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Efficient Reuse of Rare Earth Carbonate Precipitation Mother Liquor for Rare Earth Leaching in Strong Acid-Restricted Area

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Abstract: Due to the restrictions of strong acids in some regions, the reuse process of rare earth (RE) precipitation mother liquor is difficult to carry out. To achieve the straightforward and efficient reuse of precipitation mother liquor in such areas, the potential for directly reusing this liquor for rare earth (RE) leaching was explored. The results showed that when the RE concentration in the leachate ranged from 0.1 to 1.5 g/dm^3 and the RE precipitation rate exceeded 96%, the residual total carbonate content in precipitation mother liquor was less than 0.01 mol/L, and the solution pH was 7–8. Furthermore, when the total carbonate content in leaching liquor was lower than 0.01 mol/L, the presence of carbonate had a minimal impact on the RE leaching efficiency, which was observed to exceed 93%. Additionally, the process of mother liquor leaching was analyzed using dynamic models and chromatography tray theory. It was found that the leaching results were well fitted with the shrinking core model, and the apparent activation energy of RE was 5.77 kJ/mol, indicating that the reaction was controlled by diffusion, and the reaction order was 0.672 for RE. This confirms that a total carbonate content below 0.01 mol/L in the precipitation mother liquor can be directly used for the RE leaching process.

Keywords: weathered crust elution-deposited rare earth ore; reuse; RE carbonate precipitation; mother liquor

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Citation: Feng, J.; Wu, X.; Zhou, F.; Chi, R. Efficient Reuse of Rare Earth Carbonate Precipitation Mother Liquor for Rare Earth Leaching in Strong Acid-Restricted Area. *Minerals* **2024**, *14*, 1179. https://doi.org/10.3390/min14111179

Academic Editors: Gaofeng Wang, Yongqiang Yang and Hugo Marcelo Veit

Received: 18 October 2024
Revised: 13 November 2024
Accepted: 19 November 2024
Published: 20 November 2024

1. Introduction

The weathered crust elution-deposited rare earth (RE) ore is rich in medium and heavy rare earth, which is an important source of mid-heavy RE in the world [1–3]. The RE present in the ore is primarily adsorbed onto clay minerals in the form of hydrated ions or hydroxylated hydrated ions. These elements can be effectively leached using ammonium salts through an ion exchange method [4–7]. The RE leaching technology encompasses several methods, including the pool leaching process, heap leaching process, and in situ leaching process [8,9]. Among them, the in situ leaching process is widely applied in actual mining since it is more beneficial to environmental protection [10]. In the in situ leaching process, the RE leachate can be collected when ammonium salt is injected into the ore body as the leaching liquor. After that, the RE in the leachate can be recovered by using ammonium bicarbonate as a precipitator [11,12].

The RE carbonate precipitation process is to use ammonium bicarbonate instead of oxalic acid to precipitate and enrich rare earth elements in the leaching mother liquor [13]. When ammonium bicarbonate is used to precipitate rare earths, the precipitant is cheap and easy to obtain. Its solubility product is smaller than that of RE oxalate, making it easier to precipitate. The precipitation rate of rare earths is high. In addition, ammonium bicarbonate is non-toxic, has little environmental pollution, and has great industrial application prospects. In recent years, with the development and widespread application of in situ leaching, rich ores have been rapidly prioritized for mining and utilization. The grade of rare earths in the raw ore currently being mined has gradually decreased year by year, and the peak concentration of rare earths in the collected leachate is very low. In addition, there is a serious tailing phenomenon in the rare earth leaching process. The concentration of rare earths in the obtained leach solution is very low, which greatly increases the amount of ammonium bicarbonate consumed when precipitating rare earths [14,15]. Luo Xianping et al. [16] conducted a systematic study on the relationship between the precipitation and crystallization process of rare earth carbonate and the acidity of equilibrium solutions, and obtained easily filtered crystalline rare earth carbonate by adding seeds or surfactants during the precipitation process. Yu Qinghua et al. [17] investigated the influencing factors of the rare earth precipitation process using ammonium bicarbonate. By analyzing the crystal forms of rare earth carbonate formed under different conditions, they found that good rare earth carbonate crystallization can be obtained under appropriate rare earth concentration, ammonium bicarbonate dosage, stirring time, and aging time conditions. The RE carbonate precipitation mother liquor contains excessive ammonium salt and ammonium bicarbonate. The residual ammonium bicarbonate in the mother liquor is usually removed by hydrochloric acid or sulfuric acid, and then a certain amount of ammonium salt is added to the mother liquor to make the ammonium ion concentration meet the required content for leaching, and then reused in the RE leaching process [10,14]. However, due to restrictions on the use of strong acids in some areas, the reuse process of the precipitation mother liquor cannot be carried out. If the precipitation mother liquor is directly discharged, it will cause ammonia nitrogen wastewater pollution and damage the environment. In addition, if the precipitation mother liquor is not reused, the remaining ammonium in the precipitation mother liquor cannot be utilized, which will increase the consumption of the leaching agent, resulting in high operating costs. Reasonably solving the problem of regeneration and recycling of mother liquor after rare earth precipitation cannot only reduce pollution emissions and environmental impact but also save the amount of ammonium salt used, which is the key to controlling consumption and reducing costs [14]. Therefore, the reuse of the mother liquor of RE carbonate precipitation has important environmental and economic significance.

In order to realize the simple and efficient utilization of the precipitation mother liquor in these areas, the direct reuse of the precipitated mother liquor in the RE leaching process can be considered. However, when the precipitation mother liquor is directly reused for the RE leaching process, the residual ammonium bicarbonate in the precipitated mother liquor, especially the higher concentration of ammonium bicarbonate, may form RE carbonate precipitation with the leached RE ions, which will seriously affect the RE leaching efficiency.

To reduce the influence of residual ammonium bicarbonate on the RE leaching process and realize the direct reuse of the precipitation mother liquor, the dosage of ammonium bicarbonate in the precipitation process should be minimized under the premise of a high RE precipitation rate, thereby reducing the residual carbonate in the precipitation mother liquor. At the same time, the content of residual ammonium bicarbonate in the precipitation mother liquor that affects the RE leaching process should be studied. Therefore, this paper studied the RE carbonate precipitation process and the RE leaching process under ammonium bicarbonate conditions, so as to optimize the precipitation reuse process. In addition, the shrinking unreacted core model and the chromatography tray theory were used to analyze the RE leaching process using ammonium sulfate leaching solution containing carbonate ions. This research can enable the direct reuse of rare earth precipitation mother liquor in areas where strong acids are prohibited, optimize reuse processes, reduce production costs, and maximize the comprehensive utilization of resources and production benefits. It will provide theoretical and technical support for the control of ammonia nitrogen pollution in RE mining areas where strong acids are restricted.

2. Materials and Methods

2.1. Materials

The RE ore samples used in this study were collected from southern Yunnan, China. The main chemical composition of the RE ores was analyzed by X-ray fluorescence, and the results are listed in Table 1. From Table 1, the RE ore contains 0.09 wt.% REO, 32.18 wt.% Al_2O_3, and 56.52 wt.% SiO_2. It indicates that the RE ore is mainly composed of quartz and clay minerals of aluminosilicate. In addition, the RE leachate of the mine was used in the RE precipitation process and the precipitation mother liquor reuse process.

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

Component	Content
REO	0.09
Al_2O_3	32.18
MnO_2	0.08
ZnO	0.01
MgO	0.01
K_2O	5.41
SiO_2	56.52
TiO_2	0.73
Fe_2O_3	4.92
Rb_2O	0.01
SrO	0.02
ZrO_2	0.02

All chemicals used in this experiment were purchased from Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China) with analytical grade. All the solutions were prepared with deionized distilled water.

2.2. Precipitation and Column Leaching Experiments

The precipitation experiment was carried out in a 500 mL beaker. First, 200 mL of the RE leachate was placed in the beaker, and a certain dosage of ammonium bicarbonate was added under constant stirring. After standing for 2 h, the solution was filtered through a 0.22 μm filter membrane. The RE content, pH, and total carbonate content in the mother liquor were measured. The experiments were carried out at an ambient temperature of 20 ± 2 °C.

In the column leaching experiment, the glass column with a sand core filter plate at the bottom and the inner diameter of 50 mm was used as the apparatus. The RE ore sample was mixed uniformly and dried at 70 °C for 8 h before conducting leaching experiments on the column [18]. Subsequently, 250 g of dried RE ore packed into the column and two pieces of filter papers were put on the upper of the ore samples, and then 250 mL of leaching liquor was added from the top of the column at a constant flow rate by a peristaltic pump. A schematic diagram of the experimental apparatus is shown in Figure 1. The X-ray diffraction analysis results of the ore sample are shown in Figure 2. As shown in the figure, the ore is mainly composed of minerals such as quartz, feldspar, kaolinite, and illite. The leachate was collected at the bottom of the glass column. The pH and RE content of the leachate were analyzed. The experiments were carried out at an ambient temperature of 20 ± 2 °C.

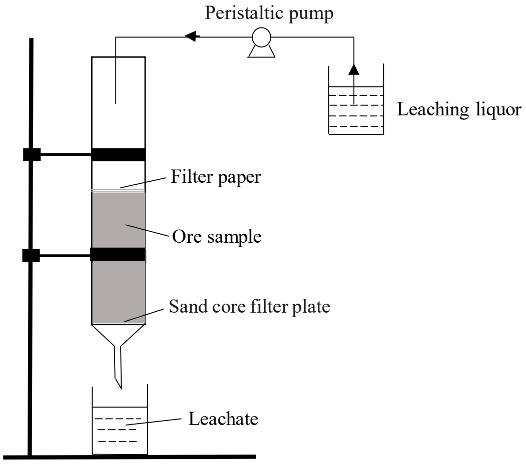

Figure 1. Schematic diagram of experimental apparatus.

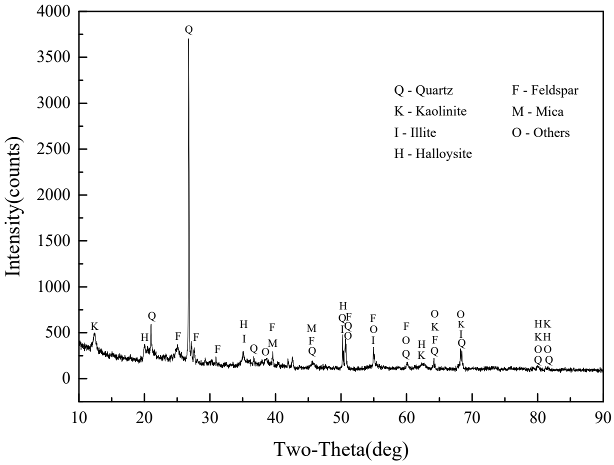

Figure 2. XRD diffraction pattern of the RE ore.

2.3. Analytical Methods

The RE content in the solution was determined by the ethylenediaminetetraacetic acid (EDTA) titration method using xylenol orange as an indicator [19]. The total carbonate content in the solution was determined by acid–base titration [20]. The ammonium ion in the solution was measured by an ammonium gas sensor (PNH3-1-01) [21]. The pH of the solution was measured with a pH meter (DELTA320). The RE precipitation rate (α) and RE leaching efficiency (γ) were calculated according to the following equations:

$$\alpha = \frac{C_0 - C_1}{C_0} \times 100\% \tag{1}$$

$$\gamma = \frac{\varepsilon_1}{\varepsilon_0} \times 100\% \tag{2}$$

where C_0 and C_1 were the RE contents before and after the precipitation process, respectively. ε_1 was the total content of RE in the leachate, and ε_0 was the total content of ion-exchangeable RE in the original ore sample.

3. Results

3.1. RE Carbonate Precipitation Process

In the RE carbonate precipitation process, the dosage of ammonium bicarbonate is an important factor affecting the RE precipitation rate. When the dosage of ammonium bicarbonate is small, the RE cannot be completely precipitated, resulting in a low RE recovery rate. However, an excessive amount of ammonium bicarbonate can result in a higher RE precipitation rate, but will increase the residual total carbonate content in the precipitation mother liquor, which may cause the formation of RE carbonate precipitation during the mother liquor reuse process, thereby reducing the RE leaching rate. Therefore, the dosage of ammonium bicarbonate in the RE precipitation process was investigated. In addition, the concentration of RE in the leachate will also affect the ammonium bicarbonate dosage during the precipitation process. The weathered crust elution-deposited RE is a clay mineral with a complex chemical composition and low RE content. Due to differences in leaching operating conditions and the chemical composition of RE minerals, the concentration of RE in the leachate varies. The minimum concentration of RE in the leachate can reach 0.1 g/dm^3, while in some areas, the concentration of RE in the leachate is as high as 1.5 g/dm^3 [22]. Therefore, the precipitation process of the leachate with different RE concentrations was studied.

The effect of the dosage of ammonium bicarbonate on the RE precipitation rate, pH, and residual total carbonate content is shown in Figure 3. The dosage of ammonium bicarbonate in the precipitation process can be expressed by the molar ratio of ammonium bicarbonate and RE. The theoretical molar ratio of the reaction between ammonium bicarbonate and RE is 1.5:1. However, to obtain a higher RE precipitation rate, the amount of ammonium bicarbonate is often higher than the theoretical amount in the actual production process. As can be seen from Figure 3, the ammonium bicarbonate dosages required for different RE concentrations were higher than the theoretical amount of 1.5:1. As the amount of ammonium bicarbonate increased, the RE precipitation rate gradually increased and then tended to plateau. The pH of the solution and the content of residual total carbonate gradually increased. When the concentration of RE in the leachate was 0.1–1.5 g/dm^3 and the RE precipitation rate was higher than 96% as it reached equilibrium, the residual total carbonate content in the precipitated mother liquor was lower than 0.01 mol/L, and the pH value of the mother liquor was 7–8.

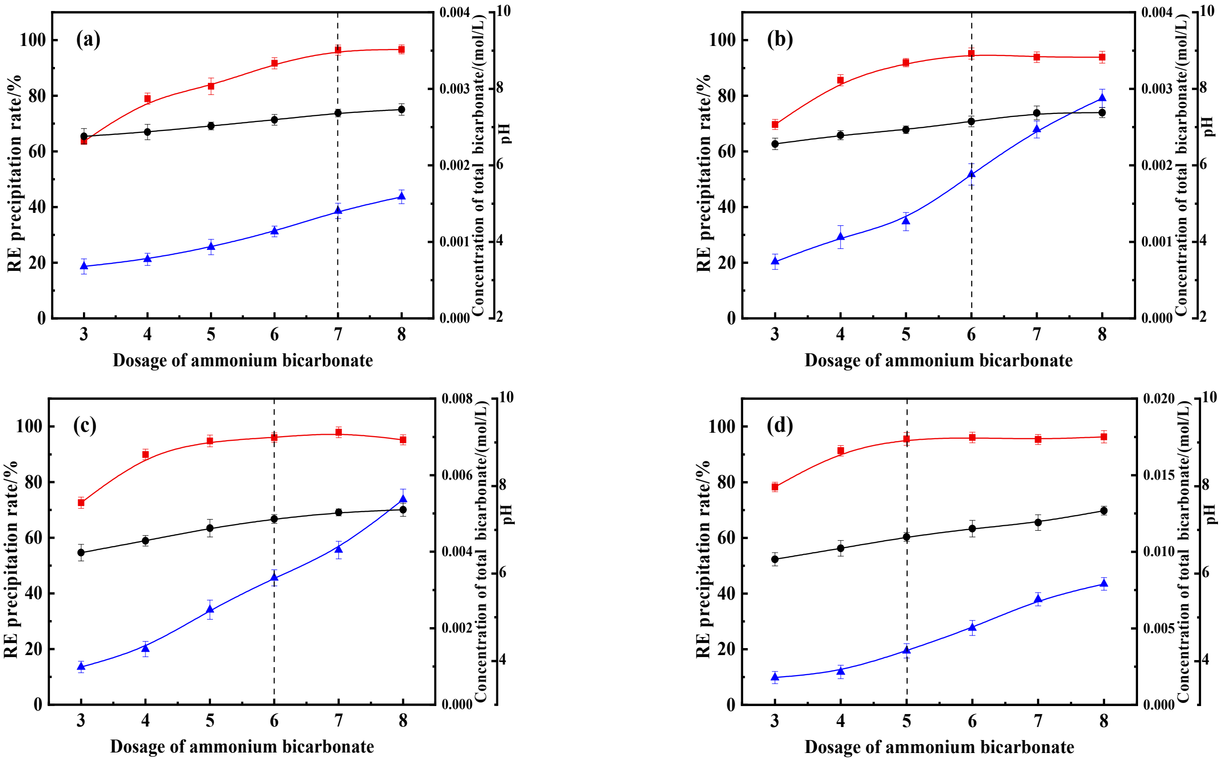

Figure 3. *Cont.*

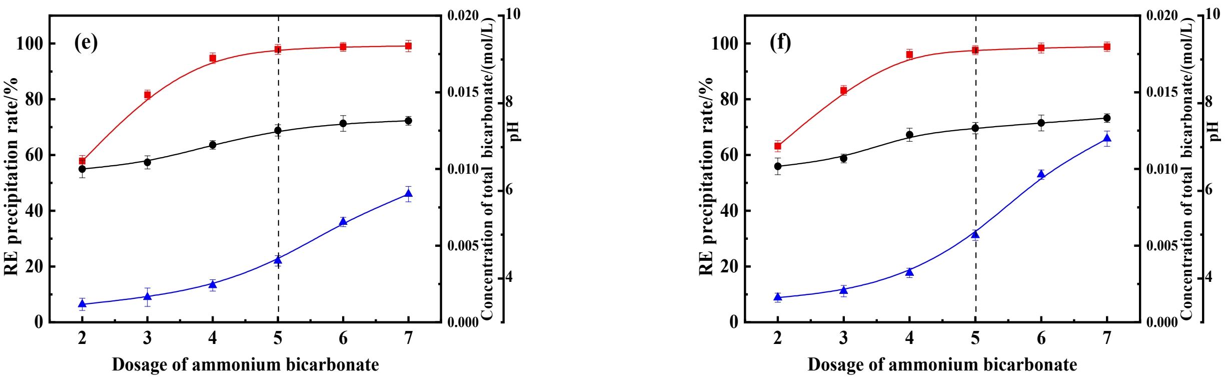

Figure 3. Effect of the dosage of ammonium bicarbonate on RE precipitation rate (■), residual total carbonate content (▲), and pH (●) (RE concentration: (**a**) 0.118 g/dm^3, (**b**) 0.227 g/dm^3, (**c**) 0.441 g/dm^3, (**d**) 0.676 g/dm^3, (**e**) 0.965 g/dm^3, (**f**) 1.470 g/dm^3).

As illustrated in Figure 3, the RE concentration in the leachate can affect the amount of ammonium bicarbonate, thus affecting the residual total carbonate content in the precipitated mother liquor. In order to facilitate the analysis of the relationship between the RE concentration and the quantity of ammonium bicarbonate involved in the process, the amount of ammonium bicarbonate was analyzed when the RE precipitation rate reached equilibrium, and the RE precipitation rate in the leachate with different RE concentrations was compared when the dosage of ammonium bicarbonate was 4:1. The outcomes are presented in Figure 4. It is evident from Figure 4 that less ammonium bicarbonate was required for the precipitation of RE with higher RE concentration in the leachate. From Figure 4, it is evident that the precipitation rate of RE escalated as the concentration of RE in the leachate increased. This phenomenon indicates that higher RE concentration in the leachate requires less ammonium bicarbonate to precipitate RE. Therefore, the quantity of ammonium bicarbonate utilized should be optimized based on the concentration of RE in the leachate. This optimization aims to enhance the precipitation rate of RE while minimizing the residual total carbonate content, which may be beneficial to the subsequent reuse process of the precipitation mother liquor.

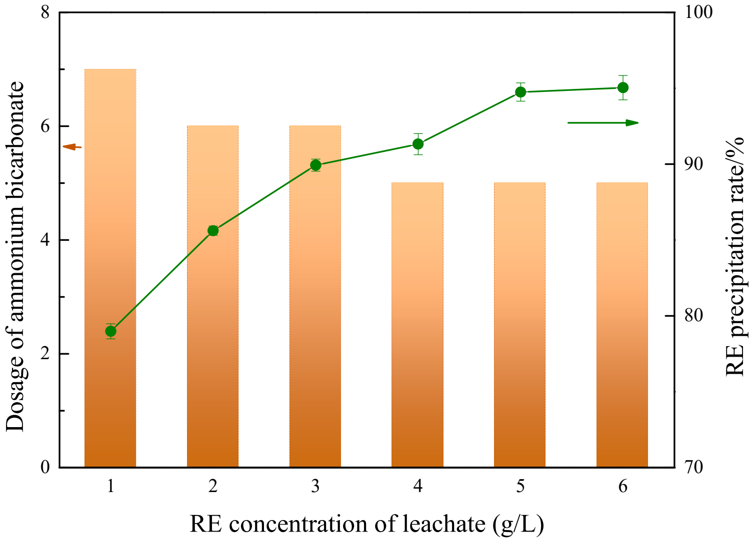

Figure 4. Effect of RE concentration on ammonium bicarbonate dosage when RE precipitation rate reached equilibrium and RE precipitation rate in the process of recovering rare earth from leachate (molar ratio of ammonium bicarbonate was 4:1).

3.2. Reuse of RE Carbonate Precipitation Mother Liquor for RE Leaching

3.2.1. Effect of Total Carbonate Content on RE Leaching Process

To study the effect of the total carbonate content in the mother liquor on the RE leaching process, an ammonium sulfate solution mixed with a certain amount of ammonium bicarbonate was used as the leaching liquor for RE leaching, the ammonium ion concentration in the leaching liquor was the same as that in the 2% ammonium sulfate solution, and the total carbonate content in the solution varied from 0 to 0.05 mol/L. The results depicted in Figure 5 indicate that when the content of ammonium bicarbonate in the leaching liquor fell below 0.01 mol/L, the RE leaching efficiency was equal to that when leaching with 2% ammonium sulfate. This result indicates that the presence of a certain amount of total carbonate has little effect on the RE leaching efficiency. Then, with the increase in the total carbonate content, the RE leaching efficiency gradually decreased. An excessive concentration of ammonium bicarbonate could affect the RE leaching efficiency during the leaching process. It can be also seen that when the total carbonate content was less than 0.01 mol/L, the pH of the leachate was basically unchanged. And then with the increasing in the total carbonate content, the pH gradually increased. This may be because clay minerals have certain acid–base buffering properties [23–25]. The acidity and alkalinity of the solution are determined by the buffering properties of clay minerals within a small range. During the leaching process, when the content of ammonium bicarbonate in the leaching agent solution is low, the pH of the leaching solution can be maintained stable at 4–5 within the buffering capacity range of clay minerals. When the content of ammonium bicarbonate in the leaching solution is high, the buffering capacity of clay minerals may be disrupted by excessive acid–base groups, resulting in a gradual increase in the pH of the leachate. It can be inferred that the precipitation mother liquor with a total carbonate content lower than 0.01 mol/L can be directly reused for the RE leaching process.

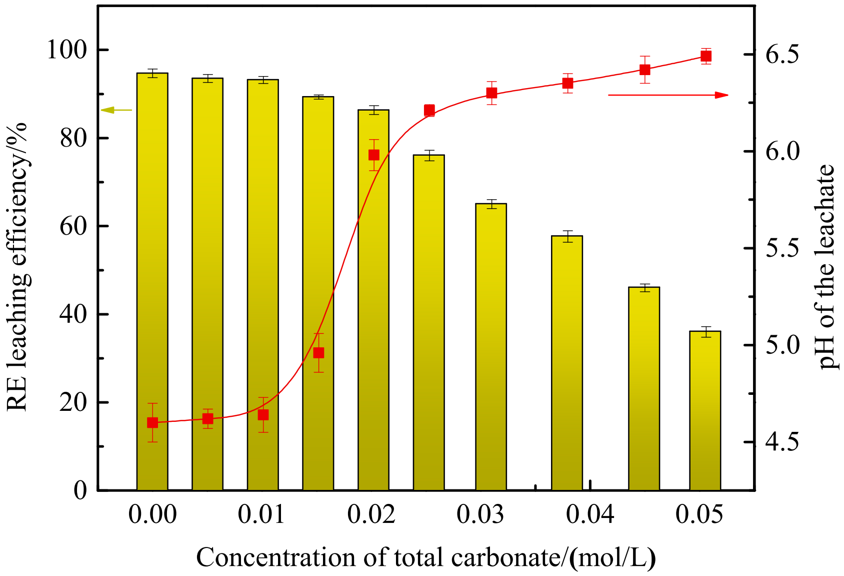

Figure 5. Effect of total carbonate content on RE leaching efficiency and pH of the leachate.

3.2.2. The Leaching Effect of the Precipitation Mother Liquor

To verify that the presence of a certain carbonate content in the precipitation mother liquor will not affect the reuse process, the precipitation mother liquor with the residual total carbonate content obtained below 0.01 mol/L was directly used in the RE leaching process after adjusting the ammonium ion concentration (the same as 2% ammonium sulfate). The results presented in Figure 6 indicate that the RE leaching efficiency obtained by utilizing the precipitation mother liquor as the leaching solution was almost equal to 2% ammonium sulfate, higher than 96%, and the pH of the leachate varied between 4 and 5. The collected leachate was clear and no precipitation occurred. This finding confirms the viability of directly reusing the RE carbonate precipitation mother liquor in the RE leaching process.

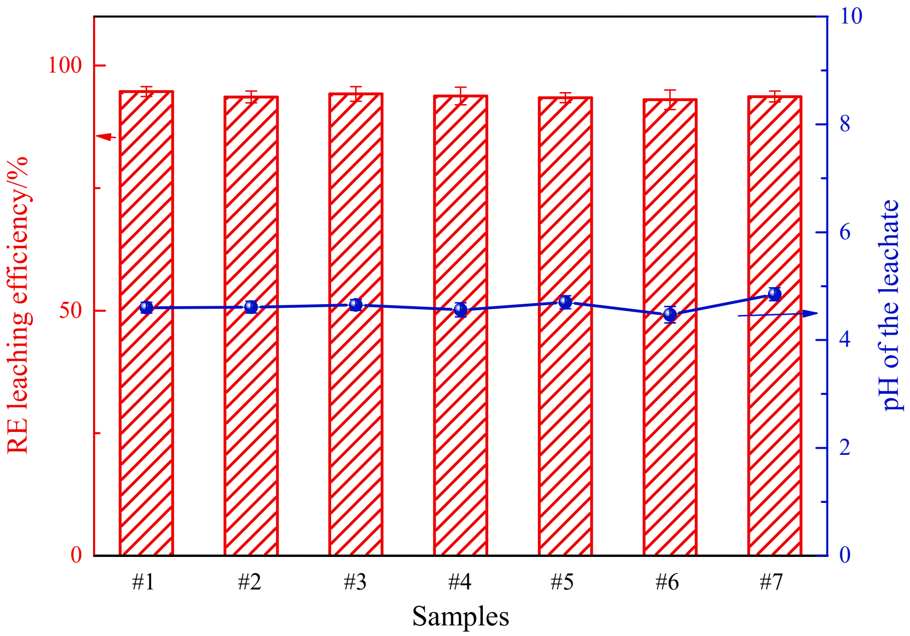

Figure 6. RE leaching efficiency and pH of leachate of different leaching solutions: #1 was 2% ammonium sulfate, #2–#7, respectively, represented the precipitation mother liquor in Figure 3a–f.

3.3. Possible Reaction Between the Residual Ammonium Bicarbonate and RE in the Leaching Process

In order to explain why the presence of a certain amount of residual precipitation agent in the mother liquor could not affect the RE leaching process, the existence of carbonic acid in the solution and the possible RE precipitation reaction during the leaching process were analyzed.

3.3.1. φ-pH of Ammonium Bicarbonate in the Aqueous Solution

Ammonium bicarbonate is an amphoteric substance, and there is an equilibrium of ionization and hydrolysis in the solution:

$$NH_4HCO_3 = NH_4{}^+ + HCO_3{}^- \tag{3}$$

$$NH_4{}^+ + H_2O \rightleftharpoons NH_3 \cdot H_2O + H^+ \qquad k_{1h} = 5.4 \times 10^{-10} \tag{4}$$

$$HCO_3{}^- + H_2O \rightleftharpoons H_2CO_3 + OH^- \qquad k_{2h} = 3.5 \times 10^{-7} \tag{5}$$

$$H_2CO_3 \rightleftharpoons HCO_3{}^- + H^+ \qquad k_1 = 4.2 \times 10^{-7} \tag{6}$$

$$HCO_3{}^- \rightleftharpoons CO_3{}^{2-} + H^+ \qquad k_2 = 5.6 \times 10^{-11} \tag{7}$$

Ammonium bicarbonate can ionize hydrogen ions in water, and can also hydrolyze to produce hydroxide ions. However, because the hydrolysis constant of hydrogen carbonate is much higher than that of ammonium ion, ammonium bicarbonate is alkaline in aqueous solution. When RE reacts with ammonium bicarbonate to form the precipitation of RE carbonate, it is mainly the reaction with the carbonate in ammonium bicarbonate. Therefore, the content of carbonate in aqueous solution is the key factor affecting the precipitation rate of rare earth carbonate. Carbonic acid is the secondary ionization product of carbonic acid, and the pH of the solution directly affects the content of carbonic acid in the solution. Ammonium bicarbonate is a weak acid and weak base salt, which rarely exists in aqueous solutions in molecular form and can be ignored. Then, the total concentration of carbonate when dissolved in water is the following:

$$[CO_3{}^{-}]_T = [HCO_3{}^{-}] + [CO_3{}^{2-}] + [H_2CO_3] \tag{8}$$

Since the component fractions of $CO_3{}^{2-}$, $HCO_3{}^{-}$, and H_2CO_3 in the ammonium bicarbonate solution are represented by Φ_0, Φ_1, and Φ_2, respectively, then

$$\Phi_0 = \frac{[CO_3{}^{2-}]}{[CO_3{}^{-}]_T} = \frac{k_1k_2}{[H^+]^2 + k_1[H^+] + k_1k_2} \tag{9}$$

$$\Phi_1 = \frac{[HCO_3{}^{-}]}{[CO_3{}^{-}]_T} = \frac{k_1[H^+]}{[H^+]^2 + k_1[H^+] + k_1k_2} \tag{10}$$

$$\Phi_2 = \frac{[H_2CO_3]}{[CO_3{}^{-}]_T} = \frac{[H^+]^2}{[H^+]^2 + k_1[H^+] + k_1k_2} \tag{11}$$

After taking the values of k_1 and k_2 into Formulas (9)–(11), the Φ-pH diagram of each component in the aqueous solution can be obtained. The result is shown in Figure 7. It can be seen from Figure 7 that in acidic solution, H_2CO_3 or $HCO_3{}^{-}$ is its main form. When the pH of the solution is high (over 10), ammonium bicarbonate mainly exists in the form of carbonate.

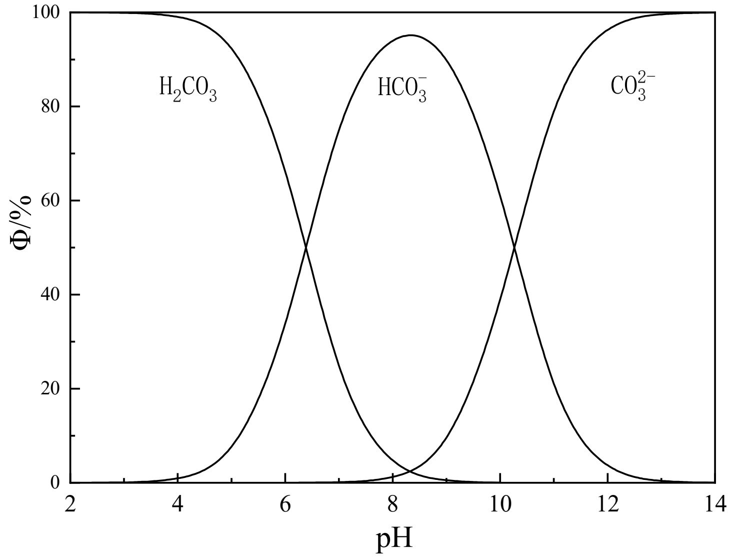

Figure 7. Φ-pH diagram of ammonium bicarbonate in the aqueous solution.

3.3.2. The Possible RE Precipitation Reaction During the Leaching Process

During the leaching process, the residual ammonium bicarbonate may interact with the leached RE to form RE carbonate precipitation, as shown in Formula (12). In addition, as the quantity of ammonium bicarbonate increases, the pH of leaching solution increases, and the RE may also react with hydroxide to form RE hydroxide precipitation, as shown in Formula (15). Formulas (14) and (17) [26] can be calculated from the precipitation solubility product, and Equations (14) and (17) are plotted to obtain the pM-pH diagram of the precipitation equilibrium of RE ions in ammonium bicarbonate solution. The findings are illustrated in Figure 8.

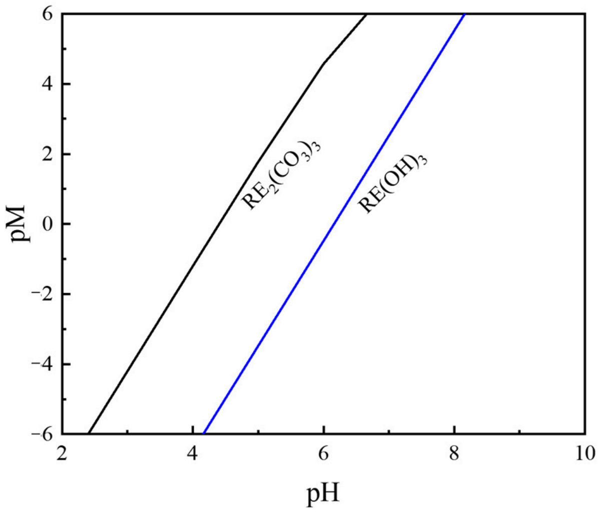

Figure 8. pM-pH diagram of ammonium bicarbonate precipitation system.

From Figure 8, the pM-pH line of RE carbonate precipitation is to the left of the pM-pH line of RE hydroxide precipitation, indicating that RE carbonate precipitation is preferentially formed under the condition of sufficient carbonate in the system. It is apparent from Figures 5 and 6 that when the total carbonate content in the leaching liquor was lower than 0.01 mol/L to leach RE, the pH of the leachate was 4–5. In this pH range, the carbonate primarily exists in the form of H_2CO_3 during the leaching process. The content of carbonate that can directly interact with RE was extremely low. Therefore, not much RE carbonate would be produced. Therefore, when the precipitation mother liquor with a total carbonate content of less than 0.01 mol/L is reused to leach RE, it exerts minimal impact on the RE leaching rate and can be directly recycled within the RE leaching process.

$$2RE^{3+} + 3HCO_3{}^{-} = RE_2(CO_3)_3 \downarrow + 3H^{+} \tag{12}$$

$$2RE^{3+} + 3CO_3{}^{2-} = RE_2(CO_3)_3 \downarrow \qquad K_{sp} = 3.12 \times 10^{-30} \tag{13}$$

$$pM_{RE^{3+}} = -13.2 - \frac{3}{2}\log\left(\left[H^{+}\right]^2 + k_1\left[H^{+}\right] + k_1k_2\right) \tag{14}$$

$$RE^{3+} + 3HCO_3{}^{-} = RE(OH)_3 \downarrow + 3CO_2 \tag{15}$$

$$RE^{3+} + 3OH^{-} = RE(OH)_3 \downarrow \qquad K_{sp} = 3 \times 10^{-24} \tag{16}$$

$$pM_{RE^{3+}}{}' = 3pH - 18.48 \tag{17}$$

3.4. Dynamics of RE Leaching Process

The leaching process of the weathered crust elution-deposited rare earth ore is a solid–liquid heterogeneous reaction, and the ore particles can be regarded as spherical. The leaching process of RE can be described by the shrinking unreacted core model [27]. The following kinetic models are commonly used to simulate the leaching process of weathered crust elution-deposited rare earth ore:

(1) Chemical reaction controls:

$$1 - (1 - \alpha)^{\frac{1}{3}} = kt \tag{18}$$

(2) Outer diffusion controls:

$$1 - (1 - \alpha)^{\frac{1}{3}} = kt \tag{19}$$

(3) Inner diffusion controls:

$$1 - \frac{2}{3}\alpha - (1 - \alpha)^{\frac{2}{3}} = kt \tag{20}$$

where α represents the leaching efficiency; k is the reaction rate constant, min^{-1}; t is the leaching time, min.

3.4.1. Effect of Carbonate Concentration on Leaching Kinetics

Under the conditions of a leaching solution flow rate of 0.6 mL/min, a liquid–solid ratio of 1:1, and room temperature, the effect of total carbonate concentration on the RE leaching process was studied by changing the concentration of ammonium bicarbonate added to a 2% ammonium sulfate solution. The results are shown in Figure 9.

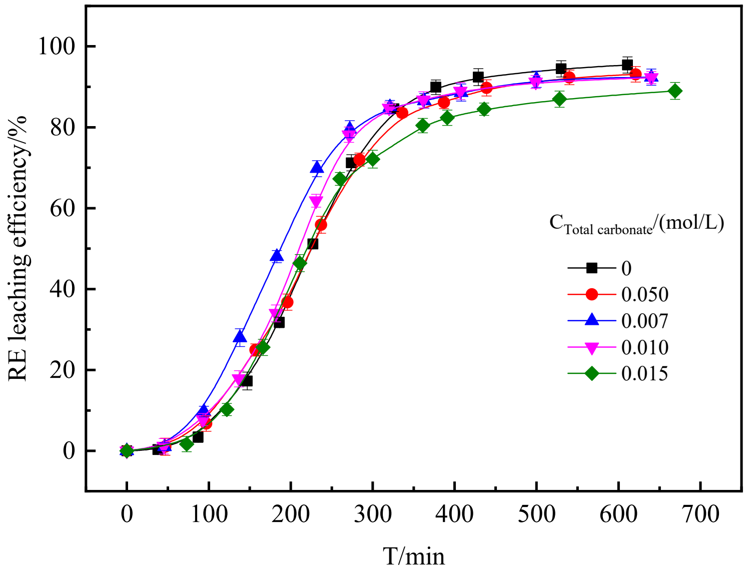

Figure 9. Effect of the total bicarbonate concentration on the kinetic curves of RE.

From Figure 9, it can be seen that the leaching efficiency of RE increases slowly in the initial stage, then increases rapidly, and then slowly tends to equilibrium with the increase in leaching time. When the maximum leaching rate is reached, it remains in equilibrium. When the total carbonate concentration in the leaching solution is less than 0.01 mol/L, the impact of the total carbonate concentration on the leaching efficiency of RE is relatively small, while excessive concentration has a significant impact on the leaching efficiency of RE. This is because when the content of carbonate ions in the leaching solution is high, it will increase the concentration difference of carbonate ions between the flow center of the leaching solution and the surface of mineral particles, enhance the diffusion effect of the leaching solution, and increase the strength of the interaction between RE ions and carbonate ions, thereby enhancing the inhibitory effect of carbonate ions on RE leaching and reducing the RE leaching efficiency.

By inputting the data from Figure 9 into the kinetic models, it was found that the linear relationship between $1 - 2\alpha/3 - (1 - \alpha)^{2/3}$ and t is better, which is more in line with the internal diffusion model. The fitting coefficients R^2 are all greater than 0.97, and the results are shown in Table 2. This result indicates that the leaching process is controlled by the internal diffusion step.

The internal diffusion kinetic equation of rare earth leaching can be expressed as follows [28]:

$$1 - \frac{2}{3}\alpha - (1 - \alpha)^{\frac{2}{3}} = (k_0 - k_{\text{RE}}C_0^n)\text{t} \tag{21}$$

By combining the original internal diffusion dynamics equation, the following can be concluded:

$$k = k_0 - k_{\mathrm{RE}} C_0^n \tag{22}$$

or

$$\ln(k_0 - k) = n\ln C_0 + \ln k_{\mathrm{RE}} \tag{23}$$

where k_0 and k_{RE} are the apparent rate constants of RE leaching when ammonium sulfate or ammonium sulfate solution containing carbonate ions are used as leaching solutions, respectively; n is the empirical reaction order of RE; C_0 is the total concentration of carbonate ions in the extraction solution, mol/L; α is the RE leaching efficiency; and t is the leaching time, min.

Table 2. Apparent rate constant and correlation coefficient values of internal diffusion.

Total Carbonate Concentration/(mol/L)	k/(min^{-1})	R^2
0	0.0009	0.9911
0.005	0.0008	0.9764
0.007	0.0007	0.9700
0.010	0.0006	0.9742
0.015	0.0005	0.9925

By substituting the data from Table 2 into Equation (23), the relationship between $\ln(k_0 - k)$ and $\ln C_0$ can be obtained, as shown in Figure 10. From Figure 10, it can be seen that there is a good linear relationship between $\ln(k_0 - k)$ and $\ln C_0$, with a fitting coefficient R^2 of 0.970, further verifying that the leaching process is controlled by internal diffusion. This result is consistent with the literature report [25]. The empirical reaction order with respect to concentration can be determined by analyzing the slope and intercept of the fitted line, which is 0.627 and k_{RE} = 0.009. Therefore, the internal diffusion kinetic equation of rare earth leaching in this process can be expressed as follows:

$$1 - \frac{2}{3}\alpha - (1-\alpha)^{\frac{2}{3}} = (0.0009 - 0.009C_0^{0.672})t \tag{24}$$

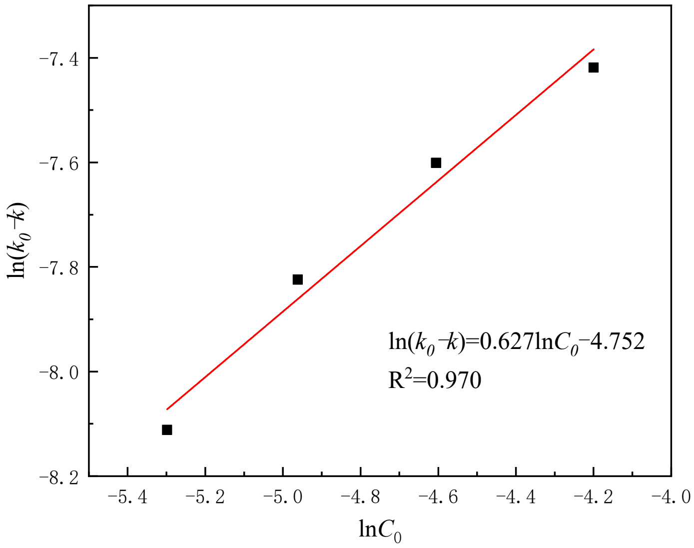

Figure 10. The relationship between $\ln k$ and $\ln C_0$.

3.4.2. Effect of Temperature on Leaching Kinetics

Under the conditions of a total carbonate concentration of 0.01 mol/L, a leaching solution flow rate of 0.6 mL/min, and a liquid–solid ratio of 1:1, the effect of leaching temperature on the RE leaching process was studied. The results are shown in Figure 11.

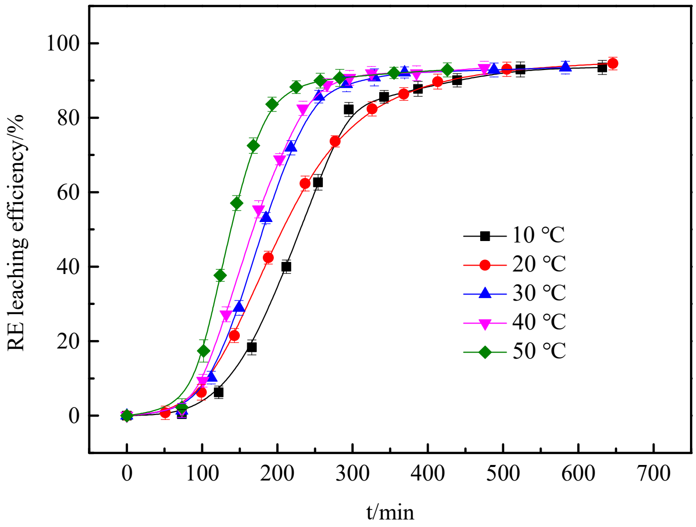

Figure 11. Effect of temperature on the kinetic curves of RE.

As can be seen from Figure 11, with the increase in leaching time, the leaching efficiency of RE increases slowly at the beginning of leaching, then rapidly increases, and maintains equilibrium when the maximum leaching efficiency is reached. In addition, the time required for the RE leaching efficiency to reach equilibrium gradually shortens with the increase in leaching temperature, and the RE leaching efficiency accelerates. This is because the increase in temperature will increase the diffusion rate of ions, increase the rate of ion exchange reaction between ammonium ions in the leaching solution and RE in the ore particles, and accelerate the RE leaching efficiency. At the same time, the increase in leaching temperature can also increase the infiltration rate of the leaching solution in the ore body and shorten the leaching time required [6]. Therefore, leaching in summer is more conducive to achieving higher leaching and production efficiency.

After fitting the data in Figure 11 into various dynamic models, it was found that there is a good linear relationship between $1 - 2\alpha/3 - (1 - \alpha)^{2/3}$ and t, and the fitting coefficients R^2 are all greater than 0.97. The findings presented in Table 3 suggest that the internal diffusion dynamics equation is effectively applicable to the rare earth leaching process.

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

Leaching Temperature/°C	k/(min^{-1})	R^2
10	0.0008	0.9786
20	0.0009	0.9701
30	0.0011	0.9790
40	0.0012	0.9806
50	0.0015	0.9804

According to the Arrhenius equation, the apparent rate constant k can be expressed as follows [29,30]:

$$k = Ae^{-\frac{E}{RT}} \tag{25}$$

or

$$\ln k = \ln A - \frac{E}{RT} \tag{26}$$

where k is the apparent rate constant, min^{-1}; A is the pre-exponential factor; E is the apparent activation energy, kJ/mol; T is the leaching reaction temperature, K; and R is the ideal gas constant.

To illustrate the relationship between ln$k$ and 1/T, the apparent rate constants derived from Table 3 were plotted, as depicted in Figure 12. Analyzing Figure 12 reveals a strong linear correlation between ln$k$ and 1/T, characterized by a fitting coefficient (R^2) of 0.978.

Furthermore, the activation energy for the rare earth leaching reaction, as deduced from the slope of the fitted line, is calculated to be 5.77 kJ/mol, ranging from 4 to 12 kJ/mol, further indicating that the leaching process is controlled by internal diffusion kinetics [31]. Based on the above analysis, the internal diffusion kinetic equations regarding concentration and temperature can be expressed as follows:

$$1 - \frac{2}{3}\alpha - (1-\alpha)^{\frac{2}{3}} = k_0\mathrm{t} - k'C_0^n e^{-\frac{E}{RT}} \cdot \mathrm{t} \tag{27}$$

If

$$k_1 = k' e^{-\frac{E}{RT}} \tag{28}$$

By fitting the linear equation, reaction activation energy, and corresponding experimental temperature in Figure 10 into Equation (28), k' can be calculated. The obtained result is substituted into Equation (27), and the kinetic equation for the RE leaching process is obtained as follows:

$$1 - \frac{2}{3}\alpha - (1-\alpha)^{\frac{2}{3}} = 0.0009\mathrm{t} - \mathrm{C}_0^{0.672} e^{-\frac{5770}{8.314\mathrm{T}}} \cdot \mathrm{t} \tag{29}$$

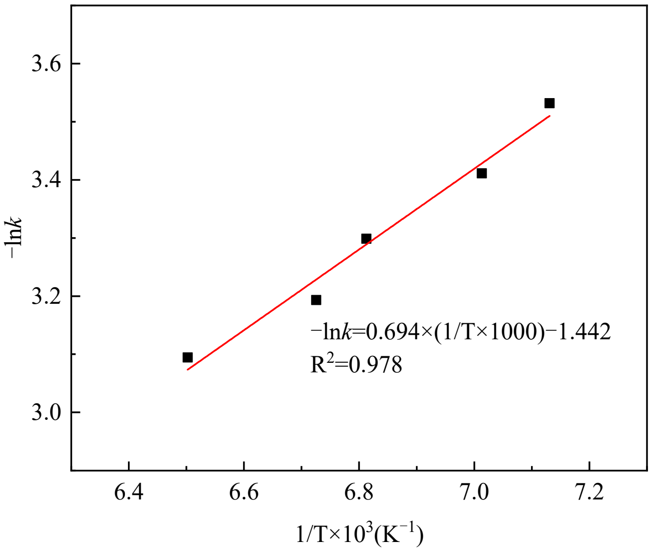

Figure 12. The relationship between plots of ln*k* versus 1/T.

3.5. Mass Transfer Analysis of RE Leaching Process

The influence of different reuse leaching conditions on the rare earth mass transfer process was studied using chromatographic tray theory. The leaching process of weathered crust elution-deposited rare earth ore can be regarded as the fixed phase being clay minerals that adsorb RE, and the mobile phase being the color layer leaching process of the leaching solution. The mass transfer process of leaching can be studied using the theory of chromatography trays. Therefore, Gaussian fitting can be applied to the mass transfer process through chromatographic tray theory. The calculation formulas for the number of theoretical plates and the equivalent height of theoretical plates are as follows [32]:

$$n = 8\ln 2 \times \left(\frac{V_R}{V_{1/2}}\right)^2 \tag{30}$$

$$HETP = \mathrm{h}/n \tag{31}$$

where n is the theoretical plate number; V_R is the retention volume of the outflow curve, mL; $V_{1/2}$ is the half peak height width of the outflow curve, mL; *HETP* is the theoretical tray height, mm; and h is the loading height, mm.

3.5.1. Effect of Carbonate Concentration on Mass Transfer Process

Under a leaching liquid flow rate of 0.6 mL/min, with a liquid–solid ratio of 1:1, and room temperature, the effect of total carbonate concentration on the mass transfer process was studied by varying the content of ammonium bicarbonate added to a 2% ammonium sulfate solution. The findings are illustrated in Figure 13 and detailed in Table 4.

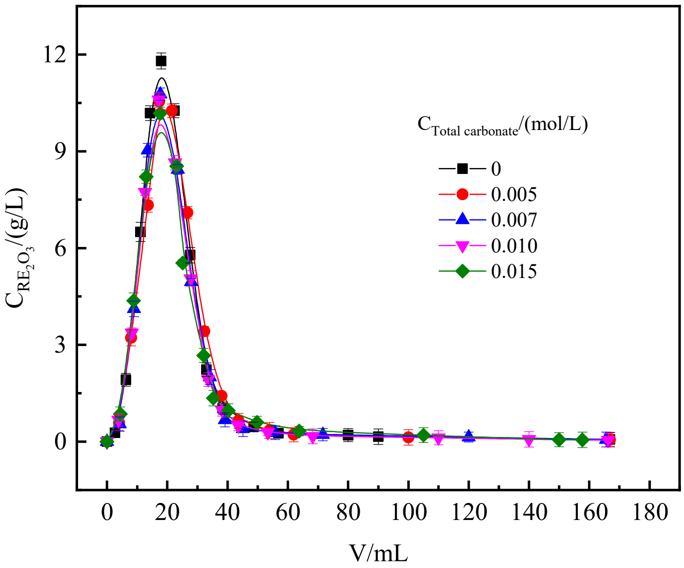

Figure 13. Effect of the total bicarbonate concentration on the leaching curves of RE.

Table 4. Leach HETP and correlation coefficient of RE under various bicarbonate concentrations.

Total Carbonate Concentration/(mol/L)	L/cm	V_R/mL	$V_{1/2}$/mL	*n*	HETP/cm
0	9.60	18.99	16.69	7.18	1.34
0.005	9.50	20.14	18.21	6.78	1.40
0.007	9.70	18.79	16.87	6.88	1.41
0.010	9.70	18.82	17.12	6.70	1.44
0.015	9.50	18.32	17.16	6.32	1.50

From Figure 13, it can be seen that as the volume of the leachate increases, the concentration of RE in the leachate first increases, then decreases, and finally approaches zero. As the concentration of carbonate ions in the leaching solution increases, the peak concentration of RE gradually decreases. The leaching curve in Figure 13 was analyzed using chromatographic tray theory to obtain the theoretical tray height, as shown in Table 4. From Table 4, it can be seen that as the concentration of carbonate ions increases, the height of the tray gradually increases. This indicates that the increase in carbonate content in the leaching solution is not conducive to the mass transfer process of RE.

3.5.2. Effect of Temperature on Mass Transfer Process

In an experimental setup involving an ammonium sulfate leaching solution with a total carbonate concentration of 0.01 mol/L, the flow rate was maintained at 0.6 mL/min and a liquid-to-solid ratio of 1:1 was employed. To investigate the influence of temperature on the mass transfer process, the leaching temperature was systematically varied. The findings from this study are presented in Figure 14 and Table 5.

From Figure 14, it can be seen that as the leaching temperature increases, the peak concentration of RE leaching shows an increasing trend, while the peak width is the opposite. This indicates that an increase in temperature can promote an increase in RE leaching efficiency. As shown in Table 5, the theoretical number of trays decreases with increasing temperature, indicating that higher leaching temperatures can promote mass transfer during the leaching process and shorten the production cycle.

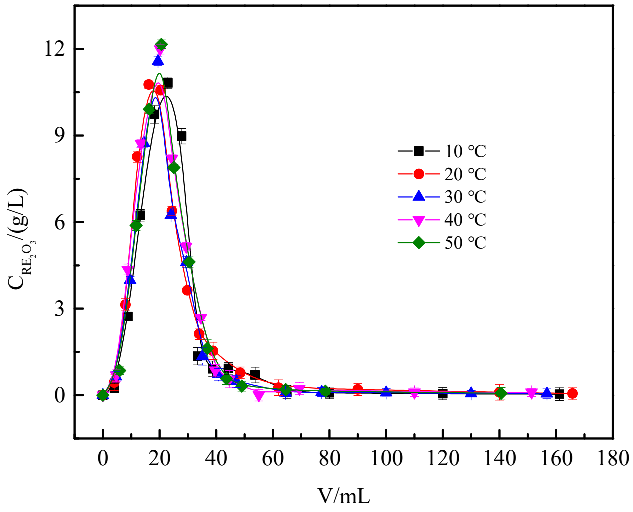

Figure 14. Effect of the leaching temperature on the leaching curves of RE.

Table 5. Leach HETP and correlation coefficient of RE under various leaching temperatures.

Temperature/°C	L/cm	V_R/mL	$V_{1/2}$/mL	*n*	HETP/cm
10	9.90	21.51	18.93	7.16	1.38
20	9.70	18.26	16.53	6.77	1.44
30	9.60	18.93	16.25	7.53	1.28
40	9.50	19.64	16.76	7.61	1.25
50	9.60	20.14	16.77	7.80	1.20

4. Conclusions

(1) In the RE carbonate precipitation process, when the RE concentration in the leachate ranged from 0.1 to 1.5 g/dm^3, and the precipitation rate of the RE attained a state of equilibrium, the RE precipitation rate was higher than 96%. And the residual total carbonate content in the precipitation mother liquor was lower than 0.01 mol/L, and the pH was 7–8.

(2) In the RE leaching process, when the total carbonate concentration in the leaching liquor was less than 0.01 mol/L, and the pH was 7–8, there was almost no effect on the RE leaching efficiency. Consequently, the mother liquor resulting from precipitation under these conditions can be directly reused in the rare earth leaching process.

(3) When the mother liquor of rare earth carbonate precipitation is used as the leaching solution, the leaching process of RE is governed by the kinetics of internal diffusion. The decrease in total carbonate content and the increase in temperature in the leaching solution are beneficial for the mass transfer process of RE leaching.

The kinetic equation for the reuse leaching process was established based on the leaching temperature and total carbonate concentration in the leaching solution, in order to guide the reuse of precipitation mother liquor for leaching rare earth ore.

Author Contributions: Conceptualization, J.F. and X.W.; methodology, J.F.; software, J.F. and X.W.; validation, X.W.; formal analysis, J.F.; investigation, J.F.; resources, R.C.; data curation, J.F.; writing—original draft preparation, J.F.; writing—review and editing, J.F. and X.W.; visualization, F.Z.; supervision, X.W.; project administration, R.C.; funding acquisition, X.W. All authors have read and agreed to the published version of the manuscript.

Funding: This research was funded by the National Natural Science Foundation of China (No. 52204278 and 22078252).

Data Availability Statement: Data are contained within the article.

Acknowledgments: Thanks for the great effort by the editors and reviewers.

Conflicts of Interest: The authors declare no conflicts of interest.

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