

## Process optimization of rare earth and aluminum leaching from weathered crust elution-deposited rare earth ore with compound ammonium salts

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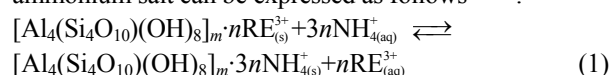
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**Abstract:** In order to intensify the leaching process of rare earth (RE) and reduce the impurities in the leachate, ammonium chloride (NH<sub>4</sub>Cl) and ammonium nitrate (NH<sub>4</sub>NO<sub>3</sub>) were mixed as a compound leaching agent to treat the weathered crust elution-deposited RE ore. Effects of molar ratio of NH<sub>4</sub>Cl and NH<sub>4</sub>NO<sub>3</sub>, ammonium (NH<sub>4</sub><sup>+</sup>) concentration, leaching agent pH and flow rate on the leaching process of RE were studied and evaluated by the chromatographic plate theory. Leaching process of the main impurity aluminum (Al) was also discussed in detail. Results showed that a higher initial ammonium concentration in a certain range could enhance the mass transfer process of RE and Al by providing a driving force to overcome the resistance of diffusion. pH almost had no effects on the mass transfer efficiency of RE and Al in the range of 4 to 8. The relationship between the flow rate and height equivalent to a theoretical plate (HETP) could fit well with the Van Deemter equation, and the flow rate at the lowest HETP was determined. The optimum conditions of column leaching for RE and Al were 1:1 (molar ratio) of NH<sub>4</sub>Cl and NH<sub>4</sub>NO<sub>3</sub>, 0.2 mol/L of ammonium concentration, pH 4–8 of leaching agent and 0.5 mL/min of flow rate. Under this condition, the mass transfer efficiency of RE was improved, but no change was observed for Al compared with the most widely used ammonium sulfate. Moreover, the significant difference value (around 20 mL) of retention volume at the peak concentration between RE and Al provided a possibility for their separation. It suggested the potential application of the novel compound leaching agent (NH<sub>4</sub>Cl/NH<sub>4</sub>NO<sub>3</sub>). It was found that the relative concentration of RE in the leachate could be easily obtained by monitoring the pH of leachate.

**Keywords:** weathered crust elution-deposited rare earth ore; aluminum; leaching process; mass transfer; ammonium chloride; ammonium nitrate

With the rapid development of advanced technologies, there is an ever-increasing demand for rare earth (RE) elements in the international markets, especially for the mid-heavy rare earth<sup>[1,2]</sup>. The weathered crust elution-deposited RE ores, also named ion-adsorption RE ore, is the main source of mid-heavy RE in the world<sup>[3]</sup>. In a warm and humid climate, original rocks contained RE are weathered and converted to clay minerals by biological, chemical and physical effects. During this weathering process, RE minerals are dissociated to be hydrated or hydroxyl hydrated RE ions and further adsorbed by the clay minerals with the migration of natural water<sup>[4,5]</sup>. Due to the metallogenic climatic condition, the weathered crust elution-deposited RE ores are mainly distributed in southern China, such as Jiangxi, Guangdong, Fujian, Hunan, Yunnan, Guangxi and Zhejiang<sup>[6]</sup>. The specific occurrence state of RE, ion-exchangeable state, decides its unique beneficiation technology<sup>[7]</sup>. RE can be easily exchanged from the weathered crust elution-deposited RE ore by monovalent cations and transferred into solution as soluble RE sulfates, chlorides, or

nitrate<sup>[8,9]</sup>. The main clay minerals in this RE ore is aluminosilicate, which can be described as [Al<sub>4</sub>(Si<sub>4</sub>O<sub>10</sub>)(OH)<sub>8</sub>]<sub>m</sub>. The ion-exchange reaction with ammonium salt can be expressed as follows<sup>[10,11]</sup>:



where *s* and *aq* represent solid phase and aqueous phase, respectively.

It shows that the clay minerals adsorbing RE can be seen as a natural ion exchange resin. The leaching process can be described as a chromatographic column elution process, in which the RE ore is a stationary phase and the leaching agent is a mobile phase<sup>[12]</sup>. When the leaching agent flows through the RE ore, the cations (NH<sub>4</sub><sup>+</sup>) in the leaching agent diffuse from solution to the ore particles, and then the RE ions adsorbed on the ore particles are substituted and transferred into the solution<sup>[13]</sup>. The ion-exchange process between the RE and NH<sub>4</sub><sup>+</sup> is a typical mass transfer process, which can be evaluated by chromatographic plate theory<sup>[14]</sup>.

The study on the intensification of RE leaching proc-

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ess can not only increase the leaching efficiency of RE and reduce the consumption of leaching agent, but also improve the production efficiency and shorten production cycle<sup>[13,14]</sup>. During the past years, much effort has been engaged in the development of the leaching techniques<sup>[15]</sup> and the improvement of the RE leaching efficiency<sup>[16]</sup>. However, limited investigations on the intensification of RE leaching process are reported. Although Tian et al.<sup>[17]</sup> introduced sesbania gum as a filter-aid reagent into ammonium sulfate solution and Qiu et al.<sup>[18]</sup> applied magnetic field to enhance RE leaching process, the high cost limited the application in the actual production.

In this work, a new leaching agent was developed to optimize the leaching process of RE, which demonstrated potential possibility to replace the most widely used leaching agent ammonium sulfate<sup>[19]</sup>. Previous study revealed that the exchangeability and permeability of ammonium chloride (NH<sub>4</sub>Cl) and ammonium nitrate (NH<sub>4</sub>NO<sub>3</sub>) both surpassed ammonium sulfate (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub><sup>[20]</sup>. However, the practical application of NH<sub>4</sub>Cl and NH<sub>4</sub>NO<sub>3</sub> were limited by the high content of impurities in the leachate, which would increase the cost of impurities removal, decrease the purity of RE product and even destroy the crystal forming of carbonate RE precipitation<sup>[21,22]</sup>. Our latest research found that the mixture of NH<sub>4</sub>Cl and NH<sub>4</sub>NO<sub>3</sub> could be used as a compound leaching agent, which not only could reduce obviously the leaching of impurities, but also could keep a high leaching efficiency of RE. The effects of molar ratio of NH<sub>4</sub>Cl and NH<sub>4</sub>NO<sub>3</sub>, ammonium (NH<sub>4</sub><sup>+</sup>) concentration, leaching agent pH and flow rate on the mass transfer process of RE were studied and evaluated by chromatographic plate theory. Aluminum (Al) as the main impurity ion in the leachate was also discussed to reveal the leaching performance of impurities.

## 1 Experimental

### 1.1 Materials and characterization

The experimental RE ores sample was collected from Dingnan (DN) County in Jiangxi Province of southern China. The main chemical composition of the RE ore was analyzed by X-ray fluorescence (Axios advanced, Panalytical B.V.) and the result is listed in Table 1. It was shown that the RE ore contained 0.10 wt.% RE and 19.53 wt.% Al. Not all the RE and Al, but the exchangeable state RE and Al can be exchanged into solution by the cations. The contents of the exchangeable state RE and Al in the RE ore were 0.09 wt.% and 0.015 wt.%, respectively. The partitioning of the ion-exchangeable state RE determined by inductively coupled plasma mass spectrometry (ICP-MS, Agilent 7700x, Agilent Technologies Inc.) are shown in Fig. 1. 52.06 wt.% of RE was the middle and heavy RE, implying the tremendous

**Table 1** Main chemical composition of the RE ores (wt.%)

Component	REO	Al <sub>2</sub> O <sub>3</sub>	MnO <sub>2</sub>	ZnO	CaO	MgO	K <sub>2</sub> O	SiO <sub>2</sub>	P <sub>2</sub> O <sub>5</sub>
Content	0.10	19.53	0.01	0.01	0.02	0.52	3.54	58.09	0.20
Component	SO <sub>3</sub>	TiO <sub>2</sub>	Fe <sub>2</sub> O <sub>3</sub>	Rb <sub>2</sub> O	SrO	ZrO <sub>2</sub>	BaO	Loss	
Content	0.04	1.40	8.07	0.02	0.01	0.02	0.04	8.36	

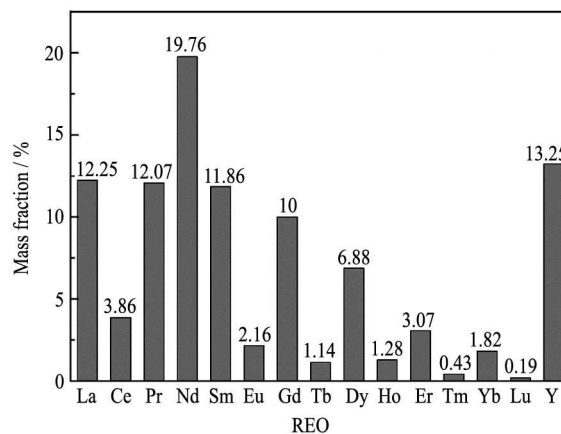


Fig. 1 Partitioning of the ion-exchangeable RE in the RE ores

commercial value.

### 1.2 Column leaching experiments

The experiments were conducted at ambient temperature (25 °C) in a glass column with 45 mm inner diameter, which can be seen as a chromatographic column. 250 g of dried RE ore sample was uniformly packed in the glass column and the packed ore height was measured. The schematic diagram of experimental apparatus is shown in Fig. 2. The RE ore sample in the glass column was eluted by the leaching agent solution with a certain concentration and pH at a desired flow rate. Leachate was collected from the bottom of the leaching column and the concentrations of RE and Al were analyzed by

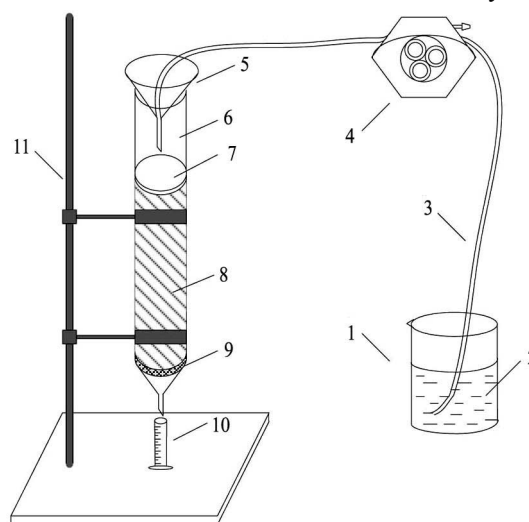


Fig. 2 Schematic diagram of experimental apparatus

1–Beaker; 2–Leaching agent; 3–Silicone tube; 4–Peristaltic pump; 5–Funnel; 6–Glass column; 7–Filter paper; 8–RE ore sample; 9–Sand core filter plate; 10–Precision measuring cylinder; 11–Iron support

titration methods. All the column leaching experiments were repeated more than three times to obtain credible leaching curves.

### 1.3 Analytical methods

The total content of RE in the leachate was determined by ethylene diamine tetraacetic acid (EDTA) titration using xylenol orange as indicator and hexamethylene tetramine as buffer. After that, excess EDTA solution was added into the studied liquid sample and placed in a water bath at 90 °C for 10 min. Then the content of Al was analyzed by back titration using a known concentration of zinc solution. All chemicals in this study were purchased from Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China) with analytical grade.

## 2 Results and discussion

### 2.1 Leaching process of RE and Al with different leaching agents

Three single ammonium salts ((NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub>, NH<sub>4</sub>Cl and NH<sub>4</sub>NO<sub>3</sub>) and a compound ammonium salts (NH<sub>4</sub>Cl and NH<sub>4</sub>NO<sub>3</sub> with the molar ratio of 1:1) were used as leaching agent to column leaching the RE ore under the condition of 0.2 mol/L of ammonium concentration, 0.5 mL/min of flow rate and pH 5.5–6.0 of leaching agent. Fig. 3 depicts the leaching process of RE and Al with different leaching agents. It was found that the concentration of RE and Al rapidly increased to maximum, and then decreased sharply to zero. When NH<sub>4</sub>Cl/NH<sub>4</sub>NO<sub>3</sub> was used as leaching agent, the leaching curve of RE showed slightly lower peak concentration (4.30 g/L) and slower retention volume at the peak concentration (37.52 mL) than that with NH<sub>4</sub>NO<sub>3</sub> (4.75 g/L, 29.29 mL); while the peak concentration of 0.51 g/L and retention volume of 57.39 mL were obtained for Al leaching, approaching to the results with (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub> which had the lowest peak concentration (0.51 g/L) and the largest retention volume

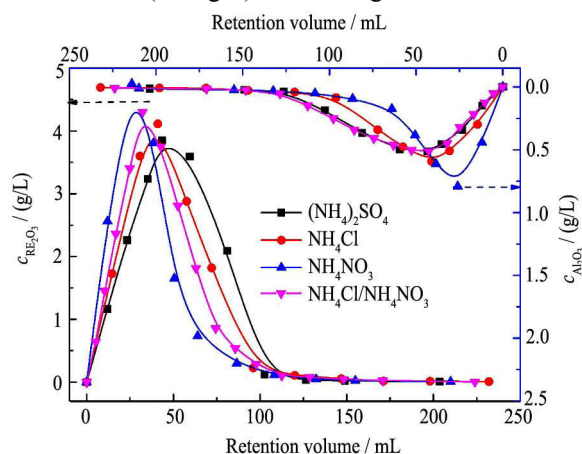


Fig. 3 Leaching curves of RE and Al with different leaching agents (250 g of RE ore,  $c_{\text{NH}_4^+} = 0.2$  mol/L,  $\mu = 0.5$  mL/min,  $T = 25$  °C, at initial pH 5.5–6.0)

(55.83 mL). Furthermore, the difference value of retention volume between RE and Al (19.87 mL) was far larger than the other studied leaching agents (1.11–4.91 mL), which was of benefit to the RE and Al separation. Therefore, NH<sub>4</sub>Cl/NH<sub>4</sub>NO<sub>3</sub> can improve the leaching process of RE and the separation of RE and Al.

The leaching curves were all similar to the chromatographic elution curves, which indicated that the mass transfer process of RE and Al can be evaluated by chromatographic plate theory<sup>[13]</sup>. The height equivalent to a theoretical plate (HETP) and plate number ( $n$ ) can be calculated by the following equations<sup>[23]</sup>:

$$\text{HETP} = \frac{L}{n} \quad (2)$$

$$n = 8 \ln 2 \times \left( \frac{V_R}{\Delta V_{1/2}^2} \right) \quad (3)$$

where HETP (mm) is the height equivalent to a theoretical plate;  $L$  (mm) is the packed ore length;  $n$  is the true plate number;  $V_R$  (mL) is the retention volume, which represents the volume of the leachate collected from the bottom of the leaching column;  $V_{1/2}$  (mL) is the peak width at half height.

The calculated HETP of RE and Al with different leaching agents are listed in Table 2. It was shown that HETP of RE decreased in the order of (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub> > NH<sub>4</sub>Cl > NH<sub>4</sub>NO<sub>3</sub> ≈ NH<sub>4</sub>Cl/NH<sub>4</sub>NO<sub>3</sub>, while HETP of Al increased in the order of NH<sub>4</sub>NO<sub>3</sub> < NH<sub>4</sub>Cl < (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub> ≈ NH<sub>4</sub>Cl/NH<sub>4</sub>NO<sub>3</sub>, which further indicated that NH<sub>4</sub>Cl/NH<sub>4</sub>NO<sub>3</sub> may work as an optimal leaching agent for a high mass transfer efficiency of RE and low mass transfer efficiency of Al.

### 2.2 Effects of molar ratio on leaching process of RE and Al

Effects of molar ratio of NH<sub>4</sub>Cl and NH<sub>4</sub>NO<sub>3</sub> on the leaching process of RE and Al are shown in Fig. 4. It was found that for RE, the highest peak concentration and the narrowest half peak width were obtained at the molar ratios of 3:7 and 1:1, while for Al, the lowest peak concentration and the broadest half peak width were obtained at molar ratio of 1:1. 1:1 may be the best molar ratio of NH<sub>4</sub>Cl and NH<sub>4</sub>NO<sub>3</sub>, since it can make not only a higher mass transfer efficiency of RE leaching, but also a

Table 2 Calculated leach HETP of RE and Al with different leaching agents

Leaching agents	Packed ore length/mm	Retention volume/mL		Half peak width/mL		Plate number		HETP/mm	
		RE	Al	RE	Al	RE	Al	RE	Al
(NH <sub>4</sub> ) <sub>2</sub> SO <sub>4</sub>	126	50.92	55.83	58.29	68.81	4.23	3.65	29.78	34.52
NH <sub>4</sub> Cl	123	42.78	45.24	48.58	54.91	4.30	3.76	28.60	32.68
NH <sub>4</sub> NO <sub>3</sub>	126	29.29	30.40	32.79	35.75	4.42	4.01	28.48	31.42
Cl/NO <sub>3</sub>	125	37.52	57.39	42.18	71.12	4.39	3.61	28.49	34.62

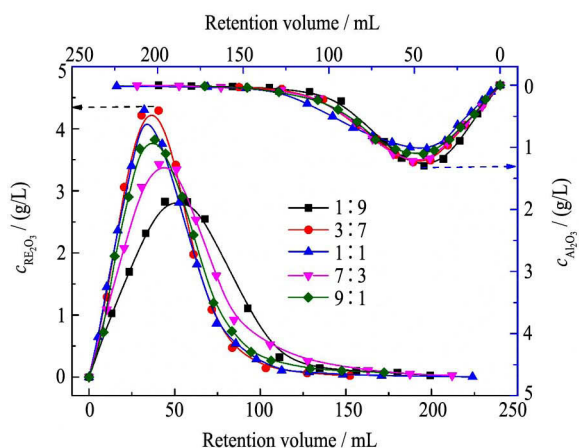


Fig. 4 Leaching curves of RE and Al under different molar ratios (250 g of RE ore,  $c_{\text{NH}_4^+} = 0.2 \text{ mol/L}$ ,  $\mu = 0.5 \text{ mL/min}$ ,  $T = 25 \text{ }^\circ\text{C}$ , at initial pH 5.5–6.0)

lower mass transfer efficiency of Al leaching.

The leach HETP of RE and Al under different molar ratios were calculated and are listed in Table 3. It was clear that the molar ratios of 3:7, 1:1 and 9:1 led to the lowest HETP of RE, while only the molar ratio of 1:1 led to the highest HETP of Al. This also further demonstrated that the high mass transfer efficiency of RE and low mass transfer efficiency of Al were achieved at molar ratio of 1:1. In addition, at 1:1 (molar ratio) of  $\text{NH}_4\text{Cl}$  and  $\text{NH}_4\text{NO}_3$ , the difference value of retention volume between RE and Al was the largest. It could provide a possible window for RE and Al separation. Thus, the optimal molar ratio of  $\text{NH}_4\text{Cl}$  and  $\text{NH}_4\text{NO}_3$  was 1:1.

### 2.3 Effects of ammonium concentration on leaching process of RE and Al

As shown in Eq. (1), ammonium ion plays a key role in the RE leaching. The effects of ammonium concentration on the leaching process of RE and Al are presented in Fig. 5. It was shown that the elution profile of both RE and Al became narrower and the peak concentration became higher with the increase of ammonium concentration, and then kept unchanged when the concentration reached to 0.4 mol/L. The mass transfer process of RE and Al can be enhanced by improving the initial ammonium concentration in a certain range. HETP and correlation parameters of RE and Al leaching under

Table 3 Calculated leach HETP of RE and Al under different molar ratios

Molar ratio	Packed ore length/mm	Retention volume/mL		Half peak width/mL		Plate number		HETP/mm	
		RE	Al	RE	Al	RE	Al	RE	Al
1:9	125	53.30	46.73	62.50	54.12	4.03	4.13	31.00	30.24
3:7	127	38.05	51.44	42.17	60.32	4.51	4.03	28.13	31.49
1:1	125	37.52	57.39	42.18	71.12	4.39	3.61	28.49	34.62
7:3	127	45.19	52.10	51.87	60.62	4.21	4.10	30.17	31.01
9:1	125	40.10	52.49	45.23	63.01	4.36	3.85	28.68	32.48

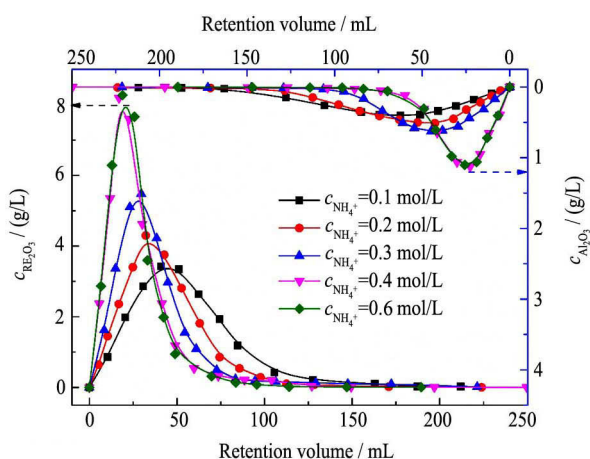


Fig. 5 Leaching curves of RE and Al under different ammonium concentrations (250 g of RE ore,  $c_{\text{NH}_4\text{Cl}}/c_{\text{NH}_4\text{NO}_3} = 1:1$ ,  $\mu = 0.5 \text{ mL/min}$ ,  $T = 25 \text{ }^\circ\text{C}$ , at initial pH 5.5–6.0)

different ammonium concentrations are listed in Table 4 to further expound the results. It could be seen that the retention volume at the peak concentration and the half peak width both decreased with the increase of ammonium concentration from 0.07 to 0.4 mol/L, and no obvious change was observed with the continued increase. Thus, the lowest HETP of RE and Al leaching was obtained at the ammonium concentration of 0.4 mol/L. HETP almost kept a constant value above 0.4 mol/L. The results above indicated that a higher ammonium concentration could have a positive effect on the mass transfer efficiency of RE and Al leaching in a certain range. This could be attributed to the higher initial concentration providing an important driving force to overcome the mass transfer resistance of ammonium diffusion from solution to ore particles<sup>[24]</sup>. The leaching rates of  $\text{RE}^{3+}$  and  $\text{Al}^{3+}$  were mainly determined by their diffusion velocities. HETP decreased with the increase of ammonium concentration. However, after the initial ammonium concentration exceeded 0.4 mol/L, the leaching rates of  $\text{RE}^{3+}$  and  $\text{Al}^{3+}$  were mainly controlled by solid-film diffusion. The mass transfer efficiency of RE and Al leaching almost remained stable with the continued concentration increasing<sup>[14]</sup>.

From Fig. 5 and Table 4, it could also be observed that the mass transfer efficiency of Al was obviously lower than that of RE due to the lower peak concentration, broader half peak width, larger retention volume and higher HETP. With the ammonium concentration increasing to 0.4 mol/L, the difference value of retention volume between RE and Al reduced visibly from 21.55 to 5.85 mL, and the difference in the half peak width decreased from 31.99 to 9.30 mL. These results indicated that the leaching of Al lagged behind the leaching of RE, and the lag was alleviated with the increasing ammonium concentration. Thus, high ammonium concentration produced negative effect for the leaching separation of RE and Al. In addition, considering that an excess initial

**Table 4** Calculated leach HETP of RE and Al under different ammonium concentrations

$C_{\text{NH}_4^+}$ / (mol/L)	Packed ore length/mm	Retention		Half peak		Plate		HETP/ mm	
		volume/mL		width/mL		number			
		RE	Al	RE	Al	RE	Al	RE	Al
0.1	127	47.57	69.12	54.73	86.72	4.19	3.52	30.32	36.05
0.2	125	37.52	57.39	42.18	71.12	4.39	3.61	28.49	34.62
0.3	124	29.71	44.83	32.49	54.34	4.64	3.77	26.74	32.86
0.4	125	20.69	26.54	22.16	31.46	4.83	3.95	25.86	31.67
0.6	125	21.16	26.48	22.58	31.33	4.87	3.96	25.67	31.56

concentration of leaching agent will not only increase the production cost and the content of impurities, but also aggravate the environmental burden<sup>[3,25]</sup>. The optimal ammonium concentration of  $\text{NH}_4\text{Cl}/\text{NH}_4\text{NO}_3$  was chosen to be 0.2 mol/L.

## 2.4 Effects of pH on leaching process of RE and Al

Fig. 6 shows the effects of pH on leaching process of RE and Al. It was found that there was almost no obvious variation on the leaching curves of RE and Al in a wide pH range from 4 to 8. The HETP of RE and Al at different pH was calculated and is shown in Table 5. The initial pH of leaching agents almost had no effects on the leach HETP of RE and Al in a pH range of 4–8. The initial pH of  $\text{NH}_4\text{Cl}/\text{NH}_4\text{NO}_3$  solution was about 5.5–6.0, thus the pH regulation can be omitted in the industrial production.

It also can be seen in Fig. 6 that pH of leachate decreased with the increase of concentration and retention volume of RE, and then increased slowly to a con-

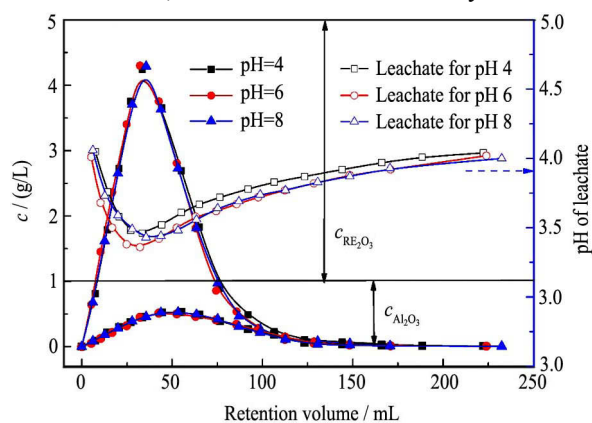


Fig. 6 Leaching curves of RE and Al at different pH (250 g of RE ore,  $c_{\text{NH}_4\text{Cl}}/c_{\text{NH}_4\text{NO}_3} = 1:1$ ,  $c_{\text{NH}_4^+} = 0.2$  mol/L,  $\mu = 0.5$  mL/min,  $T = 25$  °C)

**Table 5** Calculated leach HETP of RE and Al at different pH

pH	Packed ore length/mm	Retention		Half peak		Plate		HETP/ mm	
		volume/mL		width/mL		number			
		RE	Al	RE	Al	RE	Al	RE	Al
4	126	38.67	55.30	43.23	68.58	4.44	3.61	28.40	34.95
6	125	37.52	57.39	42.18	71.12	4.39	3.61	28.49	34.62
8	127	38.22	55.52	42.50	68.25	4.48	3.67	28.32	34.61

stant value with the concentration of RE decreasing sharply to zero. There was a minimum pH of leachate in the leaching process that corresponded to the peak concentration of RE. The phenomenon indicated that the relative concentration of RE in the leachate can be easily obtained by monitoring the pH of leachate in the continuous leaching operation of RE. In addition, the final pH of leachate was all stabilized at around 4.0, suggesting that the RE ore had a certain buffer ability to keep the leachate acidity. The broken bond on the edge of structural units of clay minerals in RE ores can accept or liberate hydrogen ion at different pH values<sup>[26]</sup>.

## 2.5 Effects of flow rate on leaching process of RE and Al

The flow rate of leaching agent as a main factor influencing the mass transfer efficiency<sup>[17]</sup> is shown in Fig. 7. It was shown that for both RE and Al, the peak concentration increased and the retention volume at the peak concentration reduced with the flow rate increasing to 0.5 mL/min, and then the peak concentration decreased and the retention volume increased with the flow rate continuing to increase. A fast flow rate of leaching agent can prevent the reabsorption of RE onto the clay minerals by taking it away timely. The mass transfer efficiency can be enhanced by a high flow rate. However, after the flow rate exceeded 0.5 mL/min, the mass transfer efficiency decreased obviously. It can be explained that too fast flow rate led to the insufficient contact of leaching agent and ore particles, and the ion exchange reaction of  $\text{NH}_4^+$  and RE could not proceed completely. The optimal mass transfer efficiency of RE and Al in the leaching process was obtained at the flow rate of 0.5 mL/min. For better expounding the result, the leaching curves of RE and Al under different flow rates were analyzed by chromatographic plate theory. The correlation parameters are listed in Table 6 and leach HETP curves of RE and Al are shown in Fig. 8. It can be found that HETP of

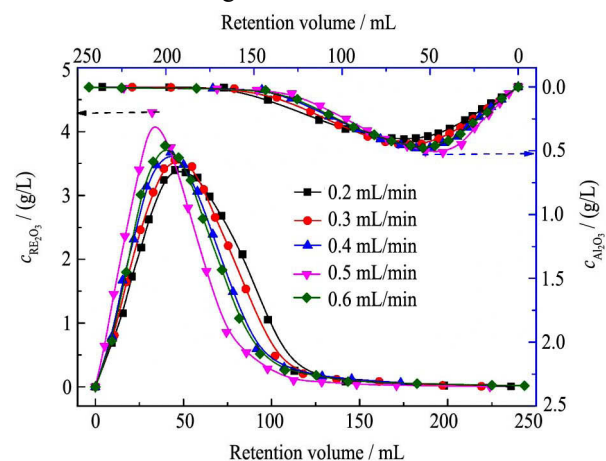


Fig. 7 Leaching curves of RE and Al under different flow rates (250 g of RE ore,  $c_{\text{NH}_4\text{Cl}}/c_{\text{NH}_4\text{NO}_3} = 1:1$ ,  $c_{\text{NH}_4^+} = 0.2$  mol/L,  $T = 25$  °C, at initial pH 5.5–6.0)

**Table 6** Calculated leach HETP of RE and Al under different flow rates

Flow rates/ (mL/min)	Packed ore length/ mm	Retention volume/mL		Half peak width/mL		Plate number		HETP/mm	
		RE	Al	RE	Al	RE	Al	RE	Al
0.2	126	53.38	71.27	63.96	92.43	3.86	3.30	32.62	38.22
0.3	127	49.69	67.13	58.05	85.46	4.06	3.42	31.26	37.12
0.4	125	45.12	62.41	51.93	78.82	4.19	3.48	29.86	35.96
0.5	125	37.52	57.39	42.18	71.12	4.39	3.61	28.49	34.62
0.6	127	43.97	61.54	49.94	77.39	4.30	3.51	29.54	36.22

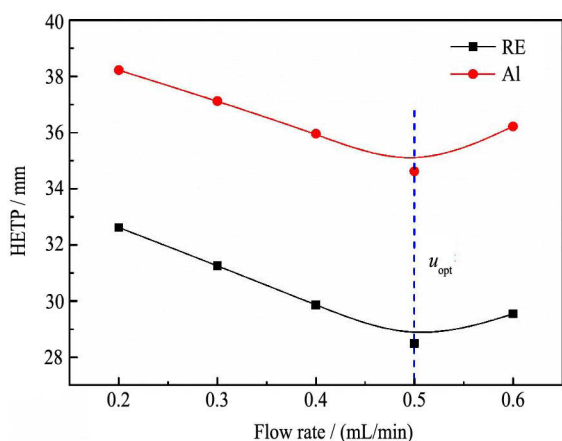


Fig. 8 Leach HETP curves of RE and Al under different flow rates (250 g of RE ore,  $c_{\text{NH}_4\text{Cl}}/c_{\text{NH}_4\text{NO}_3}=1:1$ ,  $c_{\text{NH}_4^+}=0.2$  mol/L,  $T=25$  °C, at initial pH 5.5–6.0)

RE and Al decreased firstly and then increased with the increase of the flow rate, and minimum was obtained at a flow rate of 0.5 mL/min. This can be explained by Van Deemter equation (Eq. (4))<sup>[27]</sup>.

$$\text{HETP} = A + \frac{B}{u} + Cu \quad (4)$$

where  $A$  is the multiple paths diffusion coefficient or eddy diffusion coefficient;  $B$  is the longitudinal diffusion coefficient;  $C$  is the mass transfer impedance coefficient;  $u$  is the flow rate of leaching agent. As seen in Eq. (4), there is an optimal flow rate of leaching agent ( $u_{\text{opt}}$ ) for a lowest HETP. When the flow rate was less than 0.5 mL/min ( $u < u_{\text{opt}}$ ),  $B/u$  played a leading role in HETP and  $Cu$  can be negligible. The mass transfer efficiency of RE and Al leaching was controlled by the longitudinal diffusion velocity ( $B/u$ ). HETP decreased with the increase of flow rate<sup>[14]</sup>. When the flow rate was larger than 0.5 mL/min ( $u > u_{\text{opt}}$ ),  $Cu$  played a leading role in HETP and  $B/u$  can be negligible. The mass transfer efficiency mainly depends on the diffusion rate ( $Cu$ ) of the solute between the leaching agent and the ore particle<sup>[16]</sup>. HETP increases with the increase of the flow rate. Therefore, 0.5 mL/min was chosen as the best flow rate of leaching agent for the highest mass transfer efficiency of RE.

### 3 Conclusions

For ammonium chloride and ammonium nitrate as a compound leaching agent, the optimal condition of column leaching was found to be 1:1 (molar ratio) of  $\text{NH}_4\text{Cl}$  and  $\text{NH}_4\text{NO}_3$ , 0.2 mol/L of ammonium concentration, pH 4–8 of the leaching agent and 0.5 mL/min of flow rate. High ammonium concentration could improve the mass transfer efficiency by reducing the resistance of diffusion, but excessive concentration only increased the cost and aggravated the environmental burden. pH almost had no effects on HETP of RE and Al leaching in the range of 4–8. HETP decreased firstly and then increased with the increase of flow rate. There was an optimal flow rate for the highest mass transfer efficiency.

For the novel compound leaching agent ( $\text{NH}_4\text{Cl}/\text{NH}_4\text{NO}_3$ ), the mass transfer efficiency of RE was only slightly lower than that with  $\text{NH}_4\text{NO}_3$  (owing to the lowest HETP among  $(\text{NH}_4)_2\text{SO}_4$ ,  $\text{NH}_4\text{Cl}$  and  $\text{NH}_4\text{NO}_3$ ), and the mass transfer efficiency of Al got close to  $(\text{NH}_4)_2\text{SO}_4$  (owing to the highest HETP). The retention volume of RE at the peak concentration was smaller than that of Al, providing a possibility for the separation of RE and Al. This work indicated the promising application of mixture leaching agent of  $\text{NH}_4\text{Cl}/\text{NH}_4\text{NO}_3$  in the actual exploitation of weathered crust elution-deposited RE ore.

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