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Leaching Kinetics of Weathered Crust Elution-Deposited Rare Earth Ore with Compound Ammonium Carboxylate

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Abstract: Due to the special properties of the ammonium salts, ammonium acetate and ammonium citrate were used to explore the best leaching conditions of rare earth with compound ammonium carboxylate. This paper explored the influence of the molar ratio, ammonium concentration, experimental temperature, and pH of the compound leaching agents on the leaching efficiency of rare earth and aluminum, and it analyzed the leaching process based on the leaching kinetics, which provides a new method for leaching rare earth from the weathered crust elution-deposited rare earth ore. The results showed that under the conditions where the molar ratio of ammonium acetate and ammonium citrate was 7:3 and the ammonium concentration was 0.15 mol/L, the leaching efficiency of rare earth was the highest when the pH of leaching agent was 4.0 and the experimental temperature was 313 K. Meanwhile, when CH_3COONH_4 and $(NH_4)_3Cit$ were used to leach rare earth ore, the leaching reaction kinetics equation of rare earth and aluminum were obtained. In the temperature range of 283–323 K, the apparent activation energy of rare earth was 14.89 kJ/mol and that of aluminum was 19.17 kJ/mol. The reaction order of rare earth was 0.98 and that of aluminum was 0.79. The results were in accordance with the shrinking core model and indicate that the concentration of the leaching agent had a greater influence on rare earth than aluminum. This process can reduce the use of ammonium salt, and it is of great significance to extract rare earth elements from weathered crust elution-deposited rare earth ore and improve the utilization rate of resources.

Keywords: weathered crust elution-deposited rare earth ore; leaching kinetics; rare earth; ammonium acetate; ammonium citrate

1. Introduction

The weathered crust elution-deposited rare earth ores contain a large amount of medium and heavy rare earth elements, which are the main source of medium and heavy rare earth in the world. Therefore, it has considerable commercial and industrial value and draws global attention [1]. Most of the rare earth in weathered crust elution-deposited rare earth ore is adsorbed on the surface of clay minerals in the form of hydrated or carboxyl hydrated ions [2]. It is impossible to separate rare earth concentrate by conventional and physical beneficiation, such as flotation, gravity separation and magnetic separation. Therefore, the chemical leaching technology is the suitable method to enrich rare earth from this type of rare earth ore. The clay minerals in the rare earth ore can be seen as the stationary phase, and the electrolyte can be used as the leaching agent to exchange the rare earth which has been enriched and loaded on the surface of the clay minerals. This is the theoretical basis for the chemical extraction of rare earth from the weathered crust elution-deposited rare earth ore [3,4].

Taking ammonium salt as the leaching agent as an example, the reaction of ammonium ion exchange rare earth ions can be expressed as [5] (where s stands for solid phase; aq stands for liquid phase):

$$[Al_4(Si_4O_{10})(OH)_8]_m \cdot nRE^{3+}\ (s) + 3nNH_4^{+}(aq) \leftrightarrows [Al_4(Si_4O_{10})(OH)_8]_m \cdot (NH_4^{+})_{3n}(s) + nRE^{3+}(aq).$$

Minerals $[Al_4(Si_4O_{10})(OH)_8]_m$ can be described as resin, adsorbed RE^{3+}. When the leaching agent flows through the resin, NH^{4+} in the solution starts to migrate the mineral surface to take an ion-exchange reaction with RE^{3+}.

Currently, inorganic ammonium salts are widely used as a leaching agent in industry, and the leaching process has been developed from pool leaching and heap leaching to the in-situ leaching process [6,7]. The commonly leaching agents are $(NH_4)_2SO_4$ and NH_4Cl. The selection of leaching agent is very important when extracting rare earth from weathered crust elution-deposited rare earth ore, which influences the rare earth leaching efficiency directly. The rare earth leaching efficiency with a compound leaching agent is better than that of a single leaching agent normally [8]. At present, finding a high-efficiency and environmental protection compound leaching agent to strengthen the leaching process for ensuring the rare earth leaching efficiency is still an important research direction [9,10].

Many experts have taken related research work and achieved preliminary success. Zhang et al. [11–13] used mixed inorganic ammonium salts as the leaching agent to improve the leaching efficiency of rare earth, and they studied the swelling properties of weathered crust elution-deposited rare earth ore. Xiao et al. [14,15] carried out the research on the leaching law of rare earth elements from weathered crust elution-deposited rare earth ore leaching by magnesium salt, and they realized the leaching of rare earth without ammonium. Moreover, they used a magnesium-ammonium-calcium compound leaching agent to extract rare earth, which significantly reduced the amount of ammonium salt and the leaching of aluminum impurities. Chen et al. [16,17] studied the leaching of weathered crust elution-deposited rare earth ore with magnesium salt, analyzed the kinetic model and related coefficients in the reaction process, and provided theoretical guidance for the industrial application of magnesium salt. Li et al. [18] used citrate to leach the weathered crust elution-deposited rare earth ore, explored the best process using ammonium citrate, and proved the feasibility of leaching weathered crust elution-deposited rare earth ore with citrate. Zhang et al. [19] explored the permeability characteristics of leaching rare earth from weathered crust elution-deposited rare earth ore by ammonium acetate under different experimental conditions, and they optimized the leaching process conditions through experiments. Although there was some progresses in the application of ammonium carboxylate in the leaching of weathered crust elution-deposited rare earth ore, there is still a lack of some researches on the leaching kinetics of rare earth with compound ammonium carboxylate.

In recent years, ammonium carboxylate leaching agent has become a research hotspot in the searching for the new leaching agent of weathered crust elution-deposited rare earth ore. This paper aimed to explore the optimum condition for leaching rare earth ore with compound ammonium carboxylate (CH_3COOH and $(NH_4)_3Cit$). In addition, the leaching kinetics of RE and Al were carried out and further research was taken. It provided a new technology for high efficiency, low consumption and environmental protection in the in-situ leaching of weathered crust elution-deposited rare earth ore, while enriching the theoretical basis for promoting industrial application of compound ammonium carboxylate.

2. Materials and Methods

2.1. Materials

2.1.1. Main Chemical Composition of the Rare Earth Ore

The ore samples used in the experiments were collected from the rare earth ore in Fujian Province, China. The weathered crust elution-deposited rare earth ore is mainly composed of quartz, potassium feldspar, plagioclase, white mica and clay minerals [20]. The chemical composition analysis ore sample is shown in Table 1.

Table 1. Main chemical composition of the ore samples.

Component	REO	SiO_2	Al_2O_3	Fe_2O_3	K_2O	MgO	TiO_2	MnO	Pb_2O	Loss
Content	0.13	49.32	34.84	3.42	3.19	0.30	0.35	0.10	0.02	8.30

REO, rare earth oxide.

It can be seen from Table 1 that the main chemical components in the ore are SiO_2 and Al_2O_3, accounting for 49.32% and 34.84%, respectively. The content of REO was 0.13%. Aluminum was the main impurity in the rare earth leaching solution, which would increase the difficulty of recovering rare earth and reduce the purity of rare earth products.

2.1.2. Rare Earth Partition of the Rare Earth Ore

Rare earth partition was commonly used to represent the proportional relationship between various rare earth elements in minerals. The rare earth elements partition in the rare earth ore was analyzed by ICP-AES, as shown in Table 2.

Table 2. Rare earth partition of the rare earth ore.

Component	La	Ce	Pr	Nd	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu	Y
Content	25.73	1.22	3.11	15.81	6.28	0.72	5.12	2.44	2.61	1.07	3.58	1.46	4.23	1.19	25.43

As can be seen from Table 2, the content of light rare earths such as La, Ce, Pr, and Nd was relatively low in the total rare earth content. The remaining medium and heavy rare earths accounted for 54.13%, which indicated that this rare earth mine has a great industrial utilization value.

2.1.3. Ore Particle Size Distribution of the Rare Earth Ore

The rare earth ore sample was shaped into a cone, flattened by a trowel and quartered. Then, the last two diagonal quarters were collected and remixed. The mineral particle sizes were determined by a laser particle size analyzer. The particle size distribution of the ore sample was shown in Figure 1.

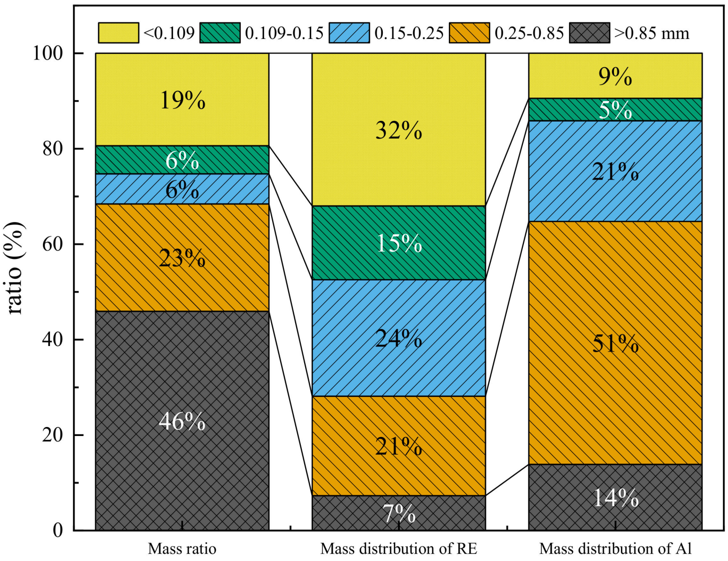

Figure 1. Mineral mass, proportion of rare earth and aluminum in different particle sizes.

It can be seen that the content of mineral particle accounted for 68.43% when their particle size was larger than 0.25 mm. Rare earth elements were mainly distributed in small and medium-sized mineral particles, while aluminum was distributed in medium-sized mineral particles.

2.2. Experimental Method

The column leaching was the main method in this experiment. Before weighing rare earth ore samples, we mixed them well and took samples by the quartering method. Then, 250 g ore samples were weighed from each group and put into the leaching column; then, we placed a filter paper on the surface to make the leaching agent flow evenly. Different concentrations and different molar ratios of composite leaching solution were configured. In accordance with the liquid–solid ratio of 2:1, the composite leaching solution was slowly added into the rare earth ore through the speed-controlled leaching device.

The main instruments in this experiment include a 50 mm glass exchange column, pH meter, constant flow pump, electronic balance, funnel, constant temperature oven, etc. The schematic diagram of the column leaching apparatus is shown in Figure 2.

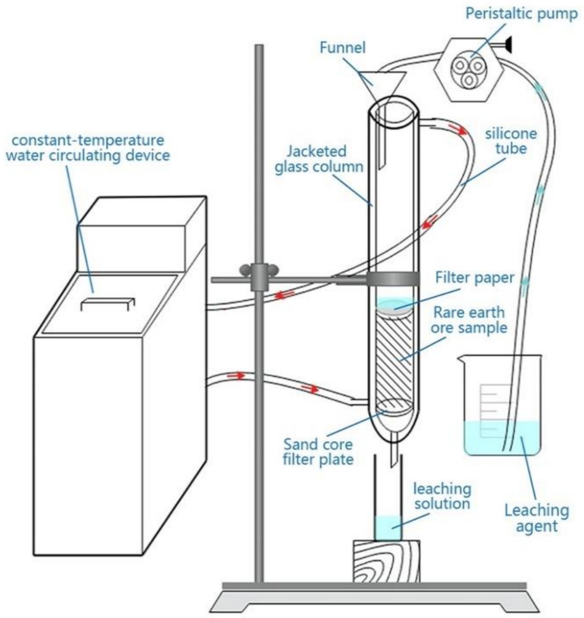

Figure 2. Column leaching apparatus.

After the leaching solution was collected and reached a certain liquid accumulation, the collecting tube was replaced and we recorded the time. The reaction equation of the leaching process can be expressed as:

$$(\mathrm{NH_4})_3\mathrm{Cit} + \mathrm{RE}^{3+} \leftrightarrows \mathrm{RECit} + 3\mathrm{NH_4}^{+}$$

$$3\mathrm{CH_3COONH_4} + \mathrm{RE}^{3+} \rightleftarrows (\mathrm{CH_3COO})_3\mathrm{RE} + 3\mathrm{NH_4}^{+}.$$

The contents of rare earth and aluminum were determined by ICP-MS (IRIS Intrepid) [21]. All the chemicals in this study were purchased from Sinopharm Chemical Reagent Co, Ltd. (Shanghai, China). The reagents used in the experiments were analytically pure. In this study, deionized water was produced by the water purification system, and all experiments were repeated three times.

2.3. Analysis Method

The leaching reaction of weathered crust elution-deposited rare earth ore is a typical liquid–solid heterogeneous reaction. The clay mineral particle in the weathered crust elution-deposited rare earth ore can be regarded as a spherical particle, and the leaching process can be described by the "shrinking core model" [22,23]. The whole leaching process can be divided into five steps: external diffusion → internal diffusion → on exchange → internal diffusion → external diffusion [24]. The kinetics of leaching can be divided into internal diffusion control and external diffusion control. It is called hybrid control when multiple rate-limiting steps control the reaction process. The schematic diagram of the RE leaching process is shown in Figure 3.

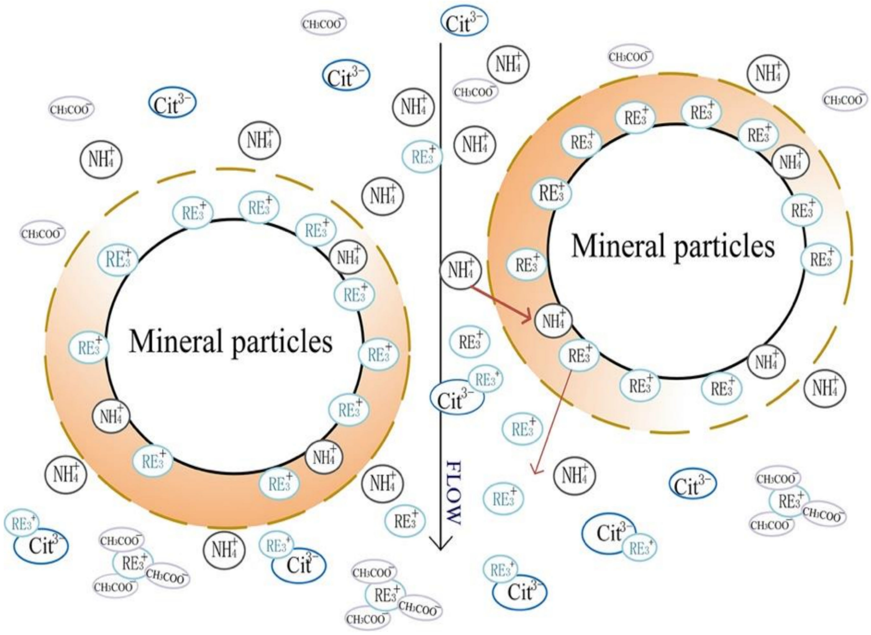

Figure 3. The schematic diagram of the RE leaching process.

There may be four dynamic control models for the leaching of weathered crust elution-deposited rare earth ore [25]:

(1) Kinetic equations for chemical reaction control

$$1 - (1 - \alpha)^{1/3} = k_1 t \tag{1}$$

(2) Kinetic equations for external diffusion control

$$1 - (1 - \alpha)^{1/3} = k_2 t \tag{2}$$

(3) Kinetic equations for internal diffusion control

$$1 - \frac{2}{3}\alpha - (1 - \alpha)^{2/3} = k_3 t \tag{3}$$

(4) Kinetic equation of hybrid control

$$1 - (1 - \alpha)^{1/3} = \frac{k_1 k_2}{k_1 + k_2} \frac{C_0 M}{r_0 p} t \tag{4}$$

where k_1, k_2, and k_3, are the reaction rate constants of different steps, which respectively represent the constants related to leaching conditions and material properties, min^{-1}. α is the rare earth leaching efficiency (%), C_0 is the initial concentration of the leaching agent, mol/L, r_0 is the particle size of the ore, mm, p is the molar density of the rare earth ore, mol/m^3, and M is the mass of the rare earth ore, g. All the units of the quantities would be transformed into international units during the calculation.

This model was restricted in the range of column leaching experiments. In this experimental design, column leaching was used to simulate in situ leaching technology.

3. Results and Discussions

3.1. Effects of Different Molar Ratios in Compound Ammonium Carboxylate on Leaching Process

In this experiment, the ammonium concentrations of compound ammonium carboxylate were set as 0.2 mol/L. On this basis, the molar ratios of ammonium acetate and ammonium citrate were 1:9, 3:7, 5:5, 7:3, and 9:1 to prepare mixed ammonium carboxylate leaching agents for pillar leaching. The influence of different molar ratios of the compound ammonium carboxylate leaching agent on the leaching rates of rare earth and aluminum are shown in Figure 4.

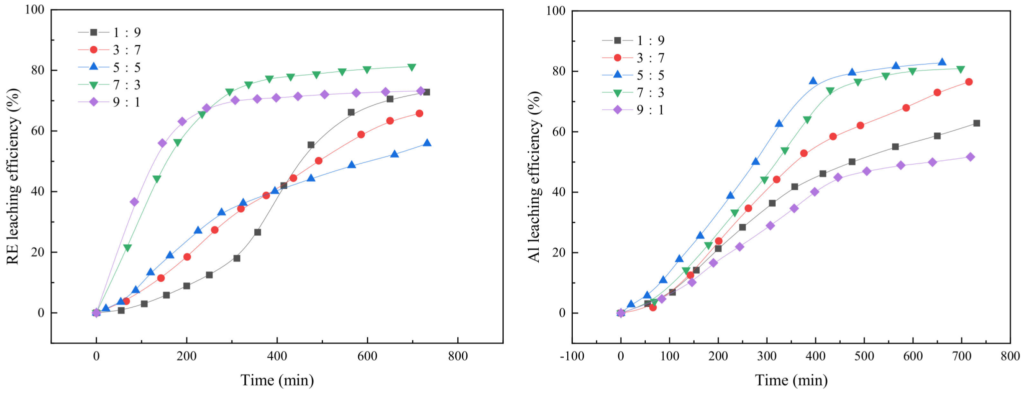

Figure 4. Effects of the molar ratio of leaching agent on the leaching processes of RE and Al.

As can be seen from Figure 4, the higher the molar ratio of ammonium acetate in the leaching agent was, the faster the leaching rate of rare earth was, and the earlier the leaching equilibrium was reached. The leaching rates of rare earth were relatively fast when the molar ratios of compound ammonium carboxylate were 7:3 and 9:1, reaching the ion-exchange equilibrium during 200–250 min approximately. In the same period, the leaching rates of the other groups were still rapid, and the leaching reaction did not reach the equilibrium state. The molar ratios of the compound ammonium carboxylate had little effect on the leaching rate of aluminum. The leaching rate of 5:5 was slightly faster than that of other groups, the leaching rate of 9:1 was the slowest, and other groups had narrow differences. The overall leaching rate of aluminum tended to balance around 400 min. In fact, due to the molar ratio of ammonium acetate and ammonium citrate changing in a relatively small range, there were narrow differences between the pH of the different solutions. The effects of different molar ratios of compound ammonium carboxylate on the leaching efficiencies of RE and Al are shown in Figure 5.

According to Figure 5, the best leaching efficiency of rare earth was 82.79% when the molar ratio of ammonium acetate and ammonium citrate was 7:3. Under this condition, the leaching efficiency of rare earth was higher and the leaching efficiency of aluminum was lower than that of the other groups at the same time. The second was 9:1, and the leaching efficiency was 78.80%. When the molar ratio of compound ammonium carboxylate was 5:5, the leaching effect of rare earth was the worst: only 68.15%. The results showed that the leaching effect of rare earth by ammonium citrate alone was better than that by ammonium acetate alone, but the leaching rate was slower. Citric acid contains three carboxyl structures and has a strong coordination effect with rare earth ions, and the complex formed is of good stability [26,27]. Adding an appropriate amount of ammonium citrate can significantly improve the leaching efficiency on the basis of ammonium acetate as the compound leaching agent.

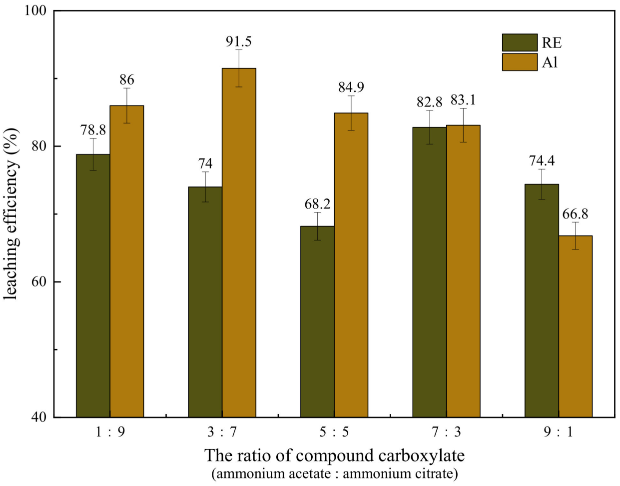

Figure 5. The leaching efficiencies of RE and Al under different molar ratios of compound ammonium carboxylate.

3.2. *Effects of the Ammonium Concentration in Compound Ammonium Carboxylate on the Leaching Process*

3.2.1. Effects on the Leaching Rate of Rare Earth and Aluminum

At the leaching temperature of 298 K, the molar ratio of compound carboxylate was set as 7:3 and the initial pH was 5.0–6.0 (without adjusting) to explore the influence of the ammonium concentration on the leaching kinetics of rare earth and aluminum, as shown in Figure 6.

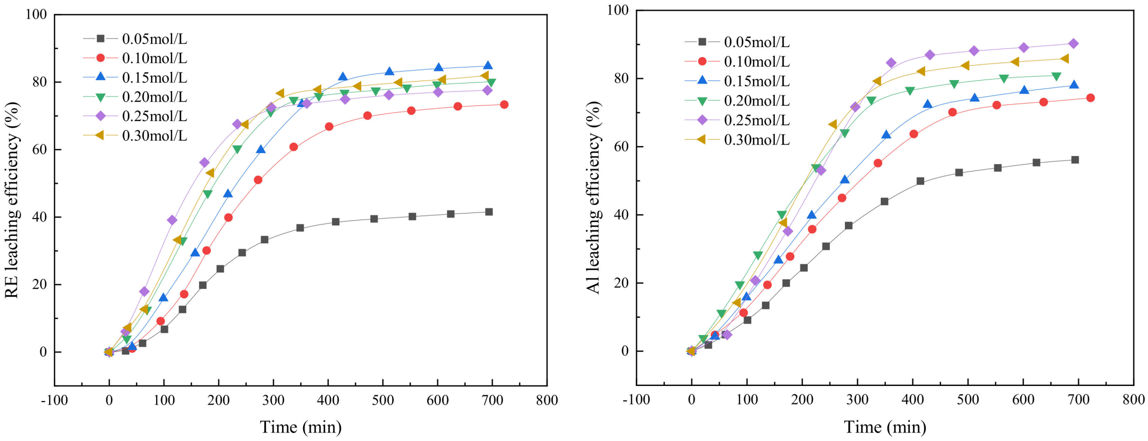

Figure 6. Effects of ammonium concentrations on the leaching rates of RE and Al.

As shown in Figure 6, with the increase of the ammonium concentration in the compound ammonium carboxylate, the rare earth leaching rate accelerated. The leaching rates of rare earth and aluminum increased with the amount of time that passed, and the equilibrium was maintained until the maximum leaching rate was reached. As the ammonium concentration continued to increase, the rare earth leaching rate showed a turning point at about 300 min of 0.2–0.3 mol/L, and the rate slowed down significantly. With the increase of the concentration of compound ammonium carboxylate, the leaching rate of rare earth and aluminum was faster and the time to reach the leaching equilibrium was shorter. The main reason is that the ammonium ion concentration difference between the flow center of the leach solution and the surface of ore particle is larger as the ammonium ion concentration in the leaching agent increases. The diffusion ability of the compound ammonium carboxylate will increase, and the enhancement of the ammonium ion concentration will increase the strength of the ion exchange reaction between NH_4^+ and RE^{3+} or Al^{3+}, thus speeding up the leaching [28,29]. In addition, the higher the ammonium concentration in the compound carboxylate, the greater its viscosity, and the slower the penetration rate of compound ammonium carboxylate in the ore body. When the ammonium concentration increased from 0.1 to 0.3 mol/L, the viscosity of the solution rose from 0.9312 $\times 10^{-3}$ to 0.9624 $\times 10^{-3}$ pa·s, which causes a little effect on the leaching rate of rare earth and aluminum. As reflected in Figure 6, the leaching rate of 0.3 mol/L at the same time of the initial stage was not as high as that of other groups, but the leaching rate was faster than that of the others. The effects of different ammonium concentrations on the leaching efficiencies of RE and Al are shown in Figure 7.

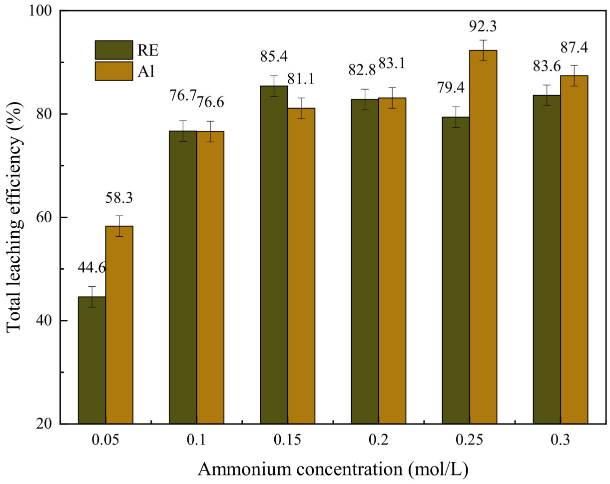

Figure 7. The leaching efficiency of RE and Al under different compound ammonium carboxylate concentrations.

According to Figure 7, when the ammonium concentration of compound ammonium carboxylate increased from 0.05 to 0.15 mol/L, the overall leaching efficiencies of rare earth and aluminum increased significantly. When the concentration continued to increase, the leaching efficiency of rare earth would not continue to increase, but aluminum would still increase, which would increase the cost of subsequent impurity removal and affect the purity of rare earth products. The leaching efficiency of rare earth was the highest at 0.15 mol/L. Therefore, when determining the ammonium concentration of compound ammonium carboxylate, appropriately increasing its concentration is beneficial to enhance the leaching efficiency of rare earth and reduce the production cost. However, the leaching concentration should not be too large. Although the high concentration of compound ammonium carboxylate has strong ion exchange ability, it will also lead to the increase of solution viscosity and reduce the rare earth leaching efficiency.

3.2.2. Dynamic Analysis

It can be seen from Figure 5 that the leaching process of rare earth and aluminum can be divided into three stages. The first stage is the initial stage of the leaching process, which is slow and unstable. The second stage is a fast and stable stage, during which the leaching rate of rare earth and aluminum increases rapidly. The third stage is the equilibrium stage, in which the leaching efficiency reaches the maximum and equilibrium. Obviously, the second stage is the key step of the reaction. The data of this stage in Figure 5 are selected and introduced into four dynamic control models to determine to which dynamic model the leaching of rare earth and aluminum belongs to. The results showed that the linear relationship between $1-\frac{2}{3}\alpha-(1-\alpha)^{\frac{2}{3}}$ and t is good, as shown in Figure 8. The slope and fitting coefficients of the fitting curve are shown in Table 3, and the fitting coefficients are all greater than 0.98. This indicated that the dynamic equation of internal diffusion control can fit the leaching process of rare earth and aluminum very well, and the leaching process of weathered crust elution-deposited rare earth ore belongs to the step control of internal diffusion.

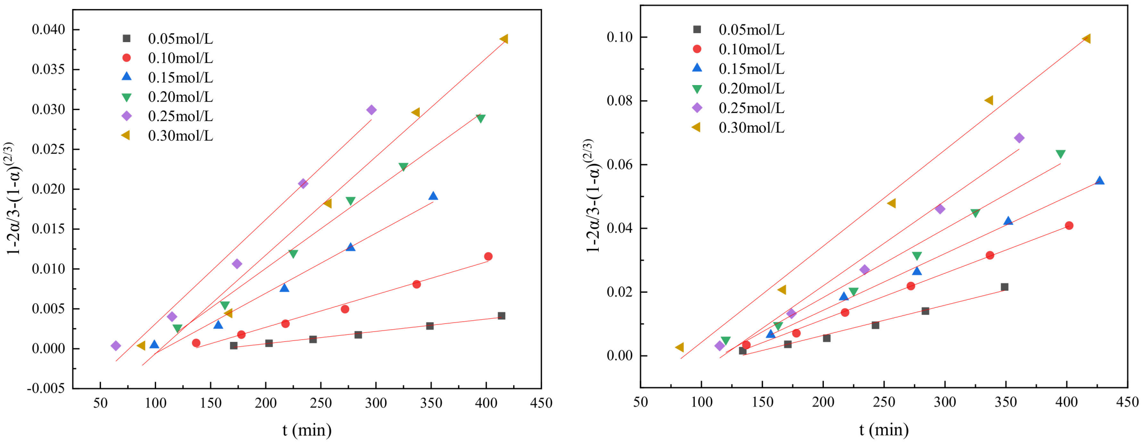

Figure 8. The fitting curve of internal diffusion control model and time.

Table 3. Apparent diffusion rate constant and correlation coefficient values.

Concentration /(mol/L)		**RE**		**Al**	
		k/min^{-1}	**R^2**	**k/min^{-1}**	**R^2**
Concentration of ammonium ion	0.05	0.00009690	0.98614	0.00010741	0.98025
	0.10	0.00021566	0.98411	0.00018680	0.99730
	0.15	0.00032639	0.98740	0.00025875	0.99682
	0.20	0.00043999	0.99500	0.00034683	0.98037
	0.25	0.00049621	0.98134	0.00037845	0.98224
	0.30	0.00053514	0.98321	0.00043948	0.99070

The internal diffusion kinetic equation can be expressed in the form related to the ammonium ion concentration, as shown in Equation (5):

$$1-\frac{2}{3}\alpha-(1-\alpha)^{\frac{2}{3}}=k_0\left(c_0+\mathrm{c_i}\right)^n t \tag{5}$$

According to the original internal diffusion dynamics equation, it can be found that:

$$k=k_0(c_0+c_\mathrm{i})^n \tag{6}$$

or

$$\ln k=n\ln(c_0+c_\mathrm{i})+\ln k_0 \tag{7}$$

where k_0 is the apparent rate constant; n is the empirical reaction order; and C_0 and C_i are the initial ammonium acetate concentration and ammonium citrate concentration in the extract.

The calculated data is substituted into the equation, and the result is shown in Figure 9.

It can be seen from Figure 9 that the logarithm of the apparent rate constant has a good linear relationship with the reciprocal of ammonium ion concentration in the compound ammonium carboxylate, and the fitting coefficient was greater than 0.97, which further verifies that the leaching process is controlled by internal diffusion. The slope of the fitting curve was the empirical reaction order about the concentration. It calculated that the reaction order of rare earth was 0.9766 and that of aluminum was 0.7943. To some extent, the empirical reaction order showed the effects of ammonium ion concentration on the ion-exchange reaction in the leaching process. The results revealed that the leaching of RE depends more strongly on the ammonium concentration than Al.

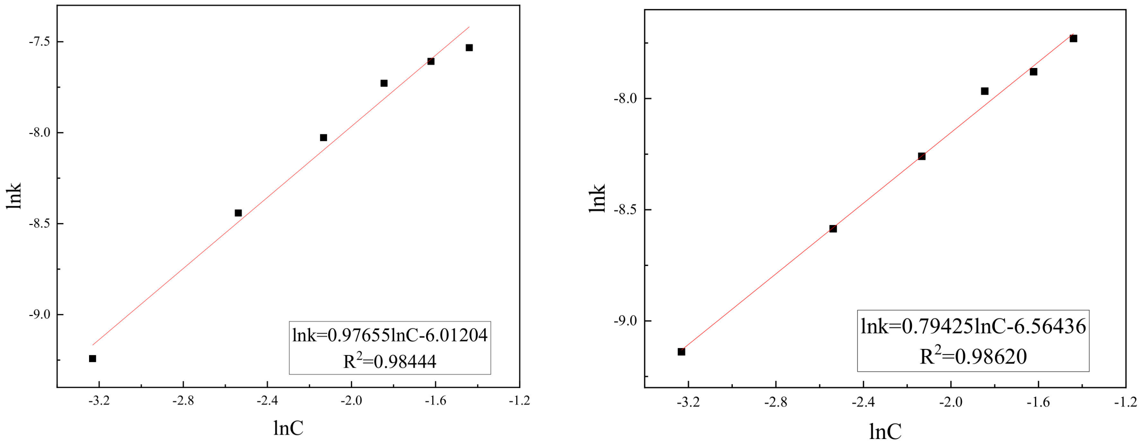

Figure 9. Relationship between ln$k$ and ln$C$ in the RE and Al leaching processes.

3.3. *Effect of Experimental Temperature on Leaching Process*

3.3.1. Effects on the Leaching Rate of Rare Earth and Aluminum

When the concentration of compound ammonium carboxylate was fixed as 0.15 mol/L and the initial pH was 5.5–6.0 (without adjusting), the leaching temperatures were changed to investigate the effects of experimental temperatures on the leaching process of RE and Al.

It can be seen from Figure 10 that in the initial stage of the reaction, the leaching rate of rare earth and aluminum increases rapidly with time. As the temperature increased, the leaching rate of rare earth and aluminum increased significantly, and the time required to reach the leaching equilibrium decreased. This is because the rise of temperature accelerates the thermal movement of ions in the leaching reaction, which increased the diffusivity of the compound ammonium carboxylate. The diffusion rate of ammonium ions in the solution moving to the ore particles and the RE or Al ions in the ore migrating to the solution both increased. In the same volume, more ammonium ions will participate in the reaction, and the leaching efficiency of rare earth and aluminum will be improved [30,31].

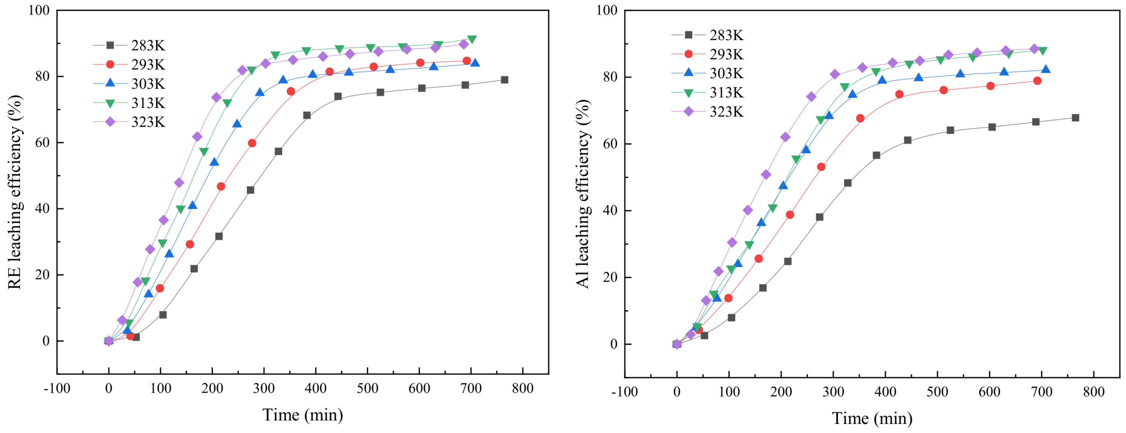

Figure 10. Effects of experimental temperatures on the leaching rate of RE and Al.

In addition, the leaching temperature also plays a decisive role in the permeation rate of the compound ammonium carboxylate in the ore body. The rise of temperature will lead to the decrease of the viscosity of compound ammonium carboxylate, and mineral particles and water will produce thermal expansion after contacting with each other. Due to the difference of their thermal expansion performance, the pore water pressure is produced [32], thus increasing the permeability of the ore body. The higher the leaching temperature, the faster the permeation rate of the compound ammonium carboxylate, thus the time required for the leaching will be greatly reduced, and the production efficiency can be significantly improved. The effects of experimental temperatures on the leaching efficiencies of RE and Al are shown in Figure 11.

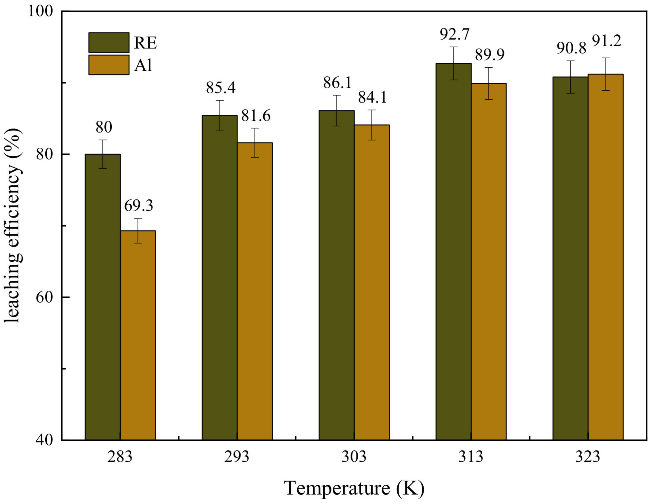

Figure 11. Leaching efficiencies of rare earth and aluminum at different temperatures.

With the increase of the leaching temperature, the leaching efficiencies of both rare earth and aluminum increased gradually. The leaching efficiency of rare earth reached the maximum value at 313 K, which is 92.70%. The results showed that the leaching effect was good at about 313 K, and the leaching efficiency of rare earth was high. Therefore, compared with winter, summer is more suitable for the leaching process.

3.3.2. Dynamic Analysis

The key stage of the leaching process was the rapid and stable reaction of rare earth and aluminum with compound ammonium carboxylate, and the leaching rate rose rapidly. After fitting the data in Figure 9, the result is shown in Figure 12. It was found that there was a good linear relationship between $1 - 2\alpha/3 - (1 - \alpha)^{2/3}$ and t, and the fitting coefficient R^2 was large: both were greater than 0.98. Its apparent rate constant and fitting coefficients are shown in Table 4, which indicated that the dynamic process of internal diffusion control can fit the leaching process of rare earth and aluminum very well, and the process of leaching weathering crust eluvial rare earth ore by compound carboxylate is controlled by the steps of internal diffusion.

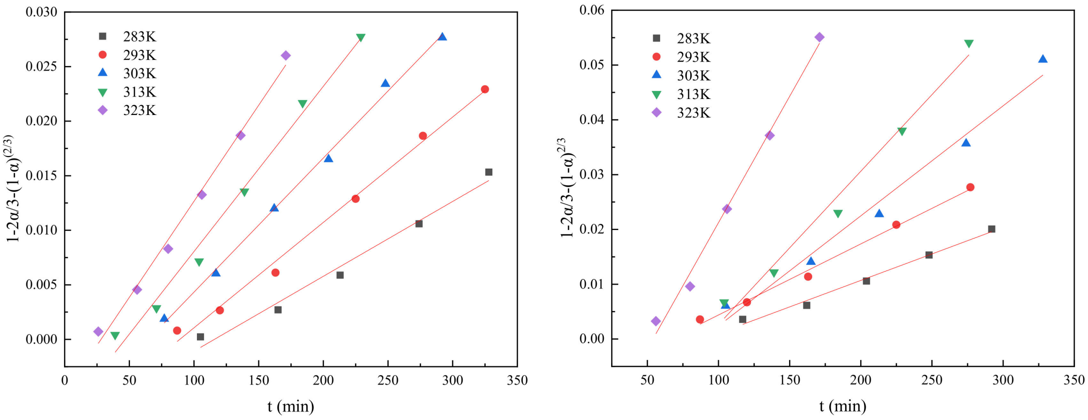

Figure 12. The fitting curve of internal diffusion control model and time.

Table 4. Internal diffusion apparent rate constant and correlation coefficient values.

Temperature /(K)		RE		Al	
		k/min^{-1}	R^2	k/min^{-1}	R^2
compound ammonium carboxylate	283	0.00030913	0.98198	0.00014884	0.98840
	293	0.00040418	0.99373	0.00020115	0.99399
	303	0.00047308	0.99694	0.00026534	0.98033
	313	0.00060235	0.98893	0.00035749	0.98302
	323	0.00067172	0.99306	0.00039135	0.99263

According to the Arrhenius equation, the apparent rate constant k can be expressed as Equation (8):

$$k = Ae^{-\frac{E_a}{RT}} \tag{8}$$

where k is the apparent rate constant, min^{-1}; A is the prefactor, E_a is the appare nt activation energy, kJ/mol; T is the reaction temperature, K; and R is the ideal gas constant.

From the obtained apparent rate constant, the relationship between ln$k$ and 1/T was drawn. It can be seen from Figure 13 that the linear relationship between ln$k$ and 1/T was good, and the fitting coefficient R^2 was greater than 0.98. The reaction activation energy of rare earth and aluminum extracted by compound ammonium carboxylate can be calculated from the slope of the fitting line. The results are shown in Table 5.

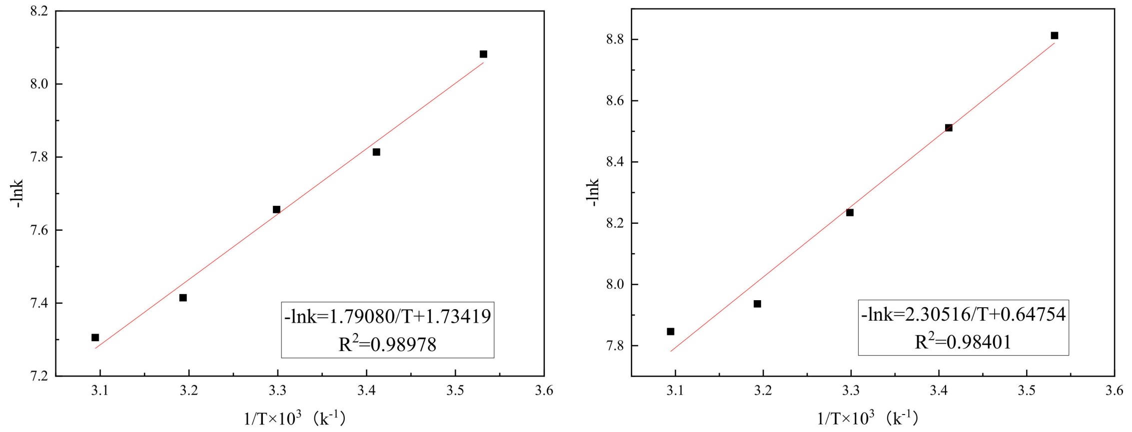

Figure 13. The relationship between ln$k$ and 1/T.

Table 5. Leaching reaction order and activation energy of RE and Al with compound ammonium carboxylate.

Compound Carboxylate	RE	Al
reaction order	0.97655	0.79425
reaction activation energy (kJ/mol)	14.8887	19.16512

As can be seen from Table 5, the empirical reaction order of rare earth was greater than aluminum, indicating that the influence of ammonium concentration on rare earth leaching was greater than that of aluminum. By comparing the leaching of rare earth and aluminum, it can be seen that the time for aluminum to reach the maximum leaching equilibrium was longer than that of rare earth. Under the same conditions, the leaching activation energy of aluminum was larger than that of rare earth, which indicated that the aluminum was more difficult to be leached. However, the apparent leaching rate constant of aluminum was higher than that of rare earth, indicating that the leaching rate of aluminum was faster than that of rare earth in the actual reaction process. The internal diffusion kinetics equations for temperature and concentration could be expressed as Equation (9):

$$1-\frac{2}{3}\alpha-(1-\alpha)^{\frac{2}{3}}=k'\cdot(C_0+C_i)^{n}\cdot e^{-\frac{E_a}{RT}}\cdot t. \tag{9}$$

In the equation $k_0 = k'e^{-\frac{E}{RT}}$, k_0 is the intercept of the fitted curve in Figure 12, and then the corresponding activation energy and reaction experimental temperature 298 K are substituted in to obtain the pre-reaction factor k'. The kinetic equations of the leaching of rare earth and aluminum by compound ammonium carboxylate were obtained, as shown in Equation (10) and Equation (11).

Compound carboxylate—RE:

$$1-\frac{2}{3}\alpha-(1-\alpha)^{\frac{2}{3}}=0.1765\cdot(C_0+C_i)^{0.9766}\cdot e^{-\frac{14889}{8.314T}}\cdot t. \tag{10}$$

Compound carboxylate—Al:

$$1-\frac{2}{3}\alpha-(1-\alpha)^{\frac{2}{3}}=0.5233\cdot(C_0+C_i)^{0.7943}\cdot e^{-\frac{19165}{8.314T}}\cdot t. \tag{11}$$

The above empirical dynamic equations are helpful to optimize the leaching process of rare earth and aluminum, which could provide some theoretical guidance for the mining and leaching of weathered crust elution-deposited rare earth ore with novel compound ammonium carboxylate.

3.4. Effects of Different pH Conditions on Leaching Process

The leaching rate of rare earth is related not only to the type of leaching agent but also to the pH of the leaching solution. At the leaching temperature of 298 K, the molar ratio of ammonium acetate and ammonium citrate was set as 7:3. Then, we changed the pH of the compound ammonium carboxylate to explore the influence of the pH on the leaching rate of rare earth and aluminum. The results are shown in Figure 14.

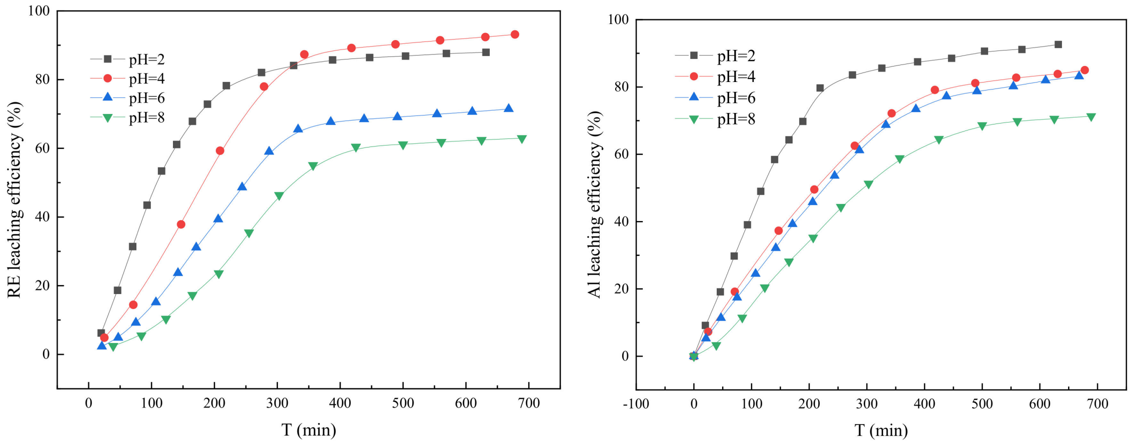

Figure 14. Effects of pH on the leaching rates of RE and Al.

As can be seen from Figure 14, the leaching rates of rare earth and aluminum are significantly different at a pH of 2–8. In the initial stage of leaching, the stronger the acidity of the compound ammonium carboxylate, the faster the rate of rare earth leaching. The leaching reached the equilibrium point firstly, and then the leaching speed began to slow down. This is because with the increase of H^+ adsorbed by the raw ore, the surface potential of mineral particles moved forward. The dissociation of organic acids could increase the affinity for rare earth ions by stimulating the internal pronation of ion-adsorbed rare earth ores, thus activating rare earth extraction. In addition, under strong acidic conditions, when pH was 2–4, rare earth in other phase states would be transferred into the leachate, leading to an increase in the leaching rate of rare earth. The dissolution of partially adsorbed hydroxyl aluminum also resulted in a significant increase in the leaching rate of aluminum. The effects of pH on the leaching efficiencies of RE and Al are shown in Figure 15.

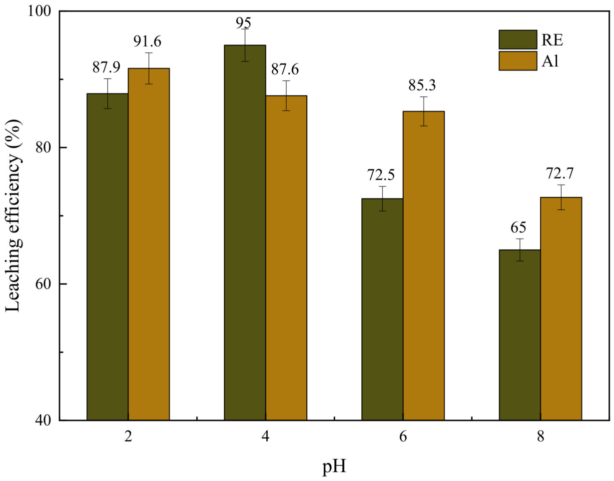

Figure 15. The leaching efficiencies of RE and Al under different pH conditions.

When pH = 4.0, the leaching effect of rare earth was the best, because H^+ can also leach rare earth ions from rare earth ore to some extent. Appropriately increasing the concentration of hydrogen ions in the leaching agent can improve the leaching efficiency of rare earth. However, lowering the pH will lead to the increase of aluminum leaching and the consumption of hydrogen ions in the solution, which would inhibit the leaching of rare earth [24,33]. At the same time, when the concentration of hydrogen ion was high, citric acid mainly exists in the form of H_3Cit and H_2Cit^-, which has a poor coordination effect on rare earth, leading to the reduction of rare earth leaching. If the pH is too high, rare earth ions would tend to hydrolyze, which would also lead to the reduction of rare earth leaching efficiency. The leaching efficiency of impurity aluminum decreased with the increase of pH. The leaching efficiency of Al was the highest when the pH was 2.0. Therefore, when the pH of compound ammonium carboxylate was 4–6, the total leaching efficiency was relatively stable. The surface of clay mineral structure contains hydroxyl groups and hydroxyl groups stripped of hydrogen ions, which show a certain acid buffering in the leaching process. As can be seen from Figure 14, the more suitable pH for rare earth leaching using compound carboxylate was 4.0.

4. Conclusions

The column leaching method was used to simulate the in situ leaching technology for extracting rare earth elements from weathered crust elution-deposited rare earth ore with compound ammonium carboxylate, and the best leaching conditions of rare earth ore with compound ammonium carboxylate were obtained: the ammonium concentration of compound ammonium carboxylate was 0.15 mol/L, the leaching pH was 4.0, and the leaching efficiency of rare earth was the highest when the ambient temperature was 313 K. The effects of compound ammonium carboxylate were better than that of the single leaching agent. Through the calculation and data fitting, it can be concluded that the leaching processes of rare earth and aluminum from weathered crust elution-deposited rare earth ore by compound carboxylate were controlled by the internal diffusion dynamics model. When the compound ammonium carboxylate was used for rare earth extraction, the reaction kinetics equations of rare earth and aluminum were

$$\mathrm{RE}: 1-\frac{2}{3}\alpha-(1-\alpha)^{\frac{2}{3}}=0.1765\cdot\left(\mathrm{C}_0+\mathrm{C}_\mathrm{i}\right)^{0.9766}\cdot e^{-\frac{14889}{8.314T}}\cdot t$$

$$\mathrm{Al}: 1-\frac{2}{3}\alpha-(1-\alpha)^{\frac{2}{3}} = 0.5233\cdot(\mathrm{C}_0+\mathrm{C}_\mathrm{i})^{0.7943}\cdot e^{-\frac{19165}{8.314T}}\cdot t$$

In the temperature range of 283–323 K, the apparent activation energy of rare earth was 14.89 kJ/mol and that of aluminum was 19.17 kJ/mol. The reaction order of rare earth was 0.98 and that of aluminum was 0.79. The activation energy of reaction between carboxylate and rare earth was less than that of the reaction with aluminum, and the influence of ammonium ion concentration on rare earth leaching was greater than that of aluminum. The study on the leaching kinetics of rare earth by compound ammonium carboxylate would provide a new way for leaching weathered crust elution-deposited rare earth ore with high efficiency, low consumption and environmental protection leaching agents. It could provide a theoretical basis for the popularization and industrial application of new leaching agents at the present stage. In the future, the complexation equilibria and acid-base reactions involving acetate and citrate ions in the ion exchange reaction would be investigated to further reflect the leaching mechanism of rare earth with compound ammonium carboxylate.

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