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Leaching Behavior of Rare Earth Elements and Aluminum from Weathered Crust Elution-Deposited Rare Earth Ore with Ammonium Formate Inhibitor

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Abstract: In situ leaching of weathered crust elution-deposited rare earth ore usually uses ammonium sulfate as the leaching agent, which poses challenges such as low mass transfer efficiency, high consumption of the leaching agent and long leaching periods. In order to intensify the leaching process of rare earth elements and reduce the impurity of leaching accompanying rare earth, ammonium sulfate and ammonium formate were mixed as a novel compound leaching agent to treat weathered crust elution-deposited rare earth ore. The effects of ammonium formate concentration, liquid/solid ratio, leaching agent pH and leaching temperature on the leaching process of rare earth (RE) and aluminum (Al) were investigated and evaluated using the chromatographic plate theory. Results showed that ammonium formate could effectively enhance the mass transfer efficiency of rare earth and significantly inhibit the mass transfer efficiency of aluminum. Leaching agent pH has a greater impact on the mass transfer efficiency of aluminum. A higher leaching temperature could enhance the mass transfer efficiency of rare earth and aluminum by providing a driving force to overcome the resistance of diffusion. The optimum conditions for leaching rare earth and aluminum are 0.1 mol/L ammonium sulfate compounded with 0.032 mol/L ammonium formate, pH 4–8 of the leaching agent, 0.8:1 liquid:solid (mL/g) ratio and room temperature. Under this condition, the mass transfer efficiency of rare earth was improved, and the mass transfer efficiency of aluminum was significantly inhibited.

Keywords: weathered crust elution-deposited rare earth ore; ammonium formate; leaching; mass transfer

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1. Introduction

Rare earth elements have an extremely wide range of uses in the field of modern new technologies and are known as the "vitamin of modern industry" [1,2]. With the development and application of new rare earth materials, the market demand for rare earth elements is increasing year by year, especially in the field of new energy. With the increasing global emphasis on "carbon emissions", it is estimated that by 2030, the demand for rare earth oxides such as Nd, Dy and Tb in the green energy industry will exceed 50,000 tons, an increase of more than 50% compared with 2020, which will greatly stimulate the exploration and development of rare earth mineral resources, especially medium- and heavy-heavy rare earth resources [3].

Weathered crust elution-deposited rare earth ore is rich in medium and heavy rare earths [4]. It has the characteristics of complete rare earth distribution, low radioactivity, simple extraction process, etc., and has extremely high mining value [5]. And, it is one of the main rare earth mineral resources that have been economically exploited at present. Granite and volcanic rocks are the main parent rocks of weathered crust elution-deposited rare earth ore [6,7]. During the weathering process, aluminosilicate minerals such as feldspar and hornblende in the parent rock are eroded into clay minerals with a large amount of negative charges on the surface, such as kaolinite and halloysite, and rare earth accessory minerals such as bastnaesite, allanite and sphene are liberated to release rare earth ions [8]. Through the accumulation of external geological processes over time, rare earth ions have enriched and integrated into clay minerals. The rare earth elements in weathered crust elution-deposited rare earth ore are mainly adsorbed on the surface of clay minerals in the form of hydrated cations and hydroxyl hydrated cations, which are difficult to enrich using conventional physical separation processes and can only be enriched and recovered via ion exchange [9].

Rare earth workers have made great efforts to develop and utilize weathered crust elution-deposited rare earth ore for a long time, have made great progress in leaching methods and leaching agents and developed three generations of leaching technologies of "pool leaching, heap leaching, and in-situ leaching" [10]. The leaching agent has also developed from sodium chloride to ammonium sulfate and magnesium sulfate [10,11]. In the process of in situ leaching, the migration of the leaching agent solution in the ore body slowly infiltrates the ore body under the action of potential energy such as gravity potential, capillary potential and macro-pressure potential [12]. At the same time, fine clay mineral particles migrate with the leaching agent, leading to blockage of the seepage channel, which results in a serious leaching tail dragging phenomenon, increased consumption of the leaching agent and a prolonged leaching cycle [13]. The leaching ability of ammonium sulfate for rare earths is not strong enough, and rare earths are prone to re-adsorption during the leaching process, which reduces the leaching efficiency of rare earth [14]. Therefore, to explore the strengthening mass transfer process and improve rare earth leaching mass transfer efficiency, shortening the leaching period is the current rare earth mine focus of the research hotspot.

Organic aids, which are renewable and easy to decompose, are regarded as green chemicals with less impact on the environment, and have been widely used in mineral processing and metallurgy. In the leaching process, a small amount of organic leaching aid is usually added to the leaching agent to enhance the rare earth leaching by improving the ion exchange, wetting and seepage diffusion properties of the leaching agent [15,16]. Researchers have selected some organic aids to study their enhanced leaching effects on rare earths, among which natural macromolecular organic compounds and some small molecular organic acids have been focused on. Luo et al. [17] found that when 0.1 wt% fulvic acid was added, the concentration of the leaching agent could be reduced by 1/4, while the leaching efficiency of rare earths increased by 8.38%. Wang et al. [18] found that six small molecule organic acids, such as acetic acid, malonic acid and citric acid, can improve the leaching efficiency of rare earths to varying degrees, and their strengthening effect is related to the coordination ability of organic acids with rare earths. Feng et al. [19] used ammonium formate to enhance the leaching rate of weathered crust elution-deposited rare earth ore, and found that ammonium formate can not only effectively strengthen the leaching efficiency of rare earth, but can also effectively inhibit the leaching of aluminum. In addition, carboxyl-containing organic acids, sulfosalicylic acid, EDTA and other complexing agents have been used as leaching aids which are beneficial to the leaching of rare earth to a certain extent [16,20,21]. In addition, some organic aids can also react with mineral surfaces to promote rare earth leaching by improving the wettability of the mineral surface, reducing the potential of the mineral surface or destroying chemical bonds. At present, there are many research projects on the leaching process of weathered crust elution-deposited rare earth ore, but there are few research studies on the leaching mass transfer process, which restricts the improvement of the efficient mining level and the technological progress of in situ leaching of weathered crust elution-deposited rare earth ore.

Ammonium formate, as a cheap and environmentally friendly surfactant, has hydrophilic groups, which can improve the hydrophilicity of the leaching agent and reduce the surface tension of the leaching agent. Therefore, in this paper, ammonium formate and the conventional rare earth leaching agent ammonium sulfate are compounded to form a composite leaching agent to explore the influence of ammonium formate concentration, temperature, liquid–solid ratio and pH on the mass transfer process of rare earth and aluminum in a column leaching simulation of in situ leaching of weathered crust elution-deposited rare earth ore, and the leaching process is analyzed by combining it with the chromatographic plate theory to reveal the mechanism of ammonium formate strengthening mass transfer. The purpose is to optimize the leaching process, reduce the consumption of the leaching agent, improve the seepage velocity of the leaching agent, shorten the leaching period and provide a theoretical basis for the development of a high-efficiency leaching agent and technology for weathered crust elution-deposited rare earth ore.

2. Materials and Methods

2.1. Materials

The experimental rare earth ore samples were collected from Guangdong province in southern China. The content of the exchangeable state rare earth (RE) and aluminum (Al) in the rare earth ore were 0.17 wt.% and 0.015 wt.%, respectively. The percentage of rare earth oxide (REO) content can reflect the utilization value of rare earth ores to a certain extent. The partitioning of the ion-exchangeable state rare earth, determined via inductively coupled plasma mass spectrometry (ICP-MS, Agilent 7700×, Agilent Technologies Inc., Shanghai, China), is shown in Figure 1. It was shown that 73.19 wt.% of rare earth was light rare earth, and the middle and heavy rare earth were 26.81 wt.%; it mainly contained light rare earth.

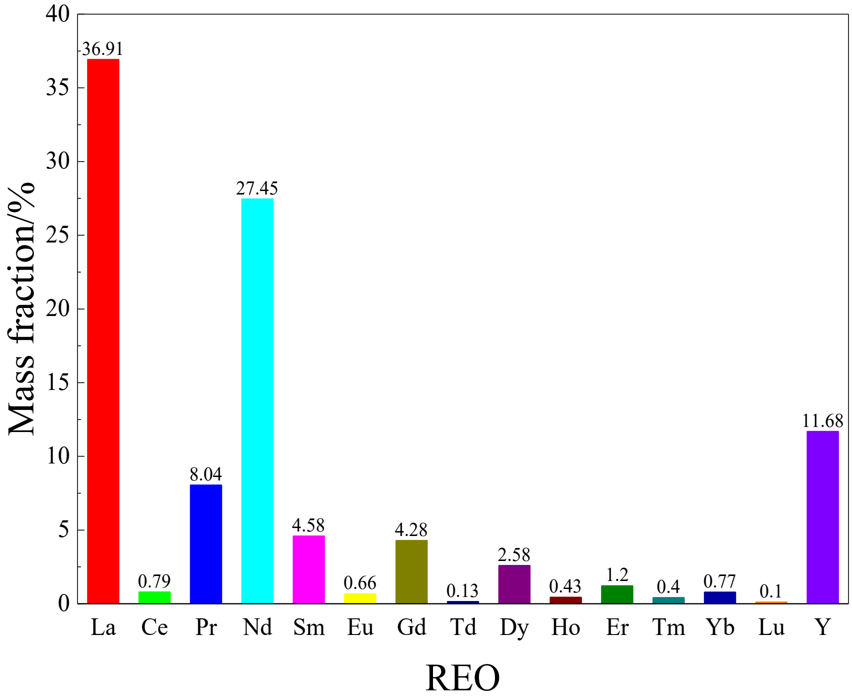

Figure 1. Partitioning of the ion-exchangeable rare earth in the rare earth ores.

Ammonium sulfate ($(NH_4)_2SO_4$), ammonium formate ($HCOONH_4$), zinc oxide (ZnO), ethylenediamine tetraacetic acid disodium, ascorbic acid, sulfosalicylic acid, xylenol orange, hexamethylenetetramine, hydrochloric acid and ammonium hydroxide were purchased from Sinopharm Chemical Reagent Co., Ltd., Shanghai, China, with analytical grade. Standard solution of zinc was purchased from National Center of Analysis and Testing for Nonferrous Metals and Electronic Materials (NCATN).

2.2. Column Leaching Experiment

The experiments were processed at ambient temperature in a glass column with an inner diameter of 45 mm and a column length of 500 mm, which can be seen as a chromatographic column. A glass column with a jacket setting, which can be applied to hot water in the jacket by using precision-type thermostat to change the temperature in the leaching process, was used. A total of 250 g of dried rare earth ore sample, which was air dried at 70 °C for 12 h, was packed uniformly in the glass column. A sand core filter plate was fixed at the bottom of the leaching column to retain soil particles and two layers of filter paper were put on the upper part of the rare earth ore sample to resist preferential flow. The leaching agent was added from the top of the leaching column at a constant flow rate using a peristaltic pump. Sulfuric acid as a pH modifier was added into the leaching solutions and the pH value of the solution was measured with pH-meter (DELTA320). Leachate was collected from the bottom of the leaching column and the concentrations of RE and Al were analyzed using the titration method.

2.3. Analytical Methods

The total content of rare earth (RE) in the leachate was determined via ethylene diamine tetraacetic acid (EDTA) titration using xylenol orange as indicator and hexamethylene tetramine as buffer [19]. 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 aluminum (Al) was analyzed with back titration using a known concentration of zinc solution.

3. Results

3.1. Screening Leaching-Aid Reagent

In order to investigate the effect of the leaching-aid agent on the rare earth leaching process, the leaching efficiency of rare earth was analyzed using a 0.1 mol/L ammonium sulfate solution compound with hydroxypropyl methylcellulose, sesbania gum phthalocyanine or ammonium formate with a strong polar formate ion as a novel compound. The results are shown in Figure 2.

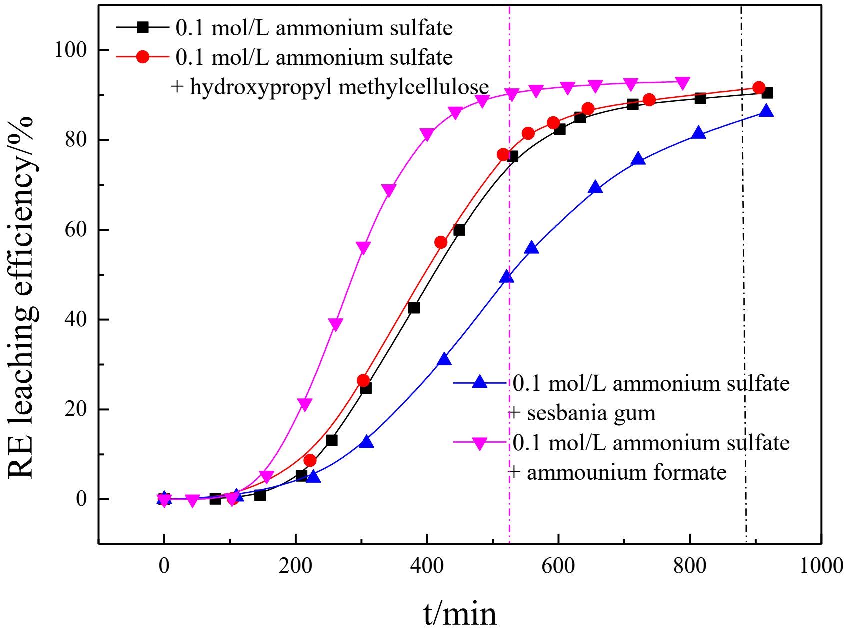

Figure 2. Effect of leaching-aid agents on the leaching efficiency of RE.

It can be observed from Figure 2 that ammonium formate as a leaching-aid agent significantly accelerates the leaching rate of rare earth, and the time for the rare earth leaching to reach equilibrium is greatly shortened. The leaching equilibrium time is shortened by nearly 350 min compared with the leaching of rare earth with single ammonium sulphate. The addition of hydroxypropyl methylcellulose can also speed up the leaching rate of rare earth to a certain extent, but compared with ammonium formate, the promoting effect is not very obvious. Therefore, comparing the leaching effects of these three leaching-aid reagents, it is concluded that the gain effect of ammonium formate is relatively higher. The effect of ammonium formate as a leaching-aid reagent on the leaching process of rare earth and aluminum from weathered crust elution-deposited rare earth ore was investigated in detail.

3.2. Effect of the Ammonium Formate Concentration on Leaching Process of RE and Al

To investigate the mass transfer process and mechanism of rare earth and aluminum from weathered crust elution-deposited rare earth ore with a compound agent of mixed 0.1 mol/L $(NH_4)_2SO_4$ with $HCOONH_4$, the effects of ammonium formate concentration on the leaching process of rare earth and aluminum are presented in Figure 3.

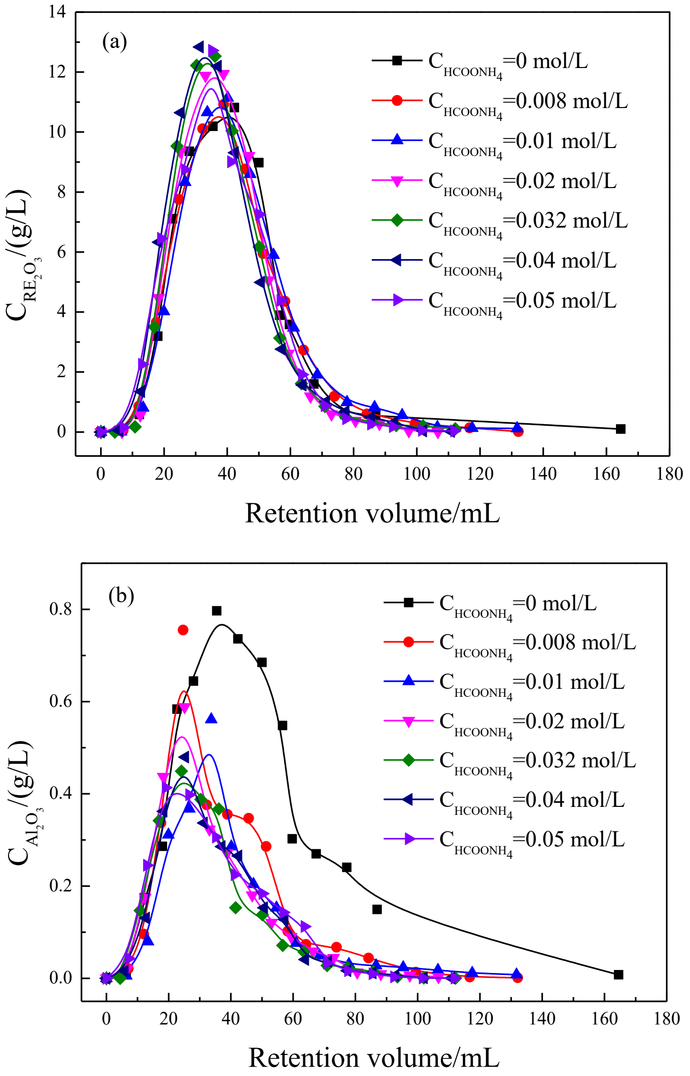

Figure 3. Effects of ammonium formate inhibitor concentration on the leaching curves of: (**a**) RE and (**b**) Al (250 g of ore, $C_{(NH4)2SO4}$ = 0.1 mol/L, μ = 0.5 mL/min and a natural pH 5.5–6.0).

It is found that the concentrations of rare earth and aluminum increase rapidly with the increase in the volume of the leaching solution until the peak value is reached, and then decrease sharply until they reach zero. From Figure 3a, it can be seen that when the compound concentration of ammonium formate is gradually increased to 0.032 mol/L, the peak concentration of rare earth in the leaching solution is gradually increased, and the peak width of the leaching curve is also narrowed. Thus, the leaching mass transfer process of rare earth is enhanced. This may be due to the increase in the concentration of ammonium ions in the leaching agent, so that the larger concentration gradient improves the ability of ammonium ions and rare earth ions to overcome the mass transfer resistance of diffusion to the ore particles and the flow center of the leachate [22]. Therefore, the reaction intensity and efficiency of the ion exchange reaction between ammonium ions and rare earth ions are enhanced. In addition, formate ions can also effectively promote the leaching of rare earth ions, thereby forming a synergistic effect, which promotes the increase in the rare earth ion peak value in the leachate with the increase in the compound concentration of ammonium formate. When the compound concentration of ammonium formate reaches 0.032 mol/L and the compound concentration continues to increase, it can be seen that the leaching curve has basically no obvious change. This may be due to the fact that the promoting effect of formate ions has little influence at this time, and the synergistic effect is weakened.

It can be seen from Figure 3b that when the compounding concentration of ammonium formate is continuously increased to 0.032 mol/L, the peak concentration of aluminum in the leaching solution is continuously decreased, the peak width of the leaching curve is also narrowed and the leaching mass transfer process of aluminum is weakened. This may be due to the fact that the formate ions in the compound leachate act on the surface of the ore particles, so that some of the exchangeable aluminum is converted into inorganic forms of aluminum such as aluminum hydroxide, which remains in the tailings and is not leached. In order to greatly reduce the content of aluminum in the leachate, the peak concentration also decreases as the concentration of the compounded ammonium formate increases. When the compounding concentration of ammonium formate reached 0.032 mol/L and continued to increase its compounding concentration, the leaching curve did not change. This may be due to the fact that continuing to increase the concentration of ammonium formate has little effect on its inhibition of aluminum leaching.

In the process of column leaching of weathered crust elution-deposited rare earth ore, the clay minerals adsorbing the rare earth are regarded as the fixed phase, and the leaching agent is regarded as the mobile phase. According to the dynamic distribution of the chromatographic outflow curve, the formulas for calculating the number of theoretical plates (n) and the height of theoretical plate (HETP) were derived as follows [23]:

$$n = 8\ln 2 \times \left(\frac{V_{\mathrm{R}}}{V_{1/2}}\right)^2 \tag{1}$$

$$\mathrm{HETP} = L/n \tag{2}$$

where 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; HETP (cm) is the height equivalent to a theoretical plate; and L (cm) is the packed ore length.

The leaching curve of the rare earth in Figure 3a was analyzed using the chromatographic tray theory. The results are shown in Table 1. It can be seen that with the increase in the concentration of ammonium formate, the retention volume corresponding to the peak concentration gradually decreases and HETP increases first and then decreases. The leaching curve of aluminum in Figure 3b was analyzed using the chromatographic plate theory, and the results are shown in Table 2. It can be seen that with the increase in the concentration of ammonium formate, the retention volume corresponding to the peak concentration gradually decreases and then increases again. HETP decreases first and then increases, and the mass transfer efficiency of aluminum increases first, then gradually decreases. The effects of ammonium formate concentrations on the rate of rare earth, inhibition rate of aluminum and aluminum ion concentration are presented in Figure 4. It can be seen from Figures 3 and 4 that when the concentration of ammonium formate is 0.032 mol/L, the mass transfer efficiency of aluminum is equivalent to that of aluminum directly leached with 0.1 mol/L ammonium sulfate, but the leaching rate of aluminum is suppressed to a large extent; the leaching rate is only 38%. At this time, the concentration of aluminum in the leaching solution is the lowest, and the leaching rate of rare earth is also high. When the concentration of compound ammonium formate is continuously increased, it can be seen that although the mass transfer efficiency of aluminum is constantly decreasing, the leaching rate of aluminum changes little, so the optimum concentration of ammonium formate is 0.032 mol/L.

Table 1. Leach HETP and correlation coefficient of RE under various ammonium formate concentrations.

Concentration/(mol/L)	Packed Ore Length/cm	Retention Volume/mL	Half Peak Width/mL	Plate Number	HETP/cm
0	11.7	38.44	32.03	3.85	3.04
0.008	11.6	37.86	32.77	4.15	2.79
0.01	12.0	38.97	32.05	3.75	3.20
0.02	12.5	36.54	29.32	3.57	3.50
0.032	12.5	35.02	28.24	3.60	3.47
0.04	12.1	33.79	28.38	3.91	3.09
0.05	11.9	36.21	33.08	4.62	2.57

Table 2. Leach HETP and correlation coefficient of Al under various ammonium formate concentrations.

Concentration/(mol/L)	Packed Ore Length/cm	Retention Volume/mL	Half Peak Width/mL	Plate Number	HETP/cm
0	11.7	40.31	40.53	5.48	2.13
0.008	11.6	31.29	32.63	5.10	2.27
0.01	12.0	32.51	27.43	7.78	1.54
0.02	12.5	26.47	24.75	6.34	1.97
0.032	12.5	27.32	27.23	5.58	2.24
0.04	12.1	29.54	31.73	4.79	2.52
0.05	11.9	29.32	36.81	3.52	3.38

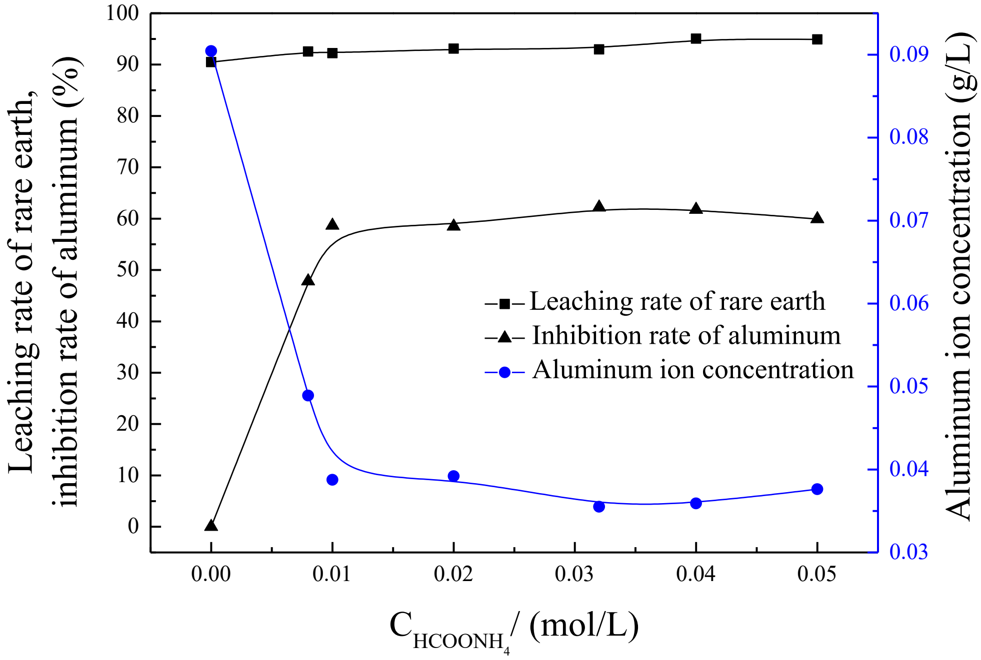

Figure 4. Effect of ammonium formate concentrations on the rate of rare earth, inhibition rate of aluminum and aluminum ion concentration (250 g of ore, $C_{(NH4)2SO4}$ = 0.1 mol/L, μ = 0.5 mL/min and a natural pH 5.5–6.0).

3.3. Effect of the Leaching Temperature on the Leaching Process of RE and Al

Under the conditions of an ammonium sulfate concentration of 0.1 mol/L, ammonium formate complex concentration of 0.032 mol/L, flow rate of 0.5 mL/min and initial pH of 5.5–6.0, the effects of the leaching temperature on the leaching process of rare earth and aluminum are shown in Figure 5. It can be seen from Figure 5 that the peak concentration of rare earth and aluminum increases with the increase in leaching temperature, which indicates that a high temperature is beneficial for the efficient mass transfer of rare earth and aluminum, and strengthens the mass transfer process. There are certain differences in the peak concentration changes of rare earths in the figure, with a higher peak concentration at 20 °C. This may be due to the better synergistic leaching effect of formate ions on the surface of mineral particles under room temperature conditions, and temperature changes have a certain impact on the effectiveness of formate ions. The increase in the leaching temperature accelerates the thermal movement of various ions, which makes the diffusion of the solution and the exchangeability of each ion enhanced [24]. The diffusion rate of ammonium ions from solution to ore particles and the diffusion rate of rare earth ions and other impurity metal ions from ore to solution increase obviously. In addition, the leaching temperature also plays a key role in the permeation rate of the leaching agent solution in the ore body. The higher the leaching temperature, the faster the leaching agent solution penetrates into the ore body.

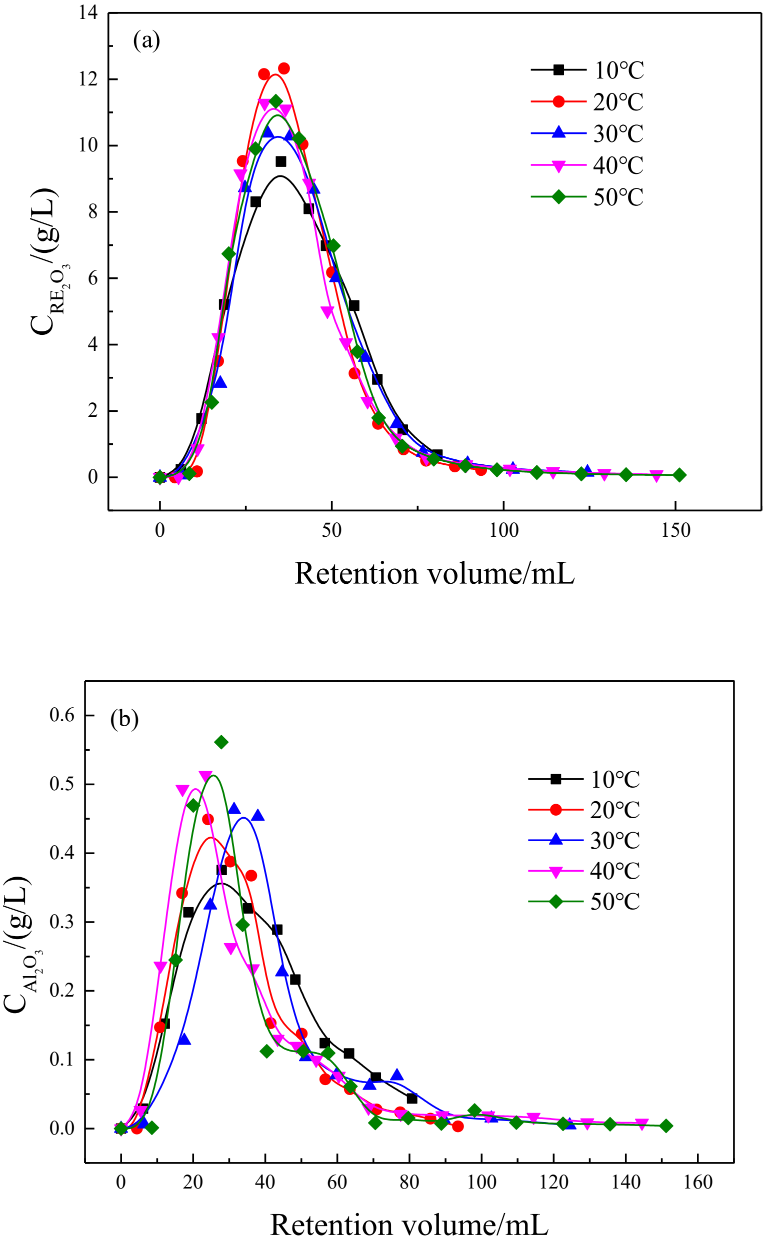

Figure 5. Effect of leaching temperature on the leaching curves of: (**a**) RE and (**b**) Al (250 g of ore, $C_{(NH4)2SO4}$ = 0.1 mol/L, $C_{HCOONH4}$ = 0.032 mol/L, μ = 0.5 mL/min and a natural pH 5.5–6.0).

The leaching curves of rare earth and aluminum in Figure 5 were analyzed using the chromatographic plate theory. The results are shown in Tables 3 and 4. It can be seen that with the increase in leaching temperature, HETP shows a decreasing trend, and the mass transfer efficiency of rare earth and aluminum is improved.

Table 3. Leach HETP and correlation coefficient of RE under various leaching temperatures.

Temperature/(°C)	Packed Ore Length/cm	Retention Volume/mL	Half Peak Width/mL	Plate Number	HETP/cm
10	12.0	37.10	35.65	6.00	2.00
20	12.1	34.97	28.21	8.52	1.42
30	12.0	36.78	32.61	7.05	1.70
40	12.2	34.21	29.09	7.67	1.59
50	11.9	36.47	32.03	7.19	1.65

Table 4. Leach HETP and correlation coefficient of Al under various leaching temperatures.

Temperature/(°C)	Packed Ore Length/cm	Retention Volume/mL	Half Peak Width/mL	Plate Number	HETP/cm
10	12.0	31.59	34.91	4.54	2.64
20	12.1	27.28	27.13	5.60	2.16
30	12.0	33.53	23.29	11.49	1.04
40	12.2	22.65	22.94	5.42	2.25
50	11.9	25.28	17.58	11.46	1.04

3.4. Effect of pH on Leaching Process of RE and Al

Under the conditions of an ammonium sulfate concentration of 0.1 mol/L, ammonium formate complex concentration of 0.032 mol/L, flow rate of 0.5 mL/min and leaching temperature of 25 °C, the pH of the leaching agent was changed to investigate the effect of leaching agent pH on the leaching mass transfer process of rare earth and aluminum. The results are shown in Figure 6.

Figure 6a,b show the effects of pH on the leaching process of RE and Al, respectively. Figure 7 shows the effect of leaching agent pH on the pH of leached-out solution.

It can be seen from Figure 6a that when the pH of the leaching agent is two and four, the peak concentration of rare earths, the retention volume corresponding to the peak concentration and the peak shape have almost no changes. When the pH of the leaching agent is six and eight, the peak concentration, the retention volume corresponding to the peak concentration and the peak shape of rare earth have almost no obvious changes. However, the peak concentration of rare earths at lower leaching agent pH was slightly higher than that at higher leaching agent pH, the half peak height width was smaller than that at higher leaching agent pH and the mass transfer efficiency of rare earths was slightly improved.

As can be seen from Figure 6b, the peak concentration of aluminum, the retention volume corresponding to the peak concentration and the peak shape were almost unchanged when the leaching agent pH was six and eight. When the leaching agent pH was reduced to four, the peak concentration of aluminum in the leaching solution increased significantly, the retention volume corresponding to the peak concentration of the leaching curve increased and the leaching rate of aluminum increased; it can be seen that the inhibition of the leaching effect of ammonium formate on aluminum in the compound system under the leaching conditions at this pH has been partially weakened. When the pH of the leaching agent dropped to two, the peak concentration of aluminum increased sharply, and the retention volume corresponding to the half peak width and peak concentration also increased sharply, resulting in a significant increase in the aluminum leaching rate. At this time, ammonium formate completely lost the effect of inhibiting aluminum leaching, and under strong acidic conditions ($pH < 3.5$), in addition to the rare earth, minerals in the ionic state of aluminum will be exchanged with the ammonium ions in the leaching agent into solution, and part of the adsorbed hydroxyl aluminum in rare earth ores will also be dissolved into the solution by acid. The amount of adsorbed hydroxyl aluminum is more than that of ionic-phase aluminum in the rare earth ore sample. Therefore, even a small amount of dissolution will have a great influence on the leaching rate of aluminum. The natural pH of the studied leaching agent is approximately 5.5–6.0 at the experimental conditions. It can be concluded that in actual mine production, the pH of the leaching agent does not require additional adjustment.

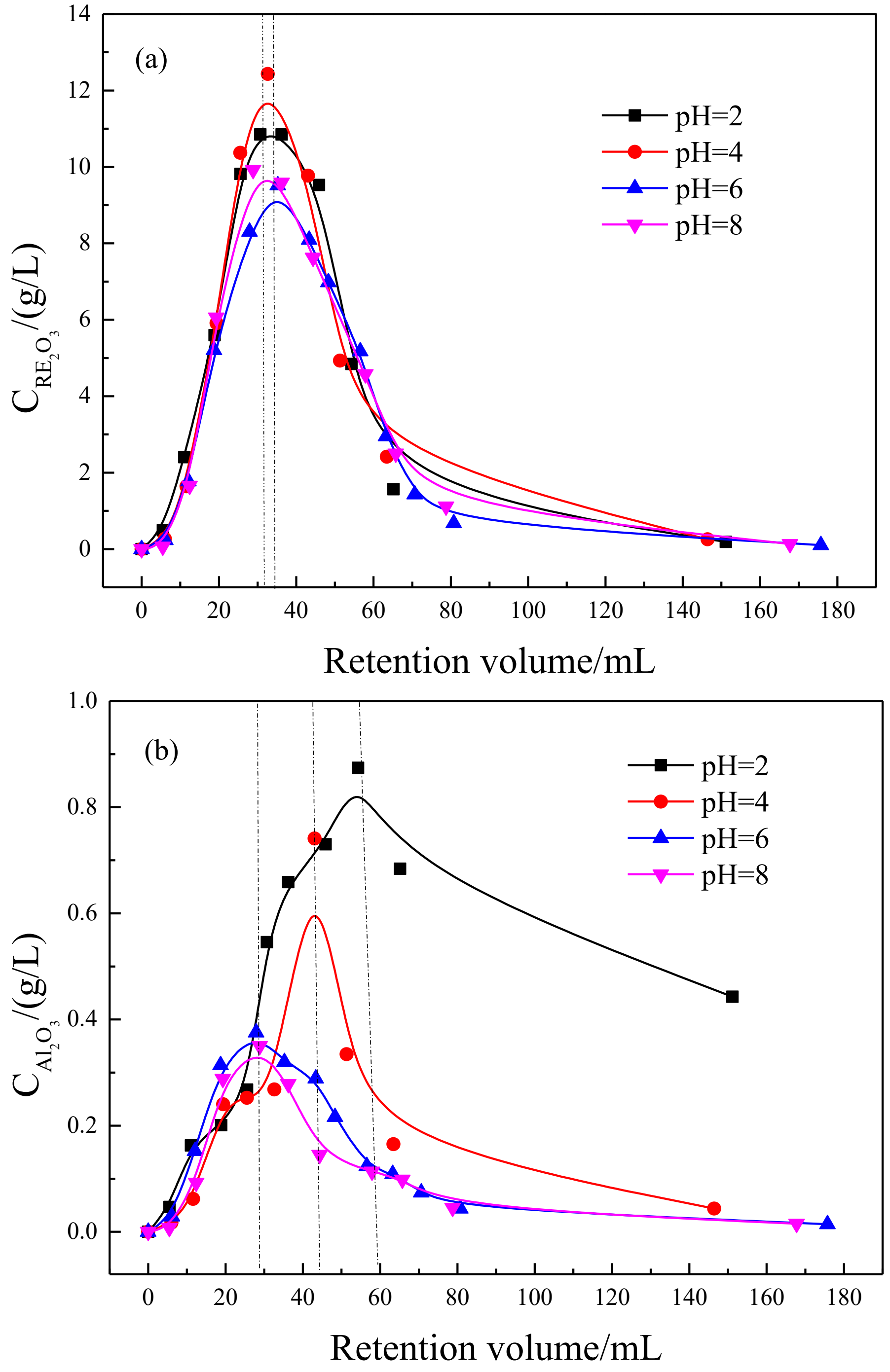

Figure 6. Effect of leaching agent pH on the leaching curves of: (**a**) RE and (**b**) Al (250 g of ore, $C_{(NH4)2SO4}$ = 0.1 mol/L, $C_{HCOONH4}$ = 0.032 mol/L and μ = 0.5 mL/min).

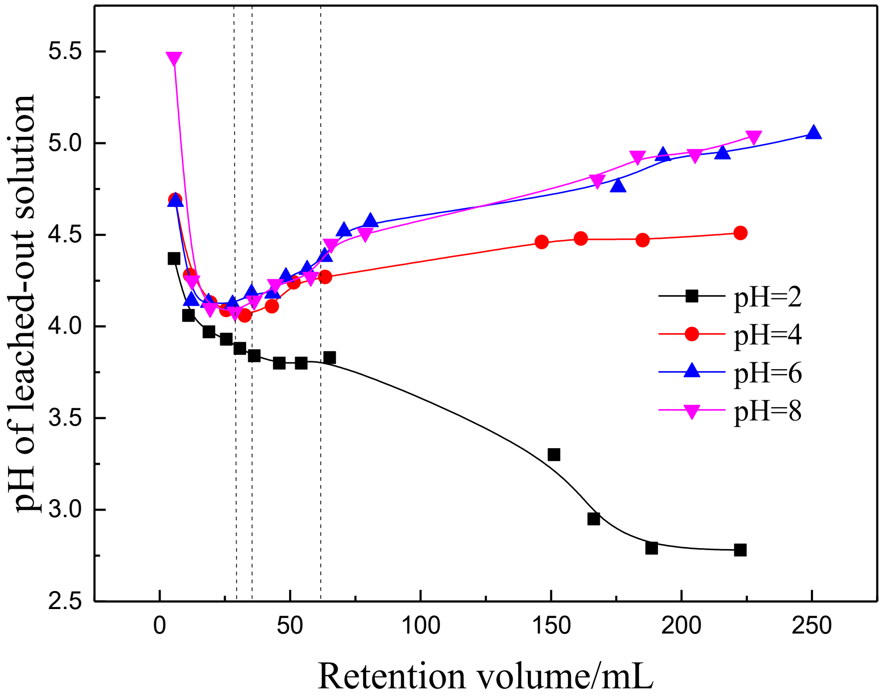

Figure 7. Effect of leaching agent pH on the pH of leached-out solution (250 g of ore, $C_{(NH4)2SO4}$ = 0.1 mol/L, $C_{HCOONH4}$ = 0.032 mol/L and μ = 0.5 mL/min).

The leaching curves of rare earth and aluminum in Figure 6 were analyzed using the chromatographic plate theory. The results are shown in Tables 5 and 6. It can be seen from the table that when the pH of the leaching agent is two and four, the HETP of rare earth and aluminum leaching is small, and the mass transfer efficiency of rare earth and aluminum is improved.

Table 5. Leach HETP and correlation coefficient of RE under various leaching agent pH values.

pH	Packed Ore Length/cm	Retention Volume/mL	Half Peak Width/mL	Plate Number	HETP/cm
2	12.2	35.80	33.15	6.46	1.89
4	12.5	34.52	28.80	7.96	1.57
6	12.0	37.75	37.19	5.71	2.10
8	12.1	36.80	36.33	5.69	2.12

Table 6. Leach HETP and correlation coefficient of Al under various leaching agent pH values.

pH	Packed Ore Length/cm	Retention Volume/mL	Half Peak Width/mL	Plate Number	HETP/cm
2	12.2	50.50	43.83	7.36	1.66
4	12.5	42.02	29.08	11.57	1.08
6	12.0	32.68	37.54	4.20	2.86
8	12.1	29.19	27.17	6.40	1.89

As can be seen from Figure 7, as the leaching solution continues to flow, the pH of the leaching solution first decreases until it reaches a minimum value and then slowly increases until it reaches an equilibrium value. However, when the pH of the leaching agent is two, the pH of the leachate will turn to a slow decrease during the later period of the slow increase until it approaches the pH of the original leaching agent. This is due to the fact that there are many -O- and -OH groups on the surface of the clay mineral structure. When the pH of the leaching agent changes, the -O- group will exhibit the ability to accept H+ or -OH groups to release H+. Therefore, it effectively reflects the acid–base buffering capacity of clay minerals to a certain extent. However, when the pH of the leaching agent is too low, the acid–base buffering property of the clay mineral will be destroyed after a certain leaching stage. Therefore, it can be seen that when the pH of the leaching agent is two, the pH of the late leachate is suddenly reduced.

The maximum value of the rare earth concentration of the leachate corresponding to the minimum pH of the leachate can be seen in Figures 6a and 7, and it is obvious that the trend of the rare earth concentration with the volume of the leachate is exactly opposite to the change in the pH of the leachate. It can be inferred that the pH value of the real-time leachate in actual production can reflect the change in the rare earth concentration in the leachate to a certain extent. It can be seen from Figures 6b and 7 that when the pH of the leaching agent is 4–8, the maximum concentration of the aluminum in the leachate is also the minimum value corresponding to the pH of the leachate. However, when the pH of the leaching agent is two, the maximum value of the aluminum concentration of the leachate corresponds to the position at which the pH of the leachate suddenly drops, and this is also the node where the acid-damping property of the ore sample is destroyed.

3.5. Effect of the Liquid/Solid Ratio on the Leaching Process of RE and Al

In this experiment, the leaching process was carried out by adding deionized water on the basis of leaching under a certain liquid–solid ratio condition. The effect of the liquid–solid ratio on the leaching process was investigated. The results are shown in Figure 8.

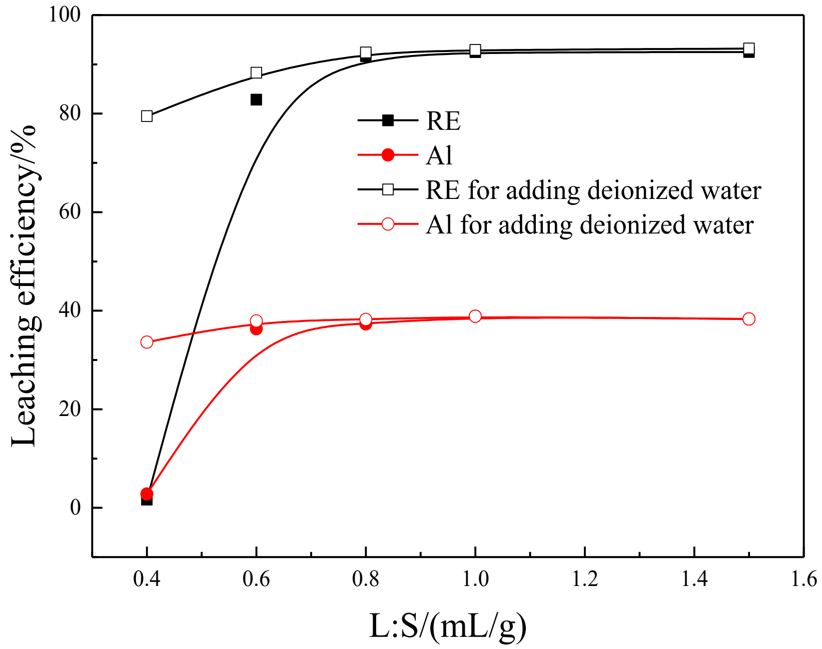

Figure 8. Effect of liquid–solid ratio on the leaching efficiency of RE and Al (250 g of ore, $C_{(NH4)2SO4}$ = 0.1 mol/L, $C_{HCOONH4}$ = 0.032 mol/L, μ = 0.5 mL/min and a natural pH 5.5–6.0).

It can be seen from Figure 8 that under different liquid–solid ratio conditions, with the addition of deionized water for secondary leaching, the leaching rate of both rare earth and aluminum is improved, and when the liquid–solid ratio is 0.4:1, the leaching rate is improved obviously. When the liquid–solid ratio reaches 0.8:1, the leaching rates of rare earth and aluminum are balanced. It can be seen that under the condition of a small liquid–solid ratio, adding deionized water for secondary leaching is beneficial for rare earth which has undergone an ion exchange reaction but is retained in the ore body to flow out the ore body; the optimal liquid–solid ratio under this condition is 0.8:1.

The effects of the liquid–solid ratio on the leaching and mass transfer process of rare earth and aluminum under different liquid–solid ratio conditions are shown in Figure 9. It can be seen from the figure that the concentration of rare earth and aluminum first increases and then decreases as the volume of the leaching solution increases. In the initial stage of leaching, due to the large amount of ammonium ions in the leach solution, it is used to exchange rare earth and other impurity metal ions in rare earth ore. In the process of continuous diffusion and seepage into the bottom of the ore body, the ammonium ion in the solution decreases until it reaches zero, and the rare earth and other impurity metal ions diffused into the solution via the ion exchange reaction with ammonium ions will be adsorbed by the clay mineral during the continuous migration to the bottom of the ore body. Therefore, the content of rare earth and other impurity metal ions in the leaching solution is very low in the initial stage. With the continuous seepage and diffusion of the leaching agent solution, the concentration of ammonium ions in the solution passing through the anti-adsorption mining area is increasing, the ion exchange reaction in this area is gradually strengthened and the anti-adsorption phenomenon is weakened. Therefore, the concentration of rare earth and impurity metal ions in the leaching solution will gradually increase until it reaches a maximum, and then will gradually decrease.

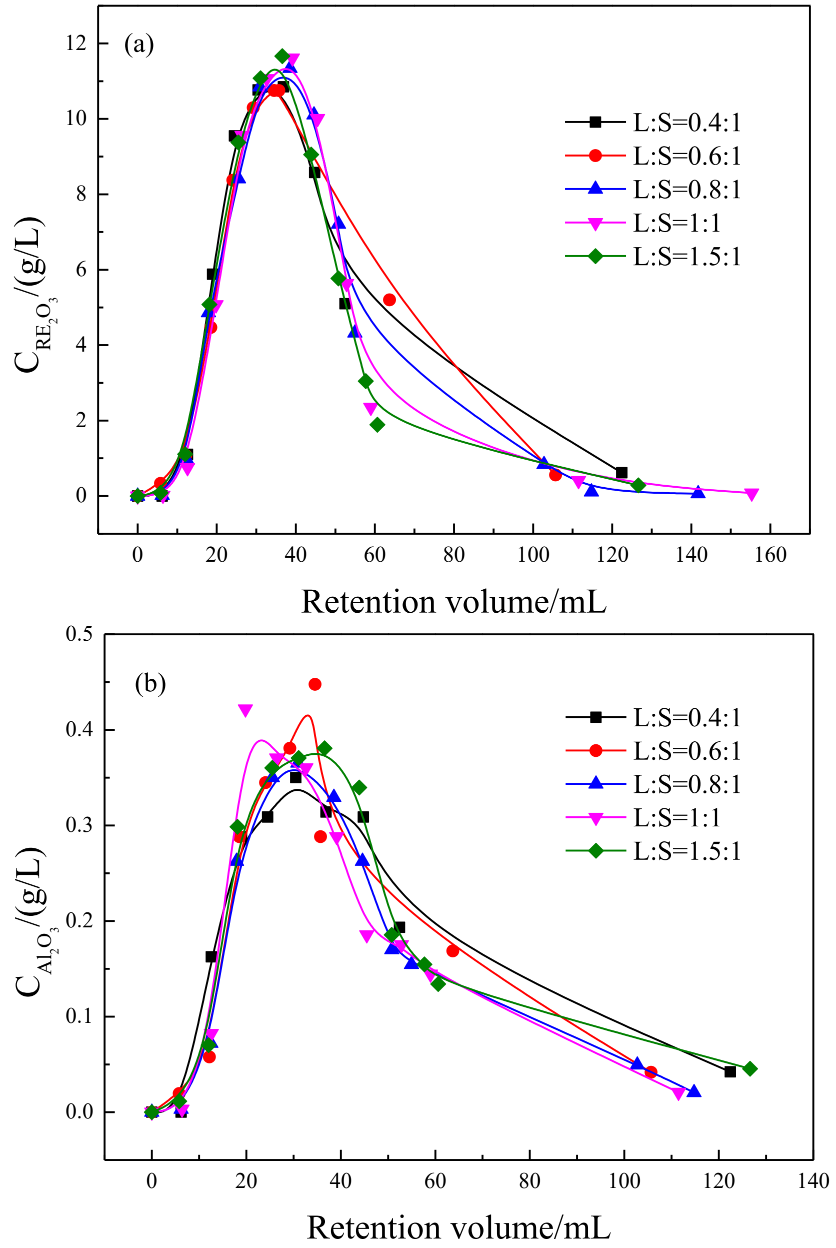

Figure 9. Effect of liquid–solid ratio on the leaching curves of: (**a**) RE and (**b**) Al (250 g of ore, $C_{(NH4)2SO4}$ = 0.1 mol/L, $C_{HCOONH4}$ = 0.032 mol/L, μ = 0.5 mL/min and a natural pH 5.5–6.0).

It can also be seen from the figure that under the liquid–solid ratio conditions, the outflow curve basically coincides in the early stage, but in the near peak concentration stage, it shows a very significant size change, and the difference in the later outflow curve is also large. This is due to the difference in the volume of the leaching agent added to the ore sample under different liquid–solid ratio conditions. When the liquid–solid ratio is small, deionized water is added for secondary leaching at a later stage. At this time, the added deionized water will push the rare earth which has been exchanged into the solution by the ammonium ion exchange in the previous stage and push out the rare earth ore. However, due to the supplement of secondary water, there are not enough ammonium ions to inhibit the reverse adsorption phenomenon and the incomplete ion exchange reaction continues, so the peak concentration of the leachate will be quite different under different liquid–solid ratio conditions, but when the liquid–solid ratio is large, there is basically no obvious change.

The leaching curves in Figure 9 were analyzed using chromatographic plate theory. The results are shown in Tables 7 and 8. It can be seen from the table that the HETP of rare earth and aluminum leaching is gradually reduced, and the leaching and mass transfer efficiency of rare earth and aluminum is gradually improved. After the liquid–solid ratio reaches 0.8:1, the liquid–solid ratio is continuously increased without much change. It can be seen that the optimum liquid–solid ratio of the leaching process is 0.8:1.

Table 7. Leach HETP and correlation coefficient of RE under various liquid–solid ratios.

Liquid–Solid Ratio	Packed Ore Length/cm	Retention Volume/mL	Half Peak Width/mL	Plate Number	HETP/cm
0.4:1	11.4	34.71	29.54	7.65	1.49
0.6:1	11.6	41.15	37.83	6.56	1.76
0.8:1	11.3	36.90	30.41	8.16	1.38
1:1	11.5	36.88	29.23	8.82	1.30
1.5:1	11.6	35.31	29.64	7.87	1.47

Table 8. Leach HETP and correlation coefficient of Al under various liquid–solid ratios.

Liquid–Solid Ratio	Packed Ore Length/cm	Retention Volume/mL	Half Peak Width/mL	Plate Number	HETP/cm
0.4:1	11.4	33.48	36.00	4.79	2.38
0.6:1	11.6	36.88	39.04	4.95	2.34
0.8:1	11.3	33.11	31.86	5.98	1.89
1:1	11.5	30.69	31.96	5.11	2.25
1.5:1	11.6	34.12	34.34	5.47	2.12

4. Conclusions

For ammonium sulfate and ammonium formate as a compound leaching agent, the optimal condition of column leaching was found to be 0.1 mol/L ammonium sulfate compounded with 0.032 mol/L ammonium formate, pH 4–8 of the leaching agent, 0.8:1 liquid:solid (mL/g) ratio and room temperature. A high ammonium formate concentration could improve the mass transfer efficiency of rare earth by reducing the resistance of diffusion and effectively reduce the mass transfer efficiency of aluminum, but excessive ammonium formate will increase the production cost and have little effect on the final leaching rate. pH almost had no significant effects on the HETP of RE and Al leaching in the range of 4–8. HETP decreased with the increase in the liquid–solid ratio.

For the new compound leaching system of ammonium sulfate and ammonium formate, the mass transfer efficiency of rare earth is close to that of the traditional ammonium sulfate leaching agent, but the mass transfer efficiency of aluminum is significantly reduced, and the leaching rate of aluminum is also greatly reduced. This indicates that the compound leaching agent of ammonium sulfate and ammonium formate has a great application prospect in the actual development of weathered crust elution-deposited rare earth ore.

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