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Application of chromatographic plate theory on the weathered crust elution-deposited rare earth ore with carboxylate

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Abstract: To improve the leaching process of rare earth and reduce the impurities in the leachate, the carboxylate ammonium, such as ammonium acetate, ammonium citrate and ammonium tartrate, were selected as lixiviant to compare the effects of concentration, flow rate, pH and temperature on leaching mass process of rare earth and aluminum. Meanwhile, the leaching behaviors of rare earth and aluminum leached by three kinds of carboxylate ammonium were analyzed by chromatographic plate theory. The relationship between the flow rate and height equivalent (HETP) could fit well with the Van Deemter equation and there was an optimal flow rate (u_{opt}) for the leaching of the rare earth and aluminum. Besides, the conditions of carboxylate ammonium lixiviant were optimized. The optimum concentrations of ammonium acetate, ammonium tartrate and ammonium citrate were 15 g/L, 25 g/L and 5 g/L respectively, the leaching flow rate was 0.50 mL/min, the pH value was approximatively 7.00 and the leaching temperature was 293 K to 303 K. At these conditions, the mass transfer efficiencies of three ammonium carboxylates for rare earth and aluminum was in the order of ammonium acetate > ammonium tartrate > ammonium citrate. Moreover, the ammonium acetate could commendably inhibit aluminum ions entering the lixivium.

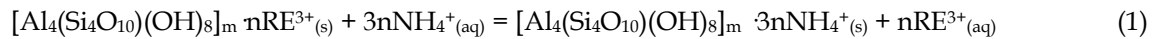
Keywords: weathered crust elution-deposited rare earth ore, carboxylate ammonium, mass transfer, theory plate, rare earth

1. Introduction

With the speedy development of science and technology, the demand for rare earth is expanding day by day. The REEs are significant raw materials which applied in renewable energy, advanced electronics, telemedicine, superconductors, aircraft, automobiles and petro-refinery catalysts, and many other high-tech fields because its special properties (Liyas, 2020, 2021). Weathered crust elution-deposited rare earth ores, also known as ion adsorption rare earth ores, are rich in medium and heavy rare earth elements which were first discovered and used industrially in China (Chi, 2012; Zhang, 2018). Due to the large content of middle and heavy rare earth in the weathered c crust elution-deposited rare earth ores, it is meaningful to take the mining process in the rare earth ores.

Under the condition of warm and humid environment, protolith which contains rare earth elements are weathered and converted into clay minerals through biological, chemical and physical processes (Gupta and Saha, 2001; Chi and Wang, 1993). Rare earth elements are mainly adsorbed on clay minerals by hydrated or hydroxyl hydrated ions (Chi, 2005). Therefore, the rare earth ions will migrate with the groundwater during the weathering process (Tian, 2010). At present, ammonium sulphate is used as the main leaching agent to recover rare earth in the in-situ leaching process. The ion-exchange process between the rare earth and ammonium ions is a typical mass transfer process, which can be evaluated

by chromatographic plate theory to further strengthen the leaching process (Tian, 2010; Bartlett, 1992). The ion exchange reaction with ammonium salts is written as (Zhang, 2016; Liu, 2013):



where: s and aq are solid phase and aqueous phase respectively.

However, there are many drawbacks when using ammonium sulfate as lixiviant (Zhang, 2018). The high concentration of ammonium sulfate would result in ammonia nitrogen pollution or soil salinization (He, 2016). The lower seepage velocity would result in long leaching process and more demand for lixiviant (He, 2017). Meanwhile, the high concentration of impurities would be leached with rare earth into the leachate. In order to improve the leaching process of rare earth, an amount of works which focus on the leaching agents were investigated. He et al. found that the optimum conditions of column leaching for rare earth and aluminium were 1:1 (molar ratio) of ammonium chloride and ammonium nitrate, 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 aluminium compared with the most widely used ammonium sulfate (He, 2016). At present, some magnesium salts lixiviant had been used in industry under some special condition (Xiao, 2015). Moreover, Chen et al. found the optimum condition for rare earth and aluminium were 0.4 mL/min of flow rate and 0.2 mol/L of magnesium ion concentration. Under this condition, the mass transfer efficiency of rare earth and aluminium with three kinds of magnesium salts follow the order of $\text{Mg}(\text{NO}_3)_2 > \text{MgCl}_2 > \text{MgSO}_4$ (Chen, 2018). Li et al. found that the 3 g/L ammonium citrate could promote the exchange of rare earth ion, improve the rare earth recovery, reduce the amount of ammonium salt, and reduce the pollution of ammonia nitrogen pollution (Li, 2015). Zhang et al. found the ammonium acetate was beneficial to increase seepage flow and shorten seepage path of lixiviant while the ammonium acetate concentration was 1.00 %, leaching temperature was 298K, and the value of pH was 7 (Zhang, 2019). On the one hand, the ammonium carboxylate salts can improve the leaching agent permeability in the ore body to increase leaching efficiency of rare earth and shorten the period of leaching process. On the other hand, the middle and heavy rare earth element can be strengthened leached by ammonium carboxylate salts. Put it all together, many investigators have researched in this field, however, the research on the mass transfer process of weathered crust elution-deposited rare earth with various carboxylate ammonium still needs to be strengthened and consummated.

In this paper, the inorganic ammonium salts are replaced by ammonium carboxylate salts to explore the mass transfer process of weathered crust elution-deposited rare earth with three kind of carboxylate ammonium. Meanwhile, the leaching mass transfer process can be evaluated by chromatographic plate theory (Tian, 2010). It is beneficial to investigate the leaching mass transfer of rare earth and aluminum. Therefore, the ammonium acetate, ammonium citrate and ammonium tartrate were used as lixiviant to discuss the effects of the ammonium ions concentration, leaching flow rate, lixiviant pH and temperature. According to the above studies, it would provide theoretical guidance and technical support for the selection and application of carboxylate ammonium salts in the industrial production.

2. Experimental

2.1. Materials and characterization

Weathered crust elution-deposited rare earth ore samples were collected in this study from Myanmar. The chemical composition of the rare earth ore was analyzed by X-ray fluorescence (Axios max). The results are shown in Table 1.

The results showed that the rare earth samples main contained 48.10 % SiO_2 and 29.64% Al_2O_3 . The amount of REO was 0.11 %, The rare earth partitioning of the ion-exchangeable rare earth ores has been determined by ICP-MS (IRIS Intrepid) and the results are shown in Fig. 1.

Table 1. Main chemical composition of the rare earth ores (wt %)

Component	REO	SiO_2	Al_2O_3	Fe_2O_3	K_2O	Na_2O	MgO	TiO_2	MnO	ZrO_2	Loss
Content	0.11	48.10	29.64	6.02	7.82	0.08	0.76	0.51	0.09	0.04	6.83

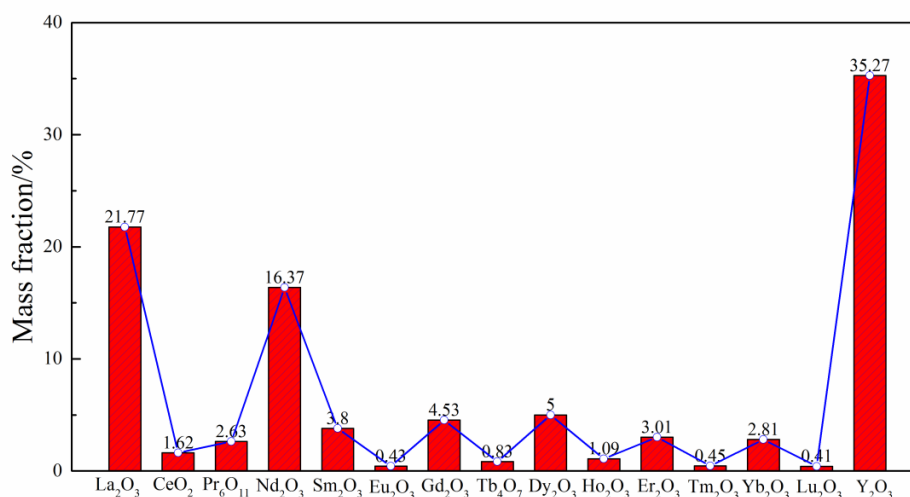


Fig. 1. The partitioning of the ion-exchangeable rare earth in the rare earth ores

It can be seen from Fig. 1 that the light rare earths included lanthanum, cerium, praseodymium and neodymium were 42.39 % totally and the rest of rare earth elements were middle and heavy rare earth, which were approximately 57.61 %.

The clay minerals were separated from rare earth ore by natural sedimentation method according to Stokes' law and then were analyzed by XRD. The results were shown in Fig. 2.

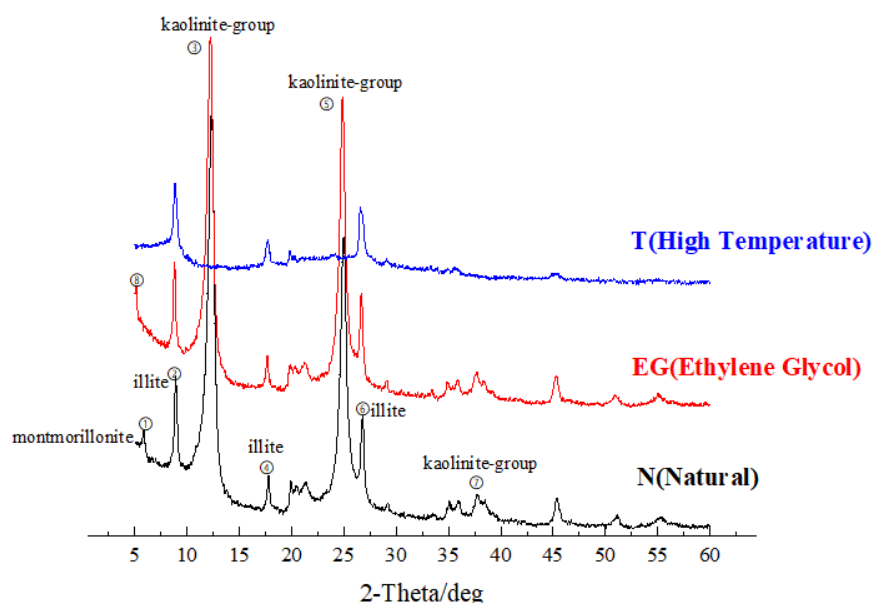


Fig. 2. XRD patterns of experiment rare earth ore sample

In Fig. 2, the peaks 3, 5, 7 were the characteristic peaks of kaolinite-group mineral. However, the characteristic peaks of kaolinite-group disappeared after sample was heated to 823 K. The lattice of kaolinite clay minerals was destroyed at high temperature, and the characteristic peak disappeared. The reaction between ethylene glycol and montmorillonite increased the layer spacing, and the characteristic peak moved to the left. It is helpful to identify different clay minerals. The peaks 2, 4, 6 were the characteristic peaks of illite. Peak 1 was the characteristic peak of montmorillonite.

In conclusion, the clay mineral species included kaolinite, halloysite, illite and montmorillonite. The kaolinite-group, illite and montmorillonite were 86.47 %, 11.64 % and 1.89 % respectively, which could be calculated by semiquantitative spectrographic analysis method.

Ammonium acetate, ammonium citrate, ammonium tartrate and other chemical reagents used in the experiments were of analytical (AR) grade and were purchased from Shanghai Chemical Reagent

Company (Shanghai, China). X-ray fluorescence (Axios max) and ICP-MS (IRIS Intrepid) were used in this research.

2.2. Column leaching experiments

The experiments were carried out in a glass column with an inner diameter of 5.0 cm. the 250 g of dried rare earth samples were uniformly packed in the double jacketed glass. A peristaltic pump was used to add the leaching agent to the column at a flow rate of 0.05 mL/min. The leachate was collected by the centrifuge tube at the bottom of the leaching column. The leaching process of weathered crust elution-deposited rare earth ore with ammonium carboxylate salts under various leaching conditions has been repeated several times. The schematic diagram of experimental apparatus is shown in Fig. 3.

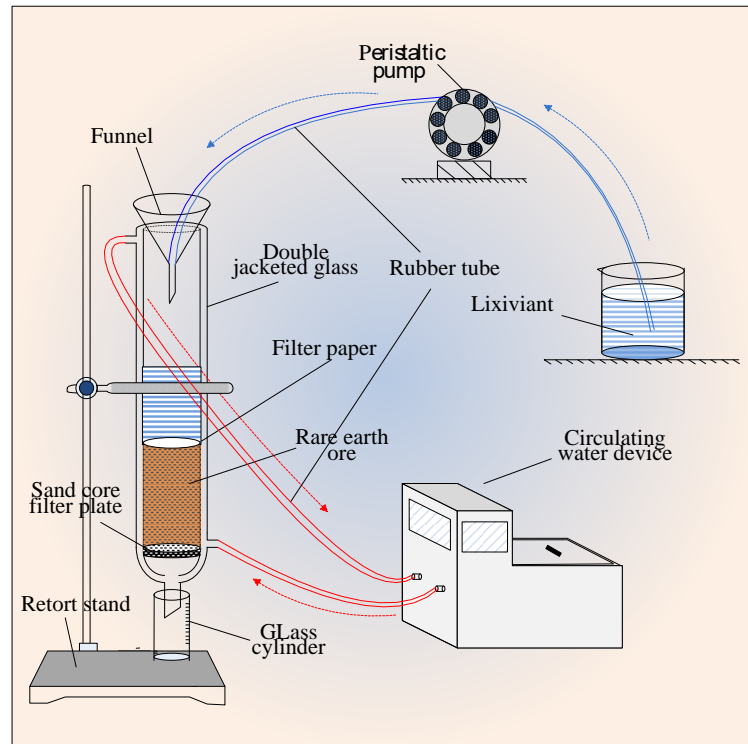


Fig. 3. Schematic diagram of experimental apparatus

2.3. Research method of mass transfer process

In order to explore the mass transfer process of leaching weathered crust elution-deposited rare earth ore with carboxylate lixiviant, the chromatographic plate theory can be used to analyze the mass transfer principle of rare earth and aluminum. Therefore, the leaching process can be seen as a chromatographic leaching process. Meanwhile, the stationary phase is clay mineral adsorbed with rare earth ions and the mobile phase is the carboxylate lixiviant. The flow process is shown in the Fig. 4.

However, the leaching curves of rare earth and aluminum are tailing peak and the chromatographic peaks don't present the normal distribution (gauss curve). Therefore, the leaching curves of slip mechanism could counteract the weaknesses of plate theory and its leaching curve's function could authentically express actual leaching curves (Didenko, 1993; Zhang, 2007).

The chromatographic slip mechanism suggests that the movement of lixiviant through the column consists of two processes. One process is slippage in which the mobile phase pushes the mechanical migration of solutes adsorbed on the surface of the stationary phase. Another process is the continuous distribution of solutes between the first adsorption layer and the second adsorption layer during the slip motion process (Dai and Xiang, 1994; Martin and Synge, 1941).

Based on the theory and research mentioned above, the binomial distribution in form of discrete function can be transformed into the form of continuous function. The equation of the leaching curve can be derived (Zhang, 2007):

$$f(n) = \frac{y}{\sqrt{2\pi} \times \sqrt{(n-c_y)xy}} e^{-\frac{(q-ny)^2}{2(n-c_y)xy}} \quad (2)$$

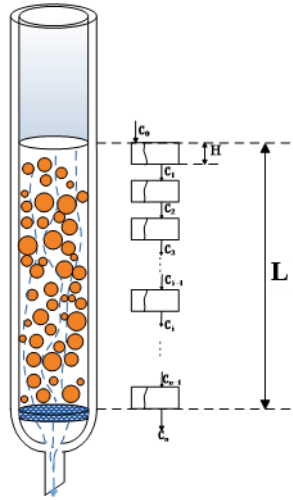


Fig. 4. Schematic diagram of plate theory model

According to the properties of the binomial distribution $c_y = \frac{c}{y}$, $q = n_R y$, where c is the number of plates reduced by solute slip motion, y is the fraction of solute in the second adsorption layer, q is the number of plates in the chromatographic column, n_R is the number that martin-singer distribution process has occurred of the solute peak reaches the outlet,

In the chromatographic leaching curve, the horizontal axis is the volume of lixiviate (v), and the vertical axis is the leaching efficiency of rare earth and aluminum. Taking a as the unit conversion factor, the Equation 2 can be transformed into the Equation 3 (Han, 1997).

$$f(v) = af(n) \quad (3)$$

At the same time, let $B = ay/x$.

The peak area of the chromatographic peak is A , so the equation of the leaching curve of the slip mechanism can be given as:

$$f(v) = \frac{A\sqrt{B}}{\sqrt{2\pi} \times \sqrt{(v-c_v)}} e^{-\frac{B(v_{nR}-v)^2}{2(v-c_v)}} \quad (4)$$

where v_{nR} is the volume of lixiviate when the solute distribution peak reached the exit of the column, c_v is the apparent slip factor.

If $c_v = 0$, and the influence of slip motion is ignored, and the slip mechanism model can be approximated as theoretical model of plate. The equation of theoretical model of plate can be represented as:

$$f(v) = \frac{A\sqrt{B_0}}{\sqrt{2\pi} \times \sqrt{v}} e^{-\frac{B_0(v_{nR}-v)^2}{2v}} \quad (5)$$

Equation 5 can describe the chromatographic peak of micro-tail.

When the equation 4 and equation 5 are used to fit the leaching curve, the $f(v)$ is correspondingly equal.

$$\frac{A\sqrt{B}}{\sqrt{2\pi} \times \sqrt{(v-c_v)}} e^{-\frac{B(v_{nR}-v)^2}{2(v-c_v)}} = \frac{A\sqrt{B_0}}{\sqrt{2\pi} \times \sqrt{v}} e^{-\frac{B_0(v_{nR}-v)^2}{2v}} \quad (6)$$

Let $v = v_{nR}$, the equation 6 may be expressed as

$$q = q_0 \left(1 - \frac{c_v}{v_{nR}}\right) \quad (7)$$

where q is the plate number of slip mechanism, q_0 is the theoretical plate number, c_v is the apparent slip factor. The value c_v should be obtained by fitting the leaching curve.

There are many choices of expressions for experimental characterization of chromatographic peak. However, the leaching curve could be approximated as a gaussian curve (Wen and Lu, 1975). After

further simplification, the real theoretical plate number can be approximated as

$$n = 5.54 \left(\frac{V_R}{V_{1/2}} \right)^2 \cdot \left(\frac{k'}{1+k'} \right) \quad (8)$$

Since the leaching curve of the plates q_0 is a trailing type and the trailing degree is small, $q_0 \approx n$. The equation of the leaching curve of the slip mechanism can be obtained as

$$q_0 = n = 5.54 \left(\frac{V_R}{V_{1/2}} \right)^2 \cdot \left(\frac{k'}{1+k'} \right) \quad (9)$$

where $V_{1/2}$ is the peak width at half height, k' is the capacity factor. When k' is infinite, the theoretical tray number n_0 can be expressed as (Lee, 1993)

$$n_0 = 5.54 \left(\frac{V_R}{V_{1/2}} \right)^2 \quad (10)$$

$$HETP = \frac{L}{n_0} \quad (11)$$

where $HETP$ is equivalent to the height of the theoretical plate, L is the packed ore length.

The chromatographic peak of leaching curve can be described as Fig. 5.

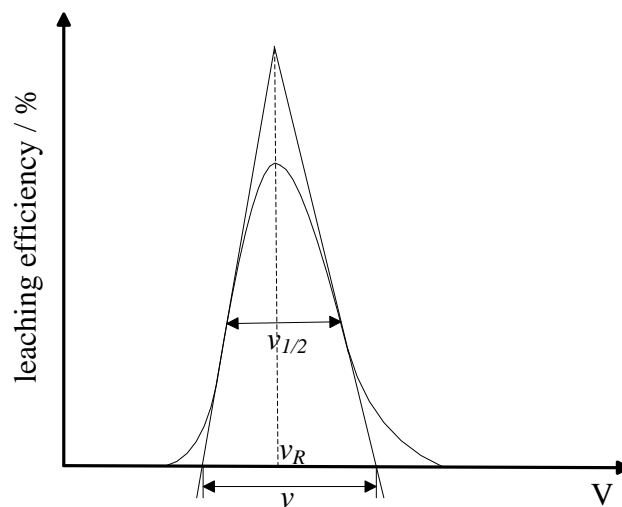


Fig. 5. Schematic diagram of chromatographic peak

When the height of ore L is constant, the theoretical plate height $HETP$ can be used to evaluate the mass transfer efficiency of rare earth and aluminum in the leaching process. The smaller the $HETP$ is, the higher the mass transfer efficiency of leaching is (Su, 2015).

3. Results and discussion

3.1. Effects of concentration of ammonium carboxylate on mass transfer.

To investigate the effects of different carboxylate ammonium salt on the mass transfer of rare earth and aluminum, the different concentrations of ammonium acetate, ammonium tartrate and ammonium citrate were to compare the mass transfer of rare earth and aluminum. The results are shown in Fig. 6.

The concentration of ammonium carboxylate plays a significant role in the leaching process, which could influence the performance of ion-exchange and diffusion (Tang, 2013). As shown in the Fig. 6, the peak value of rare earth concentration distinctly increased with the concentration enhancement of three kinds of the carboxylate ammonium salt. The peak values of rare earth were 5.56 g/L, 1.82 g/L and 3.12 g/L, respectively. It could indicate that the leaching efficiency of rare earth and aluminum increased and the mass transfer curve of rare earth and aluminum became narrower with the concentrations increasing of the carboxylate ammonium salt. Therefore, the leaching process of rare earth and aluminum could be improved by increasing the concentration of ammonium. This is because the concentration difference between the lixiviant and the mineral surface rose with the increasing of the concentration gradient of ammonium ion, which led to the exchange capacity of ammonium ion

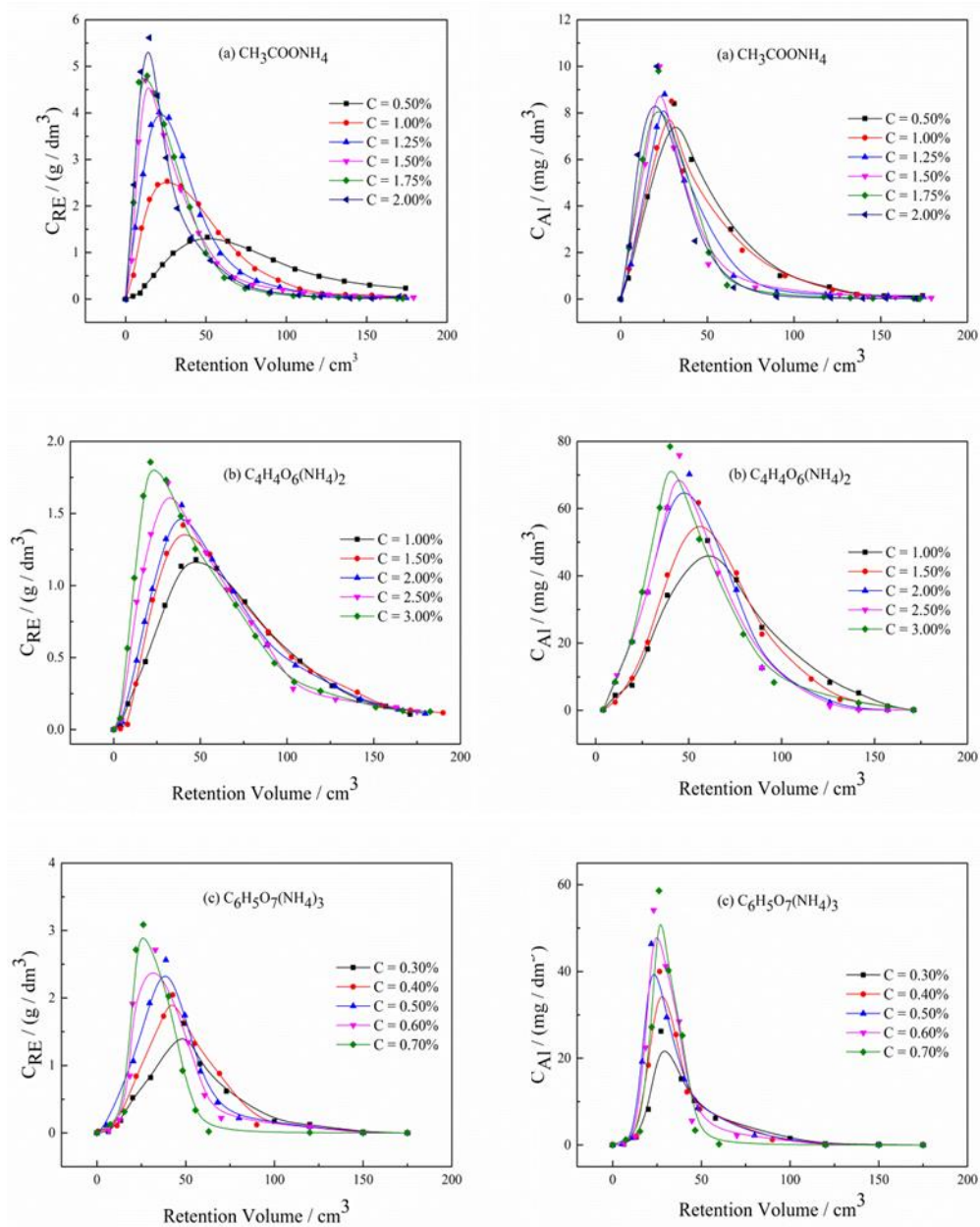


Fig. 6. Leaching behaviors of RE and Al under different mass concentrations (250g of ores, L/S = 2/1 mL/g, μ = 0.50 mL/min, T = 298K, pH = 7.00). (a) $\text{CH}_3\text{COONH}_4$, (b) $\text{C}_4\text{H}_4\text{O}_6(\text{NH}_4)_2$, (c) $\text{C}_6\text{H}_5\text{O}_7(\text{NH}_4)_3$

improve. Meanwhile, the carboxylate ammonium was beneficial for accelerating the seepage velocity in the leaching process (Zhang, 2019), which led to the intensity of ion exchange reaction be enhanced in the leaching process (Guo, 2017).

As results, in order to interpret the mass transfer regularities of rare earth and aluminum, the theoretical plate height HETP of rare earth and aluminum shown in the Fig. 7.

It was illustrated in Fig. 7 that the theoretical plate heights of rare earth and aluminum gradually decreased to the bottom. Therefore, based on the chromatographic plate theory, the mass transfer efficiency of rare earth and aluminum would be enhanced with the increasing of carboxylate ammonium concentration. When the concentrations of ammonium acetate, ammonium tartrate and ammonium citrate were 15 g/L, 25 g/L and 5 g/L respectively, the theoretical plate height were 26.51 mm, 26.98 mm, 29.47 mm, respectively. Moreover, the HETP of rare earth was higher than that of aluminum, which means the effect of carboxylate ammonium on extracting rare earth was better than that of aluminum. The higher concentrations of carboxylate ammonium have effect on the leaching mass transfer efficiency of rare earth and aluminum. This is since the higher concentrations could provide a

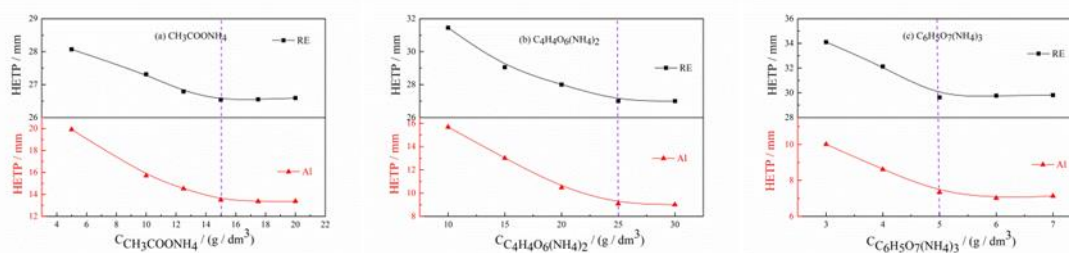


Fig. 7. The HETP of RE and Al under different ammonium concentrations

driving force to make the ammonium ion diffuse from the solution to the ore particles more easily (Tang, 2013). The exchange reaction between ammonium and rare earth ions was strengthened. Therefore, the mass transfer efficiency was accelerated. However, the excessive concentration would increase the lixiviant viscosity and the permeability of the lixiviant would be decreased by the high viscosity lixiviant (Yuan, 2005). When the carboxylate ammonium salts have reached their optimum concentrations, the leaching efficiency of rare earth and aluminum reached equilibrium. The mass transfer efficiencies of rare earth and aluminum were almost stable under the optimal concentration. During the experiment, it was found that some fine clay particles would enter the leachate under the adsorption of tartrate and citrate, which would influence the precipitation process.

The optimum concentrations of ammonium acetate, ammonium tartrate and ammonium citrate were compared with each other. The HETPs of rare earth and aluminum were calculated and shown in Table 2.

Table 2. Calculated HETP of RE and Al under different lixiviants

leaching agents	C/ (g/L)	Packed ore length/mm	Retention volume/mL		Half peak width/mL		Plate number		HETP/mm	
			RE	Al	RE	Al	RE	Al	RE	Al
CH ₃ COONH ₄	15.00	90.14	19.29	22.81	22.28	21.50	4.16	6.24	26.51	13.36
C ₄ H ₄ O ₆ (NH ₄) ₂	25.00	90.22	35.81	23.18	42.14	40.10	4.00	8.01	26.98	9.11
C ₆ H ₅ O ₇ (NH ₄) ₃	5.00	90.30	39.73	24.07	52.28	15.71	3.20	13.02	29.47	7.32

By comparing the mass transfer process of the three ammonium carboxylate salts, it can be seen from the above Table 2 that the mass transfer behavior of ammonium acetate rare earth has a higher peak concentration, a narrower half-peak width, a lower retention volume and a smaller HETP among ammonium carboxylate. The leaching mass transfer efficiencies were followed the order: ammonium acetate > ammonium tartrate > ammonium citrate. Therefore, ammonium acetate has great promoting effect on the leaching of rare earth. It could be found that ammonium acetate has great inhibition effect on the leaching of aluminum in the same way. Ammonium acetate could shorten the leaching process of rare earth and aluminium and improve mass transfer efficiency.

3.2. Effect of flow rate of ammonium carboxylate on mass transfer

In order to investigate the effects of ammonium carboxylate on the mass transfer of rare earth and aluminium, the different flow rates of ammonium acetate, ammonium tartrate and ammonium citrate were analysed to compare the mass transfer of rare earth and aluminium. The results are shown in Fig. 8.

As shown in Fig. 8, the peak concentration increased and the retention volume of the rare earth and aluminium reduced with the flow rate increasing to 0.50 mL/min, and then the peak concentration and the retention volume were nearly invariable with the flow rate continuing to increase when carboxylate ammonium salts were used as lixiviant. This was due to the fact that the fluid flow of lixiviant solution in the surface of ore body would be accelerated with the enhancing of the flow rate of ammonium carboxylate, which lead to the rare earth and aluminium be left in the ore surface quickly (Sameni and Morshedi, 2000). Meanwhile, the re-adsorption phenomenon of rare earth ions would be

alleviated (Huang, 2018). The rare earth peak concentration of three kinds of ammonium carboxylate followed the orders: ammonium acetate > ammonium citrate > ammonium tartrate. The HETPs of rare earth and aluminum at different flow rates were calculated and shown in Fig. 9.

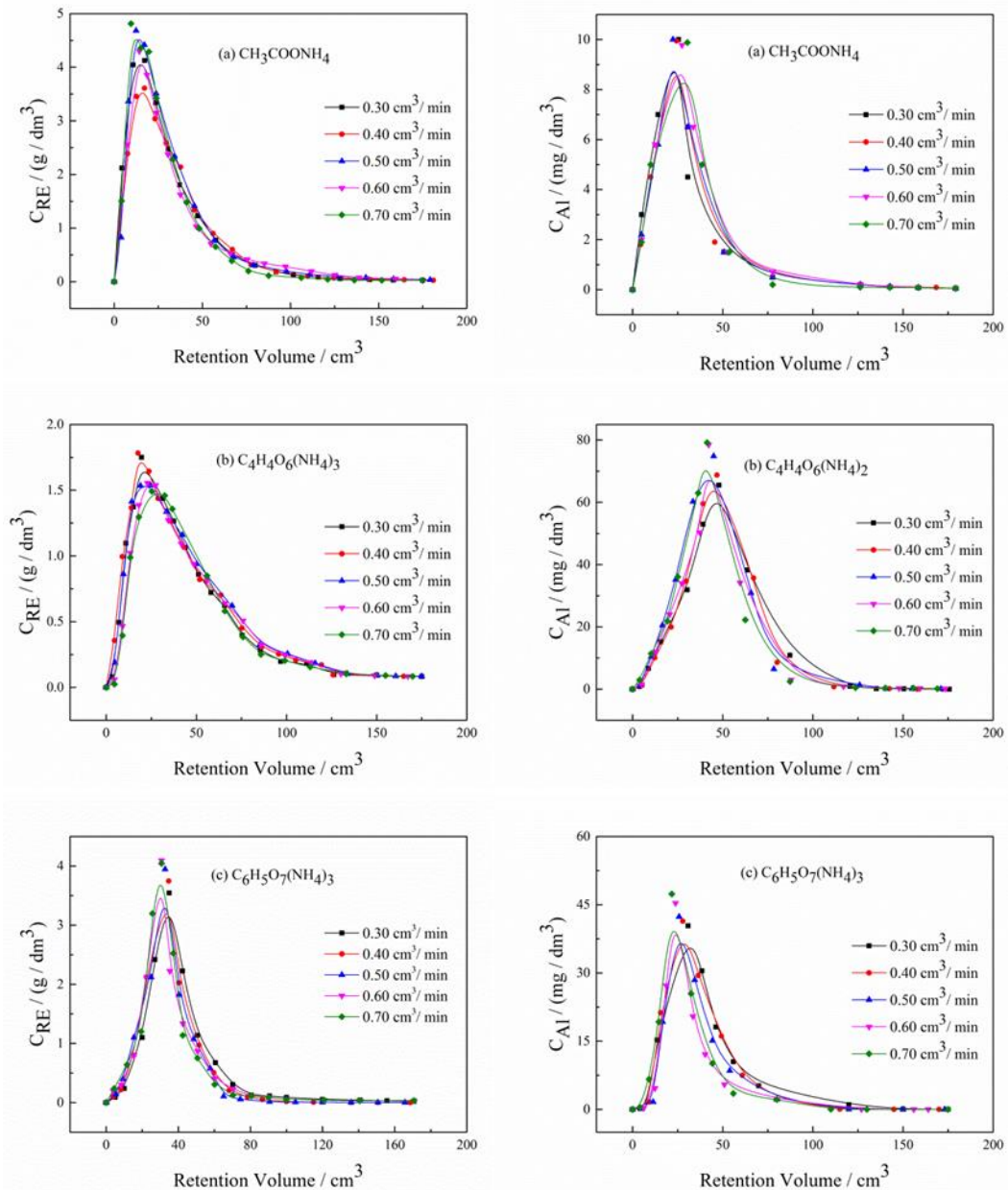


Fig. 8. Leaching behaviors of RE under different flow rates (250 g of ores, $L/S = 2/1$ mL/g, $T = 298$ K, $pH = 7.00$. (a) $CH_3COONH_4 = 15$ g/L, (b) $C_4H_4O_6(NH_4)_2 = 25$ g/L, (c) $C_6H_5O_7(NH_4)_3 = 5$ g/L)

Under the same condition, the height of theoretical plate would be largely determined by the flow rate (Didenko, 1993). It was illustrated in Fig. 9 that the HETP of the rare earth and aluminum decreased with the flow rate increasing to 0.50 mL/min, and then increased with the flow rate continuously increasing when carboxylate ammonium salts were used as lixiviant. This was because the exchanged rare earth ions would be re-adsorbed to the surface of clay minerals when the flow rate was low, resulting in poor mass transfer efficiency (Li, 2017). And the ammonium ions have not exchanged with the rare earths and aluminum and then flow out immediately under a high flow rate. As a result, ammonium ions could not contact with mineral particles fully, which is not conducive to the formation of the exchange reaction between ammonium ions and rare earth ions (Luo, 2014).

Therefore, as seen from Fig. 9, there was an optimal flow rate (u_{opt}) for the leaching of the rare earth

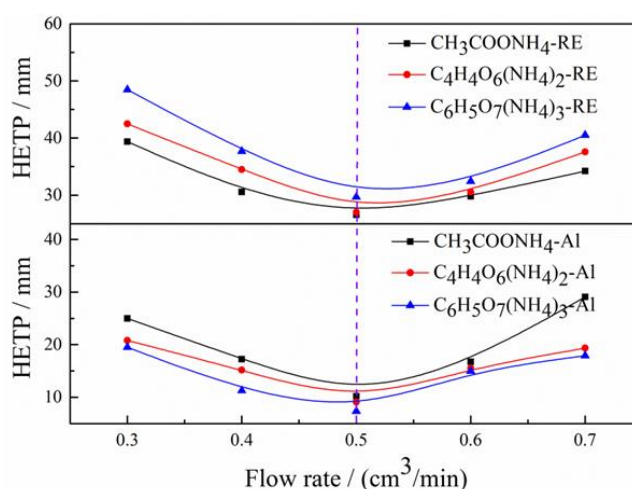


Fig. 9. The HETP of RE and Al under different flow rates

and aluminum, which can be explained by the Van Deemter equation (Dai and Xiang, 1994).

$$HETP = A + B/u + Cu \quad (12)$$

where A, B and C are the three factors that affect the column efficiency.

In the Eq. 12, A is the multipath diffusivity or eddy diffusivity. The degree of channeling phenomenon in the leaching process can be reflected by A. B is the longitudinal diffusivity. C is the mass transfer impedance coefficient; u is the flow rate of lixiviate. Therefore, the B/u played a leading role in calculating the HETP and the Cu was negligible while the flow rate was less than optimal flow rate (u_{opt}). On the contrary, the Cu played a leading role in calculating the HETP and the B/u was negligible while the flow rate was more than optimal flow rate (u_{opt}). According to the Fig. 9, the height of the theoretical plate increased while the leaching flow rate was too slow, which leading to the decrease of mass transfer efficiency of rare earth and aluminum. Therefore, the optimal flow rate (u_{opt}) was 0.50 mL/min. Therefore, in order to obtain the highest mass transfer efficiency of RE, the 0.50 mL/min flow rate of lixiviate was chosen to leach the rare earth ore.

3.3. Effects of ammonium carboxylate pH on the mass transfer

In order to investigate the effects of ammonium carboxylate pH on the mass transfer of rare earth and aluminium, the different pH of ammonium acetate, ammonium tartrate and ammonium citrate were to compare the mass transfer of rare earth and aluminium. The results are shown in Fig. 10.

According to Fig. 10, the peak values of rare earth and aluminum were decreased with the increasing of pH value of the carboxylate ammonium salt. The concentration of rare earth was the highest and the concentration of aluminum was the least among various carboxylate ammonium salts. Therefore, the ammonium acetate has the best inhibiting effect on aluminum. The effects of pH were evident on the mass transfer in the leaching process when ammonium citrate was used as leaching agent. Because the citrate was in the form of H_3Cit , H_2Cit in acidic condition. The H_3Cit and H_2Cit were difficult to produce complexation reaction with rare earth ions. The content of $HCit^{2-}$ and Cit^{3-} would increase with increasing of the pH value, which was beneficial to the mass transfer of rare earth and aluminum (Bian, 2011). However, the rare earth ions and aluminum ions would hydrolyze into rare earth hydroxide and aluminum hydroxide under the studied range of pH value up to 9, leading to the fall of the concentration of rare earth and aluminum. In order to analyze the effects of pH on the mass transfer of the rare earth and aluminum, the HETPs of rare earth and aluminum at different pH were calculated and shown in Fig. 11.

The HETP of rare earth and aluminum remained stable at the pH value of 4 to 7. However, the HETP of rare earth and aluminum increased when the pH value was over 7. As shown in Fig. 11, the height of the theoretical plate of rare earth was the lowest while the ammonium acetate was selected as

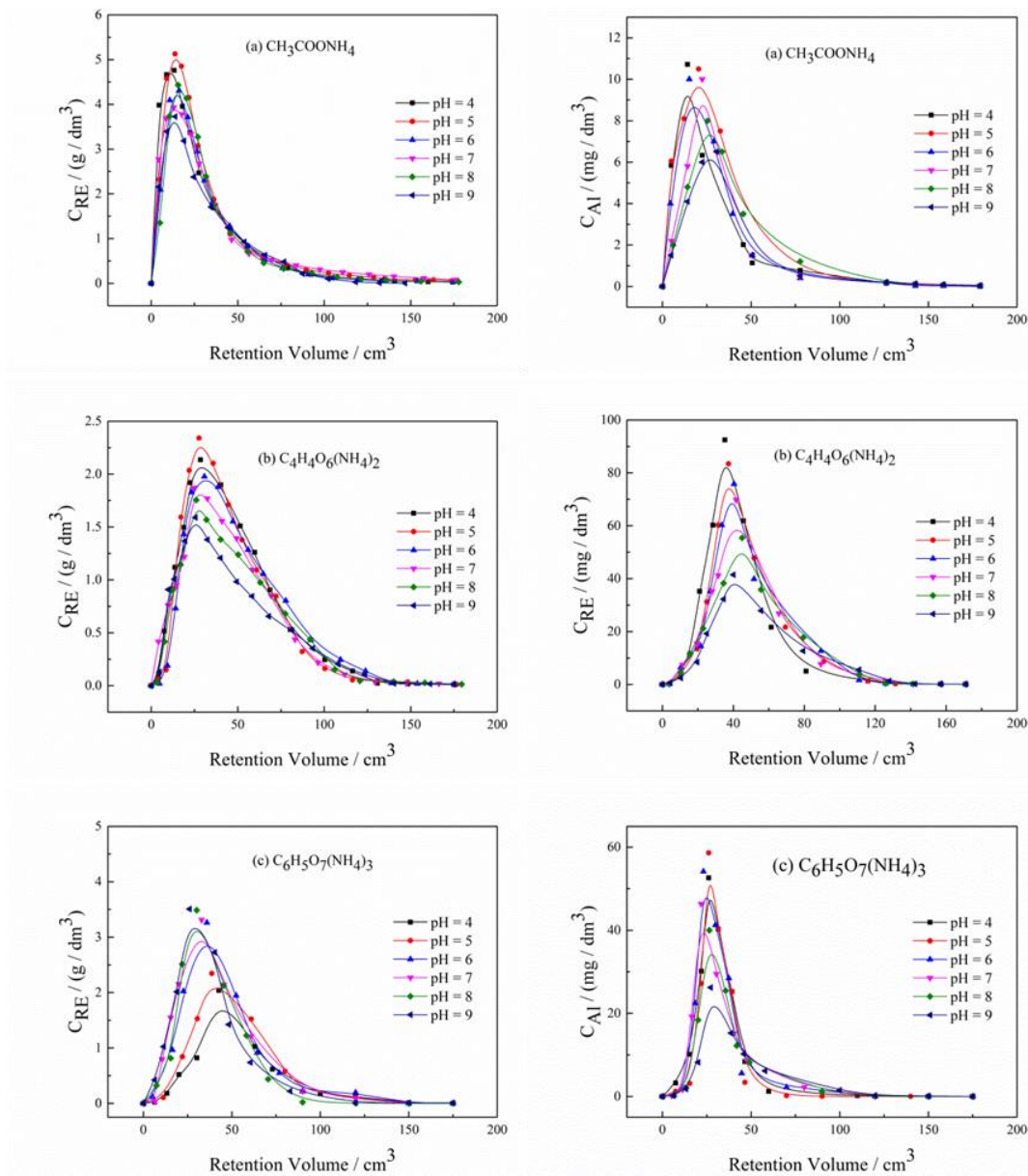


Fig. 10. Leaching behaviors of RE and Al under different pH (250g of ores, L/S = 2/1 mL/g, μ = 0.50 mL/min, T = 298K. (a) $\text{CH}_3\text{COONH}_4$ = 15 g/L, (b) $\text{C}_4\text{H}_4\text{O}_6(\text{NH}_4)_2$ = 25g/L, (c) $\text{C}_6\text{H}_5\text{O}_7(\text{NH}_4)_3$ = 5 g/L)

lixiviant, which means the mass transfer of rare earth would superior to the ammonium citrate and ammonium tartrate. On the contrary, the height of the theoretical plate of aluminum leached with ammonium acetate was lower than that of ammonium tartrate and ammonium citrate. The mass transfer process and height of the theoretical plate indicated that the ammonium acetate was the best one among the three kind of carboxylate ammonium salt. Moreover, the mass transfer efficiency of rare earth followed the orders: ammonium acetate > ammonium tartrate > ammonium citrate. The mass transfer efficiency of aluminum followed the orders: ammonium tartrate > ammonium citrate > ammonium acetate. This was mainly because of the inhibitory effect of ammonium acetate on aluminum. Therefore, the mass transfer of aluminum leached with ammonium acetate would be reduced, which would reduce the cost of the mining production.

3.4. Effects of temperature on mass transfer with ammonium carboxylate

In order to investigate the effects of temperature on the mass transfer of rare earth and aluminium, the different temperatures of lixiviant were to compare the mass transfer of rare earth and aluminium. The results are shown in Fig. 12.

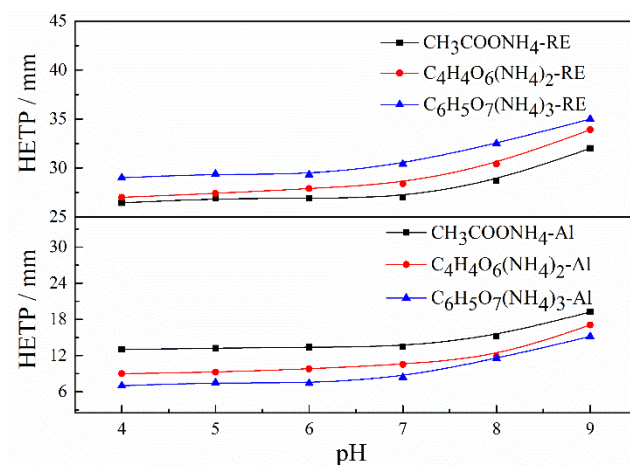


Fig. 11. The HETP of rare earth and aluminum under different pH

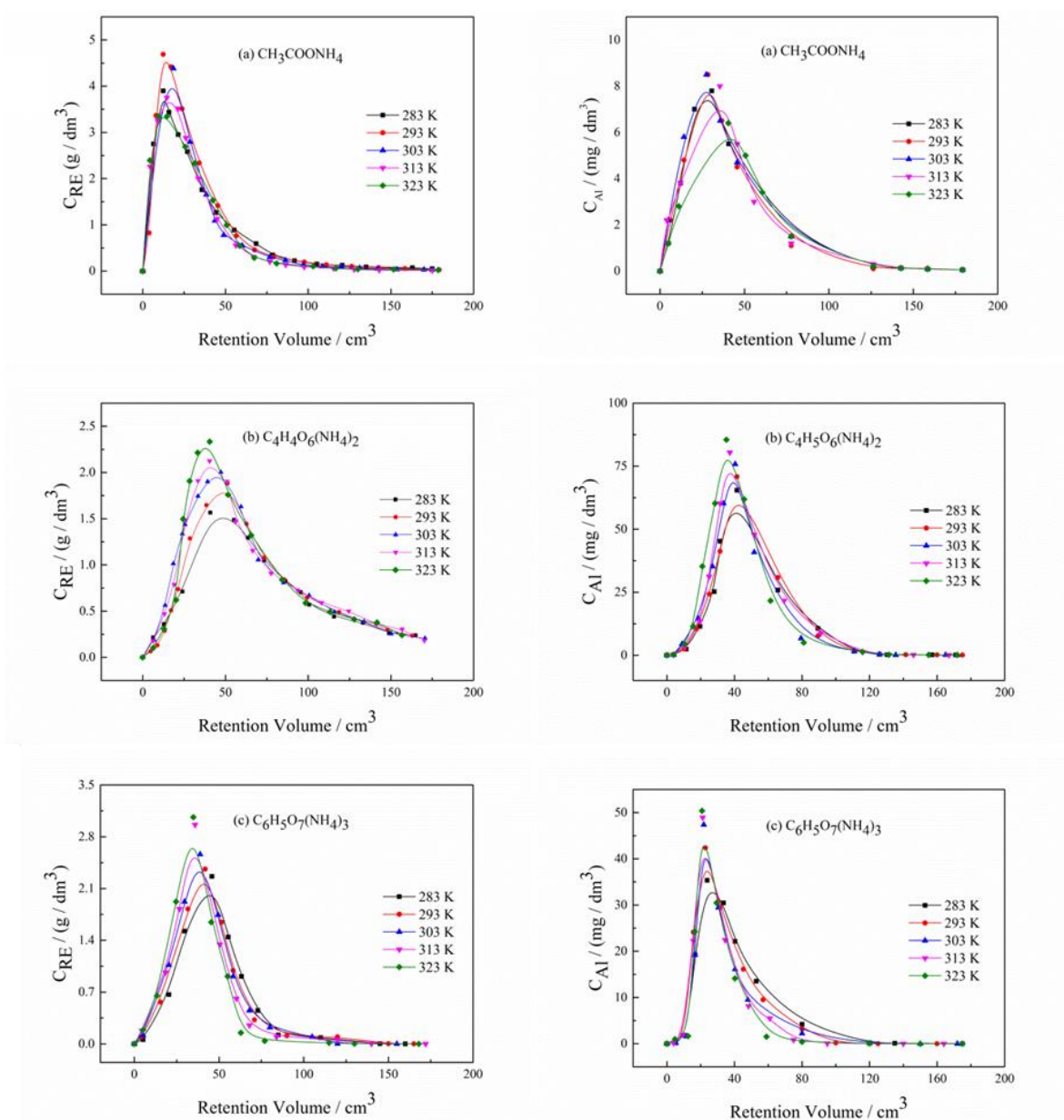


Fig. 12. Leaching behaviors of RE and Al under different temperatures (250 g of ores, $L/S = 2/1$ mL/g, $\mu = 0.50$ mL/min, pH = 7.00. (a) $\text{CH}_3\text{COONH}_4 = 15$ g/L, (b) $\text{C}_4\text{H}_4\text{O}_6(\text{NH}_4)_2 = 25$ g/L, (c) $\text{C}_6\text{H}_5\text{O}_7(\text{NH}_4)_3 = 5$ g/L)

Fig. 12 illustrated the effects of lixiviant temperature on mass transfer of ammonium carboxylate. According to the Fig. 12(a), the peak concentrations of rare earth and aluminum gradually decreased with the temperature increasing and the peak concentration of rare earth and aluminum was the highest while the temperature was 293K when the lixiviant was ammonium acetate. This was since the ammonium acetate tended to decompose easily with the increasing of temperature. Meanwhile, the solubility of ammonium acetate in the solution decreased with the increasing of temperature (Tang, 2002). Therefore, exchange reactions between ammonium acetate and rare earth (aluminum) would be reduced. The Fig. 12 shown that the peak concentrations of rare earth and aluminum that leached with ammonium tartrate and ammonium citrate increased with the temperature increasing. The thermal motion of ion speed would be raised because of the leaching temperature increasing. In addition, the solution diffusivity and ions exchangeability would be improved (Aydogan, 2006). Elevating leaching temperature was conducive to the exchange reaction between ammonium ions and rare earth ions when ammonium tartrate and ammonium citrate were used as lixiviant (Chen, 2018). In order to analyze the effects of the leaching temperature on the mass transfer of the rare earth and aluminum, the HETPs of rare earth and aluminum at different temperature were calculated and shown in Fig. 13.

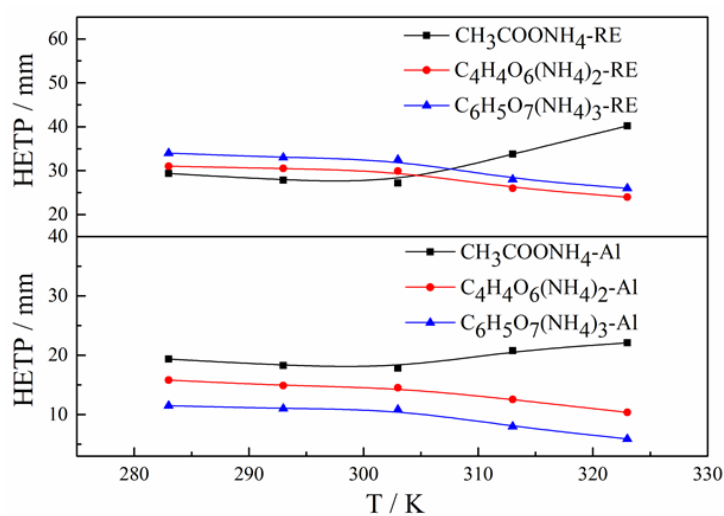


Fig. 13. The theory plate number curves and HETP of RE and Al under different temperature

It could be seen from Fig. 13 that the effects of temperature on the mass transfer of ammonium acetate were different from the ammonium tartrate and ammonium citrate. The HETP of ammonium acetate increased with the increasing of temperature, which means the mass transfer of rare earth and aluminum leached by ammonium acetate decreased with the increasing of temperature. The HETP of ammonium citrate and ammonium tartrate decreased with the increasing of temperature, which means the mass transfer of rare earth and aluminum leached by ammonium acetate increased with the increasing of temperature. The conditions that elevated leaching temperature were conducive to the exchange reaction between ammonium ions and rare earth ions. Therefore, the natural temperature from 283 K to 303 K was suitable for the rare earths' extraction.

4. Conclusions

The carboxylate ammonium, such as ammonium acetate, ammonium citrate and ammonium tartrate, were selected as lixiviant to compare the concentration, flow rate, pH and temperature on leaching mass process of rare earth and aluminum. Results showed that the optimum concentrations of ammonium acetate, ammonium tartrate and ammonium citrate were 15 g/L, 25 g/L and 5 g/L respectively, the leaching flow rate was 0.50 mL/min, the pH value was approximately 7.00 and the leaching temperature was 293 K to 303 K. Meanwhile, the leaching behaviors of rare earth and aluminum leached by three kinds of carboxylate ammonium were analyzed by chromatographic plate theory. The relationship between the flow rate and height equivalent to HETP could fit well with the Van Deemter equation and there was an optimal flow rate (u_{opt}) for the leaching of the rare earth and aluminum. The

mass transfer efficiencies of three ammonium carboxylates for rare earth and aluminum was in the order of ammonium acetate > ammonium tartrate > ammonium citrate. Moreover, the ammonium acetate could commendably inhibit aluminum ions from entering the lixivium.

Compared with the traditional ammonium inorganic salts and magnesium salts, besides effectively recovering the middle and heavy rare earth elements and shortening the leaching period for reducing the cost, three ammonium carboxylate salts showed better mass transfer efficiencies and utilizations of leaching agents were lower. The experimental results can not only optimize the leaching conditions of carboxylate, but also applicable in other leaching agents. It is reasonable to apply the chromatographic plate theory to guide the practical mining production in the industry.

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References

- ILYAS, S., KIM, H., SRIVASTAVA, R. R., et al. *Cleaner production of rare earth elements from phosphorus-bearing sulfuric acid solution of vein deposit monazite*. Journal of Cleaner Production, 2021, 278:123435.
- ILYAS, S., KIM, H., SRIVASTAVA, R. R. *Extraction equilibria of cerium (IV) with Cyanex 923 followed by precipitation kinetics of cerium (III) oxalate from sulfate solution*. Separation and Purification Technology, 2020, 254:117634.
- CHI, R. A., TIAN, J., LUO, X. P., XU, Z. G., HE, Z. Y., 2012. *The basic research on the weathered crust elution-deposited rare earth ores*. Nonferrous Metals Science & Engineering, 3(04), 1-13.
- ZHANG, Z. Y., SUN, N. J., HE, Z. Y., CHI, R. A., 2018. *Local concentration of middle and heavy rare earth elements on weathered crust elution-deposited rare earth ores*. Journal of Rare Earths. 36(5), 552-558.
- GUPTA, C. K., SAHA, S., 2001. *Extractive metallurgy of beryllium*. Mineral Processing and Extractive Metallurgy Review. 22(4/6), 413-451.
- CHI, R. A., WANG, D. Z., 1993. *Study of adsorption properties and enriching RE on clay minerals by quantum chemical calculation*. Journal of Rare Earths. 02, 64-69.
- CHI, R. A., TIAN, J., LI, Z. J., PENG, C., WU, Y. X., LI, S. R., WANG, C. W., ZHOU, Z. A., 2005. *Existing state and partitioning of rare earth on weathered ores*. Journal of Rare Earths. 23, 756-759.
- TIAN, J., CHI, R. A., YIN, J. Q., 2010. *Leaching process of rare earths from weathered crust elution-deposited rare earth ore*. Transactions of Nonferrous Metals Society of China. 20(5), 892-896.
- TIAN, J., YIN, J. Q., CHEN, K. H., RAO, G. H., JIANG, M. T., CHI, R. A., 2010. *Optimisation of mass transfer in column elution of rare earths from low grade weathered crust elution-deposited rare earth ore*. Hydrometallurgy. 103(1), 211-214.
- BARTLETT, R. W., 1992. *Simulation of ore heap leaching using deterministic models*. Hydrometallurgy. 29(1), 231-260.
- ZHANG, Z. Y., HE, Z. Y., YU, J. X., XU, Z. G., CHI, R. A., 2016. *Novel solution injection technology for in-situ leaching of weathered crust elution-deposited rare earth ores*. Hydrometallurgy. 164, 248-256.
- LIU, K., DENG, X. Y., ZUO, X. H., 2013. *Leaching process and development trend of weathered crust elution-deposited rare earth ore*. Journal of Hubei Polytechnic University. 29(02), 32-36.
- ZHANG, Z. Y., HE, Z. Y., ZHOU, F., CHI, R. A., 2018. *Swelling of clay minerals in ammonium leaching of weathered crust elution-deposited rare earth ores*. Rare Metals. 37(1), 72-78.
- HE, Z. Y., ZHANG, Z. Y., YU, J. X., XU, Z. G., XU, Y. L., ZHOU, F., CHI, R. A., 2016. *Column leaching process of rare earth and aluminum from weathered crust elution-deposited rare earth*. Transactions of Nonferrous Metals Society of China. 26(11), 3024-3033.
- HE, Z. Y., ZHANG, Z. Y., CHI, R. A., XU, Z. G., YU, J. X., WU, M., BAI, R. Y., 2017. *Leaching hydrodynamics of weathered elution-deposited rare earth ore with ammonium salts solution*. Journal of Rare Earths. 35(08), 824-830.
- HE, Z. Y., ZHANG, Z. Y., YU, J. X., XU, Z. G., CHI, R. A., 2016. *Process optimization of rare earth and aluminum leaching from weathered crust elution-deposited rare earth ore with compound ammonium salts*. Journal of Rare Earths. 4, 413-419.
- XIAO, Y. F., FENG, Y. Z., HU, G. H., HUANG, L., HUANG, X. WEI., CHEN, Y. Y., LI, M. L., 2015. *Leaching and mass transfer characteristics of elements from ion-adsorption type rare earth ore*. Rare Metals. 34(5), 357-365.

- CHEN, Z., ZHANG, Z. Y., HE, Z. Y., CHI, R. A., 2018. *Mass transfer process of leaching weathered crust elution-deposited rare earth ore with magnesium salts*. Physicochemical Problems of Mineral Processing, 54(3). 1004-1013.
- LI, Q., HE, Z. Y., ZHANG, Z. Y., ZHANG, T. T., ZHONG, C. B., CHI, R. A., 2015. *Studies on coordination leaching of weathered crust elution-deposited rare earth ore with citrate*. Chinese Rare Earths, 1, 18-22.
- ZHANG, H., ZHANG, Z. Y., LIU, D. F., CHAI, X. W., CHI, R. A., 2019. *Permeability characteristics of weathered crust elution-deposited rare earth ores in-situ leaching with ammonium acetate*. Mining and metallurgical engineering, 04, 110-114.
- DIDENKO, A. N., KOZLOV, E. V., SHARKEEV, Y. P., TAILASHEV, A. S., RJABCHIKOV, A. I., PRANJAVICHUS, L., AUGULIS, L., 1993. *Observation of deep dislocation structures and "long-range effect" in ion-implanted α -Fe*. Surface & Coatings Technology, 56(2), 97-104.
- ZHANG, D. L., LU, L. Z., KE, J. J., 2007. *Discussing chromatographic plate number with slip mechanism*. China Science and Technology Information, 20, 278-281.
- DAI, C. Z., XIANG, Z. Y., 1994. *Study on the properties of chromatographic leaching curve of plate theory*. Acta Chimica Sinica, 52, 64-70.
- MARTIN, A. J. P., SYNGE, R. L. M., 1941. *A new form of chromatogram employing two liquid phases*. Biochemical Journal, 2(11), 245.
- HAN, Z. W., HE, Z. M., YU, G. Z., 1997. *Expression of column plate model of normal trailing chromatographic peak*. Chinese Journal of Chromatography, 15(6), 532-533.
- WEN, C. Y., LU, P. Z., 1975. *Basic principles of chromatography*. M. Bei Jing: Science Press, 20.
- LEE, W. C., TSAI, G. J., TSAO, G. T., 1993. *Analysis of chromatography by plate theory*. Separations Technology, 3(4), 178-197.
- SU, Z. H., 2015. *Research on the theory and application of chromatography-economic analysis method*. D. Wuhan University.
- TANG, X. K., TIAN, J., YIN, J. Q., LUO, X. P., 2013. *Research on acid-leaching rare earth from low-grade weathered crust elution-deposited rare earth ore with sesbania gum*. Nonferrous Metals Science and Engineering, 4, 85-89.
- GUO, Z. Q., JIN, J. F., WANG, G. S., QIN, Y. H., WANG, X. J., ZHAO, K., 2017. *Basic theory of leaching kinetics on the weathered crust elution-deposited rare earth ores*. Nonferrous Metals Science and Engineering, 05, 131-136.
- YUAN, M., JIA, Z. W., YUAN, C. Y., 2005. *Research on influential factors to viscoelasticity of polymer solution*. Petroleum Geology & Oilfield Development in Daqing, 05, 74-76+108-109.
- SAMENI, A. M., MORSHEDI, A., 2000. *Hydraulic conductivity of calcareous soils as affected by salinity and sodicity. II. Effect of gypsum application and flow rate of leaching solution*. Communications in Soil Science and Plant Analysis, 31(1-2), 69-80.
- HUANG, W. F., ZOU, Z. Q., WU, H., HUANG, L. J. H., HUANG, X. L., 2018. *Study on anti-adsorption of ion adsorption type rare earth ore*. Chinese Rare Earths, 39(05), 102-109.
- LI, Y. X., WANG, X. J., XIAO, W. J., DENG, S. Q., CAO, S. R., HAN, J. W., 2017. *Study on variation regularity of permeability in leaching process of ion-type rare earth ore*. Metal Mine, 08, 104-108.
- LUO, S. H., HUANG, Q. Q., WANG, G. S., HU, S. L., HONG, B. G., 2014. *Permeability change rule of ion-adsorption rare-earth in ore leaching process*. Nonferrous Metals Science and Engineering, 5(02), 95-99.
- DAI, C. Z., Xiang, Z., YUN., 1994. *Research into character of chromatographic eluting curve by plate theory*. Acta Chimica Sinica, 52, 64-70.
- BIAN, X., YIN, S. H., ZHANG, F., WU, W. Y., TU, G. F., 2011. *The separation of rare earth oxide and celeium fluoride with the method of citric acid complex leaching*. Journal of Materials & Metallurgy, 10(04), 244-248.
- TANG, M. T., XI, X. M., CHANG, J. W., HUANH, Z. S., 2002. *Rusting rate of manganese in water catalyzed by different ammonium salts*. Journal of Central South University (Science and Technology), 06, 576-579.
- AYDOGAN, S., UCAR, G., CANBAZOGLU, M., 2006. *Dissolution kinetics of chalcopyrite in acidic potassium dichromate solution*. Hydrometallurgy, 81, 45-51.