *REE* ore sample was determined at the National Tungsten & Rare-Earth Product Quality Supervision Testing Center, Ganzhou, China, using ICP-AES (Table 2). The ore contained yttrium and *MREE*s. The precision of ICP-AES analyses varies between 1.3% and 5.5% (Ai *et al*., 2001). The mineralogical composition of the sample was identified

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TABLE 1. The chemical compositions (%) of the ore sample.

Element	REO	MgO	Al_2O_3	CaO	SiO_2	Fe_2O_3	Na_2O	K_2O
Content	0.11	0.14	15.06	0.036	73.23	5.29	0.12	1.7

REO = rare earth oxide.

by X-ray diffraction (XRD; PANalytical EMPYREAN) using Cu-*K*α radiation in the range 5 to 90°2θ with a scanning speed of 2°2θ/min. Fourier-transform infrared (FTIR) spectra of the sample were collected with a Nicolet-740 FTIR spectrometer using KBr pellets.

The leaching reagent used in this experiment was the magnesium sulfate ($MgSO_4$) solution. All chemicals used in the analysis were of analytical reagent grade.

Apparatus and experimental procedure

A given weight (100 g) of ground *REE* ore was placed into a tri-neck glass flask and then the leaching solution of known concentration was added at the desired L:S. Leaching experiments were conducted under stirring at the specified conditions. After completion of the experiments, the suspensions were centrifuged and the supernatant collected. The total *REE* content and individual *REE* concentrations were determined by ICP-AES.

The fraction of the ion-exchangeable *REE*s was determined as follows: 100 g of the *REE* ores was leached by 20 g/L $(NH_4)_2SO_4$ for 12 h in a beaker, with magnetic stirring at 100 rpm. Subsequently, the suspension was filtered through a quantitative neutral filter paper. The concentration of the *REE*s in the filtrate was determined by EDTA volumetric titration.

The rare earth leaching efficiency (η) was calculated according to equation 1:

$$\eta = \frac{\varepsilon_t}{\varepsilon_o} \times 100\% \qquad (1)$$

where ε_τ is the total amount of leached *REE*s at a reaction time *t* and ε_o is the ion-exchangeable *REE* fraction in the original ore sample.

RESULTS AND DISCUSSION

Characterization of the weathered crust elution-deposited rare earth ores

The XRD pattern of the ore sample is presented in Fig. 1. The ore consists mainly of quartz (~53%) and kaolinite (29%) and minor illite-mica (~6%) and K-feldspar (~6%). REOs or other *REE* minerals were not detected probably due to their low abundance. Quantitative estimation of the minerals present in the ore was obtained from the chemical composition of the ore (Table 1) and from the fact that the detection limit for illite-mica with XRD would be 5%.

According to the research results published by Chi *et al.* (2005), the surface hydroxyls of kaolinite react with *REE* ions, so the trivalent rare earth ions behave as divalent or monovalent cations:

$$RE^{3+} + OH^- \rightarrow (RE\mathrm{OH})^{2+} \qquad (2)$$

$$\text{or} \quad RE^{3+} + 2\mathrm{OH}^- \rightarrow (RE\mathrm{OH})^{+} \qquad (3)$$

In this case, kaolinite may adsorb *REE* ions at a ratio of 2:1 or even 1:1, rather than 3:1. Consequently, the cation exchange capacity (CEC) of kaolinite increases with the decrease in the valence state of rare earth cations. Moreover, the CEC of kaolinite is ~0.03–0.05 mmol/g (Chi *et al.*, 2005) and the total CEC of the ore sample would be ~8.855–14.759 mmol/kg. The average molecular weight of *MREE*s is 152, which means that the total CEC of this sample might be ~1.346–2.243 g/kg. The detection limit of *RE*O by ICP-AES of 1.1 g/kg is slightly lower than the average level.

The FTIR spectrum (Fig. 2) shows characteristic absorption bands for the clay minerals present. The large bands observed from 3600 to 4000 cm^{-1} are attributed to the OH-stretching vibration modes, and those at 1600–1660 cm^{-1} to bending vibrations of adsorbed water molecules. The absorption bands at 912 and 778 cm^{-1} are attributed to the stretching vibration of Al–OH and Si–O, respectively. The band at 467 cm^{-1} is assigned to the stretching vibration of Fe–O (Meng *et al.*, 2004). The FTIR results are in accord with the mineralogical composition (Fig. 1).

Leaching experiments

The leaching agent, $MgSO_4$, is less expensive than Na_2SO_4 and K_2SO_4 and it has a higher leaching efficiency because the adsorption capacity of the clay

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TABLE 2. Partitioning of the ion-exchangeable phases, in the Chongzuo rare earth ore (mass fraction %).

Element	La_2O_3	CeO_2	Pr_6O_{11}	Nd_2O_3	Sm_2O_3	Eu_2O_3	Gd_2O_3	Tb_4O_7	Dy_2O_3	Ho_2O_3	Er_2O_3	Tm_2O_3	Yb_2O_3	Lu_2O_3	Y_2O_3
Content (%)	20.55	10.85	5.43	21.28	4.41	0.62	4.41	0.73	3.98	0.80	2.19	0.30	1.84	0.26	22.35

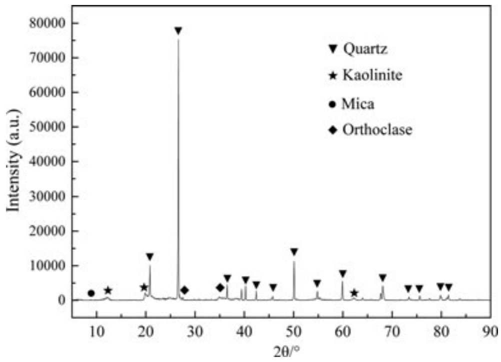

FIG. 1. XRD pattern of the *RE*O sample.

is stronger for bivalent than for monovalent cations (Jiang *et al*., 1992). When comparing $MgSO_4$ with $MgCl_2$ in usual hydrometallurgy systems, the stability constants of sulfates are an order of magnitude greater than those of chlorides, making $MgSO_4$ a good choice for forming *REE* complexes (de Carvalho & Choppin, 1967; Wood, 1990; Millero, 1992).

The original pH of 3% $MgSO_4$ solution was set as the leaching acidity based on the analysis in Fig. 3. The Al^{3+} concentration decreases with increasing pH (Fig. 3). Excessive leaching of Al^{3+} might cause low rare earth yield, low product purity and an increase in difficulty in subsequent processes. The *REE* leaching efficiency is maximum at pH 4.4 (original 3 wt.% $MgSO_4$), declining thereafter. In addition, the pH should be less than the hydrolysis pH of rare earth ions, because otherwise it may result in a lower leaching efficiency of *REE*. The pH value was kept constant by adding dilute H_2SO_4 or NaOH.

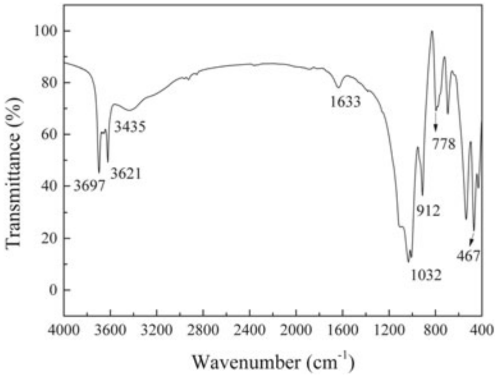

FIG. 2. FTIR spectrum of the rare earth ore sample.

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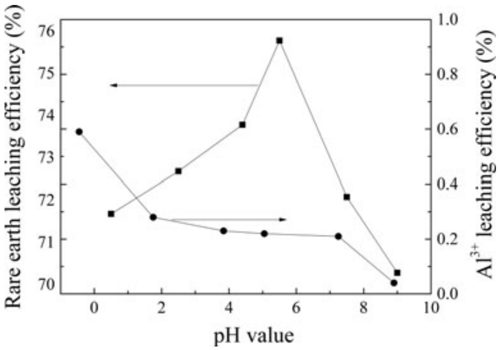

FIG. 3. Effect of the acidity of the leaching agent on rare earth leaching and Al^{3+} concentration. $MgSO_4$ concentration: 3%, L:S ratio = 3:1, room temperature.

The effect of temperature on the leaching efficiency of *REE*s was tested over the range 25–85°C (Fig. 4). The leaching efficiency of *REE*s was virtually constant after 30 min in the temperature range used. Based on these results, room temperature was selected in further experiments.

The effect of stirring speed on the leaching process is shown in Table 3. Stirring did not affect the leaching efficiency, suggesting that the leaching rate is controlled by inner diffusion, which provides the basis of analysis in studying the effect of $MgSO_4$ concentration on leaching (Xiao *et al*. 2015). A stirring speed of 500 rpm was selected as optimal for the leaching experiments.

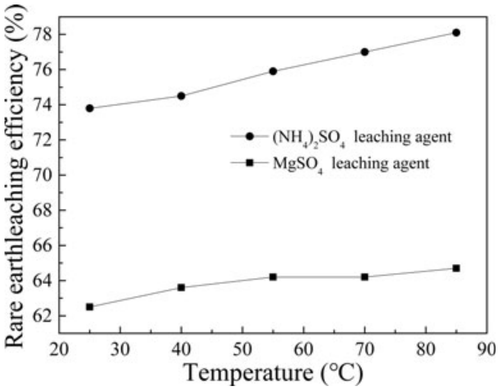

FIG. 4. Effect of temperature on the leaching efficiency using $MgSO_4$ and $(NH_4)_2SO_4$ lixiviants. $MgSO_4$ and $(NH_4)_2SO_4$ concentration: 3 wt.%, L:S ratio = 3:1, pH = 4.4.

Leaching chemistry in the weathered crust elution-deposited rare earth ore

*REE*s exist mainly in the ion-exchangeable phase adsorbed on clay minerals in the weathered crust elution-deposited ore, accounting for 75–95% of total *REE*s, and is the only part that can be extracted at present (Chi *et al*., 2005; Tian *et al*., 2013). Therefore, ion-exchange leaching is the only method to extract *REE*s from this type of ore. The *REE*s are adsorbed on kaolinite ($[Al_2Si_2O_5(OH)_4]\cdot nRE^{3+}$), halloysite ($[Al_2Si_2O_5(OH)_4]\cdot xH_2O\cdot nRE^{3+}$) and muscovite ($[KAl_2\ [AlSi_3O_{10}](OH)_2]\cdot nRE^{3+}$) (Yang & Zhang, 2015). The absorbed *REE*s might be easily and selectively desorbed and substituted on the substrate by the cations of the leaching agent and transferred into the solution as soluble *REE* sulfates (Moldoveanu & Papangelakis, 2012). The leaching reaction of the ion-exchangeable *REE*s in the ore with $MgSO_4$ is as follows:

$$\begin{aligned}&2\mathrm{Clay}-RE(\mathrm{s})+3\mathrm{MgSO_4}(\mathrm{aq})\\&\quad\rightarrow \mathrm{Clay_2}-\mathrm{Mg_3}(\mathrm{s})+RE_2(\mathrm{SO_4})_3(\mathrm{aq})\end{aligned}\qquad(4)$$

where 's' and 'aq' represent solid phase and aqueous phase, respectively, and 'Clay' stands for the clay mineral.

Leaching time, the concentration of leaching agent and L:S are the three main factors affecting the leaching process. These three aspects were studied in detail.

Effect of leaching time on rare earth leaching

The leaching reaction in equation 4 is a typical non-catalytic heterogeneous reaction in solid–liquid systems. To investigate the leaching process with $MgSO_4$ solution, the effect of leaching time on the leaching efficiency was examined with 2.0% or 3.0% (w/v) concentration $MgSO_4$ solution and 5:1 or 3:1 L:S ratio. The *REE* leaching efficiency increased rapidly initially before subsequently decreasing with time, indicating that the rare earth leaching behaviour was controlled by kinetics in the initial stage (Fig. 5). After 7 min, the leaching efficiency increased slowly, suggesting that the leaching process approached equilibrium.

The equilibrium time above is in accordance with results reported in the literature. The adsorption of Nd onto the kaolinite surface at 25°C is relatively fast and remains essentially unchanged after a reaction time of 15 min (Aja, 1998). Leaching of 1% H-montmorillonite for 5 min led to the same retention

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TABLE 3. Effect of stirring speed on rare earth leaching (temperature = 25°C, $MgSO_4$ concentration = 3 wt.%, L:S ratio = 3:1).

	Rare earth leaching efficiency (%)				
Leaching time (min)	100 rpm	300 rpm	500 rpm	700 rpm	900 rpm
15	76.7	73.6	74.7	73.3	74.7
30	76.3	75.5	75.5	75.6	73.2
45	75.6	75.4	74.7	74.5	74.7

of *REE*s as leaching for 3 h (Bruque *et al*., 1980). In view of other experimental factors such as pH or temperature, it was decided that there is no need to study the above conditions because the process kinetics were very fast (Moldoveanu *et al*., 2013). Based on the experimental results, 30 min was considered to be sufficient for reaching maximum extraction of *REE*s.

Effect of concentration of the leaching agent on REE *leaching*

The effect of leaching-agent concentration on the leaching efficiency is illustrated in Fig. 6. The leaching efficiency increased slowly at low concentrations of $MgSO_4$ and tended to be stable at increasing initial concentrations.

As mentioned above, the leaching process was controlled by inner diffusion. According to Fick's law, the leaching rate of inner diffusion control is described by equation 5 (Ma, 2007):

$$\mu = \frac{d\varphi}{dt} = SD_0\frac{d_c}{d_r} = \frac{4\pi r_0^2 D_0}{\delta}(C_l - C_s) \quad (5)$$

where S is the surface area of the ore-sample particle, D_0 (a function of temperature) is the mass transfer diffusivity coefficient of the product layer, C_l and C_s are the concentrations of the leaching agent in the liquid phase and the surface of the ore sample particles, respectively, r_0 is the average initial radius of the ore sample and δ is the thickness of the liquid film, which is a function of the flow rate of the leaching agent and the radius of the ore-sample particle. Clearly, the leaching process might be enhanced by raising the reaction temperature, enlarging the contact area, increasing the concentration of the leaching agent and so on.

Based on equation 5, increasing the leaching agent concentration decreases the resistance of diffusion and improves the leaching reaction rate. When the concentration of the leaching agent is <3%, the

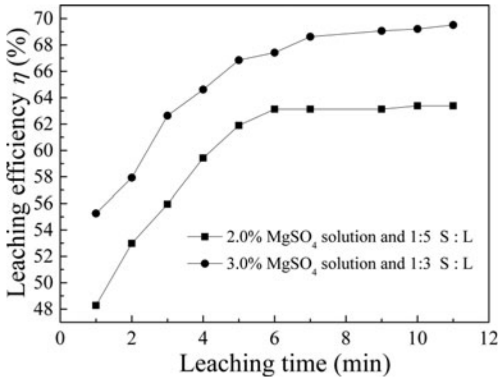

FIG. 5. The effect of leaching time on the leaching efficiency. $MgSO_4$ concentration: 3 wt.%, L:S ratio = 3:1, ω = 500 rpm, pH = 4.4.

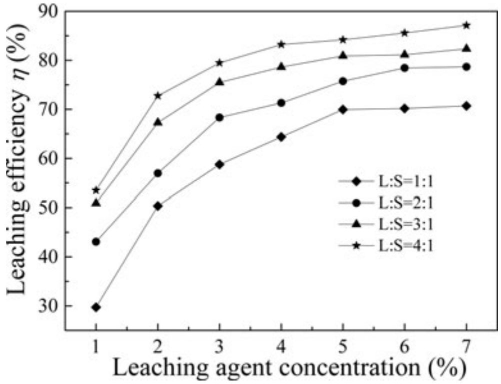

FIG. 6. The effect of concentration of the leaching agent on the leaching efficiency (L:S ratio = 3:1, 30 min leaching time, ω = 500 rpm, pH = 4.4.

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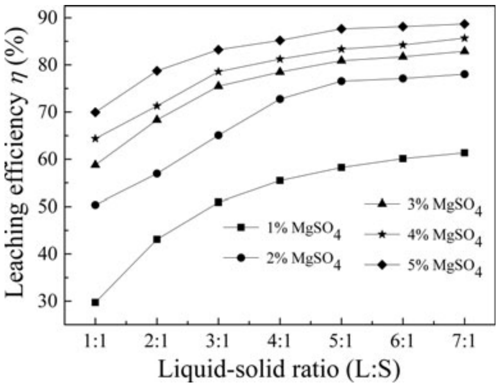

FIG. 7. The effect of L:S ratio on the leaching efficiency. $MgSO_4$ concentration: 3 wt.%, 30 min leaching time, ω = 500 rpm, pH = 4.4.

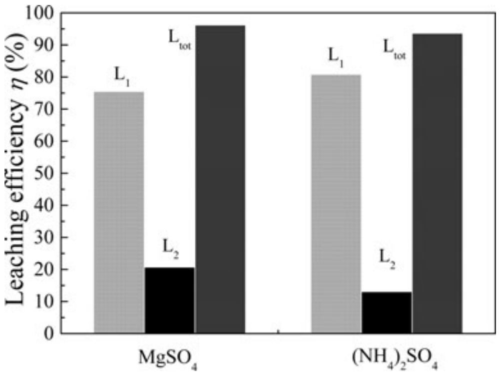

FIG. 8. Influence of two-stage leaching on overall rare earth-extraction levels using different lixiviants.

leaching efficiency is low because of the small concentration gradient. When the concentration of the leaching agent is >3%, the concentration gradient is large enough for efficient diffusion, so the leaching efficiency would remain stable with increasing leaching agent concentration. When the leaching agent concentration is adequate, the effect of the leaching agent concentration on mass transfer is insignificant. This indicates that the leaching reagent concentration should not be too high in real production. Considering the consumption, the concentration of $MgSO_4$ solution should be 3%.

Effect of L:S ratio on rare earth leaching

The L:S affects the probability of contact of the rare earth ion with the leaching agent. These experiments were carried out in 3% $MgSO_4$ solution for 30 min of leaching time. The mass of ore was 100 g and the volume of $MgSO_4$ solution was such to keep an L:S of 1:1–7:1. The results are shown in Fig. 7. The leaching efficiency increases with increasing L:S, reaching a maximum value at L:S = 3:1 and becoming relatively constant at higher L:S values. This behaviour might be explained by the mass transportation equilibrium between RE^{3+} and Mg^{2+}.

In practice, a higher L:S is sometimes used to ensure complete slurry suspension (*i.e.* high solid–liquid contact interface) and efficient agitation. However, a larger electrolyte fraction is not deemed necessary because sufficient stoichiometric excess is delivered by using greater L:S and material consumption. In the present study, however, L:S = 1:1 led to a viscous slurry that was impossible to mix due to the extremely fine nature of the clays used and the general tendency of dry clays to adsorb water and expand. Therefore, L:S = 3:1 was chosen here, and the leaching efficiency exceeded 75% (Fig. 7).

Leaching efficiency

In practical applications, leaching is a continuous process. If the leaching efficiency in stage 1 is unsatisfactory, the leaching operation may be prolonged. Figure 8 shows the detailed two-stage leaching process.

The two-stage leaching process was employed to improve the overall leaching efficiency. The ore sample was initially leached in 3% $MgSO_4$ solution for 30 min to obtain the stage 1 leaching solution (L_1). The residue

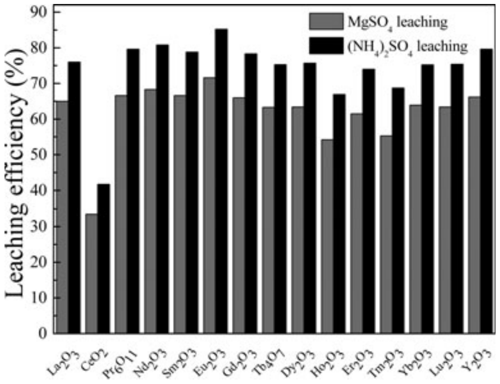

FIG. 9. Individual lanthanide leaching with $MgSO_4$ lixiviants. $MgSO_4$ concentration: 3 wt.%, 30 min leaching time, L:S ratio = 3:1, ω = 500 rpm, pH = 4.4.

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Table 4. Individual rare earth partitioning in leaching solution under various conditions ($MgSO_4$ concentration = 3 wt.%, L:S ratio = 3:1, leaching time = 30 min).

	Mass fraction (%)														
Condition	La_2O_3	CeO_2	Pr_6O_{11}	Nd_2O_3	Sm_2O_3	Eu_2O_3	Gd_2O_3	Tb_4O_7	Dy_2O_3	Ho_2O_3	Er_2O_3	Tm_2O_3	Yb_2O_3	Lu_2O_3	Y_2O_3
Raw ore	20.55	10.85	5.43	21.28	4.41	0.62	4.41	0.73	3.98	0.80	2.19	0.30	1.84	0.26	22.35
Temperature 25°C, pH 4.4	21.85	5.82	5.78	23.24	4.70	0.71	4.51	0.74	4.20	0.81	2.22	0.26	1.81	0.23	23.65
Temperature 40°C, pH 4.4	21.13	5.93	5.78	23.31	4.73	0.74	4.22	0.82	4.22	0.82	2.24	0.26	1.80	0.23	23.69
Temperature 55°C, pH 4.4	21.00	6.05	5.77	23.29	4.75	0.72	4.45	0.74	4.21	0.82	2.24	0.26	1.80	0.23	23.69
Temperature 70°C, pH 4.4	20.90	6.29	5.74	23.27	4.71	0.71	4.45	0.73	4.23	0.81	2.25	0.26	1.80	0.23	23.64
Temperature 85°C, pH 4.4	20.82	6.97	5.74	23.02	4.69	0.71	4.39	0.73	4.17	0.81	2.21	0.26	1.79	0.22	23.48
Temperature 25°C, pH 0.5	20.10	6.01	5.57	22.28	4.58	0.70	4.19	0.71	4.05	0.78	2.14	0.25	1.73	0.21	22.40
Temperature 25°C, pH 2.5	20.87	6.08	5.71	23.24	4.75	0.71	4.47	0.74	4.24	0.82	2.26	0.27	1.81	0.23	23.81
Temperature 25°C, pH 4.4	21.85	5.82	5.78	23.24	4.70	0.71	4.51	0.74	4.20	0.81	2.22	0.26	1.81	0.23	23.65
Temperature 25°C, pH 4.5	21.08	5.82	5.75	23.38	4.76	0.72	4.41	0.74	4.23	0.82	2.25	0.26	1.80	0.23	23.79
Temperature 25°C, pH 7.5	21.27	5.78	5.76	23.34	4.75	0.71	4.45	0.74	4.22	0.81	2.22	0.26	1.80	0.23	23.67
Temperature 25°C, pH 9.0	21.36	5.91	5.80	23.40	4.69	0.71	4.40	0.72	4.13	0.81	2.18	0.25	1.72	0.22	23.70

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from stage 1 was re-leached in fresh 3% $MgSO_4$ solution under the same conditions to produce the stage 2 leaching solution (L_2). As was expected, the overall leaching efficiency of the two-stage leaching ($L_{tot} = L_1 + L_2 = 96.19\%$) was higher than that of one-stage leaching ($L_1 = 75.48\%$). Furthermore, one-stage leaching employing 3% $(NH_4)_2SO_4$ solution achieved 80.8% extraction. After application of a second stage, the leaching efficiency improved to 93.87% (*i.e.* slightly less than the 96.19% achieved by the 3% $MgSO_4$ system).

Effect of partitioning of rare earths on rare earth leaching

The individual *REE* leaching efficiencies using different leaching agents are shown in Fig. 9. Leaching varies from element to element, with Ce presenting the lowest leaching efficiency. This may be attributed to the fact that Ce^{3+} is easily oxidized to Ce^{4+} by atmospheric oxygen (O_2) (electrode potential $\varphi_{Ce3+/Ce4+} = -1.72$ V; Bard *et al.*, 1985). The Ce^{4+} precipitates as CeO_2, inhibiting the extraction of CeO_2 in the leaching liquor.

Table 4 lists the partitioning of *REE*s in the leaching solution at different temperatures and pH values in order to clarify the leaching behaviour of individual *REE*s. The partition in the leaching solution under different conditions barely changes with temperature and pH, which is almost in agreement with the *REE* partitions of the ion-exchangeable phase in the raw ore, except for Ce.

CONCLUSIONS

This study investigates the influence of experimental conditions such as leaching time, lixiviant concentration and L:S on the leaching efficiency of *REE*s using $MgSO_4$ instead of $(NH_4)_2SO_4$ as a lixiviant. It was observed that:

(1) The leaching efficiency for *REE* increases with increasing leaching time, lixiviant concentration and L:S within a certain range of conditions (1–7 min leaching time, lixiviant concentration of 1–3 wt.%, L:S from 1:1 to 3:1).
(2) The leaching efficiency for *REE*s is up to 75.48% for optimal conditions of a leaching time of 30 min, a lixiviant concentration of 3% and an L:S ratio of 3:1. The leaching efficiency of *REE*s reaches 96.19% by extending the leaching stages.
(3) Leaching of individual lanthanides varies from element to element, with Ce presenting the lowest leaching efficiency, and with the partition in the leaching solution being in agreement with that in raw ore, except for Ce.

These results will be useful for finding a novel approach to improving *REE* leaching efficiency and reducing NH_4^+–N pollution towards green chemistry.

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