Article

Removal of Sulfate Ions from Calcium Oxide Precipitation Enrichment of a Rare Earth Leaching Liquor by Stirring Washing with Sodium Hydroxide

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ABSTRACT: The use of calcium oxide as a precipitant can achieve a nonammonia enrichment of a rare earth leaching liquor. However, an alkaline rare earth sulfate forms during the precipitation process, thus resulting in excessive SO_4^{2-} content in the mixed rare earth oxides. Therefore, a stirring washing process for precipitation enrichment, which was obtained from calcium oxide precipitation, was investigated using a sodium hydroxide solution. It was determined that the Gibbs free energy of the stirring washing reaction, which was calculated by a group contribution method, was between −60 and −300 kJ/mol, depending on the different rare earth elements. The above results indicated that the reaction was thermodynamically feasible. The optimum conditions of the washing process were obtained, namely, a feed ratio of 2.85, a liquid−solid ratio of 6.5 mL/g, a stirring washing temperature of 35 °C,

and a stirring washing time of 20 min. Under the optimal conditions, the purity and the SO_4^{2-} content of the mixed rare earth oxides were 94.38% and 3.48%, respectively, and the stirring washing process with the sodium hydroxide solution had good recyclability. Moreover, the washing product was tested using thermogravimetry-differential thermal analysis (TG-DTA), X-ray diffraction (XRD), and scanning electron microscopy-energy-dispersive spectrometry (SEM-EDS), which verified that the stirring washing process with NaOH could effectively remove SO_4^{2-} from the precipitation enrichment into solution. On this basis, a new extraction process of the ion-adsorption-type rare earth ore by magnesium salt leaching−calcium oxide precipitation−sodium hydroxide stirring washing is proposed. This new process can eliminate the traditional aluminum-removal process and effectively reduces the rare earth loss in the process. It can also solve the problem of the excessive SO_4^{2-} content in the mixed rare earth oxides caused by the calcium oxide precipitation process. The research in this paper can have great significance for green, efficient extraction of the ion-adsorption-type rare earth ore and the improvement of resource utilization.
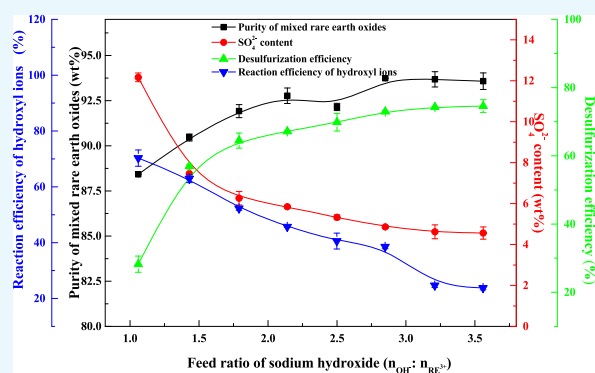
1. INTRODUCTION

Rare earth elements have unique physical and chemical properties, and they have been widely used in magnetics, optics, and many other fields.[1] Among them, middle and heavy rare earth elements are indispensable raw materials that are highly associated with many high-technology fields.[2] The ion-adsorption-type rare earth ore, mainly located in China, is the main resource of middle and heavy rare earth elements in the world. Currently, rare earth is extracted from the ion-adsorption-type rare earth ore by leaching with ammonium sulfate, which is followed by aluminum-removal and the precipitation process with ammonium bicarbonate. The use of $(NH_4)_2SO_4$ and NH_4HCO_3 has generated serious ammonia−nitrogen pollution. High ammonium−nitrogen contamination in both groundwater (3500−4000 mg/L) and surface water (80−160 mg/L) has been reported,[3,4] which leads to eutrophication and biodiversity decline in streams. To solve the above problems, nonammonia leaching agents,[5−7] such as

magnesium sulfate, iron sulfate, and aluminum sulfate, and nonammonia precipitants,[8−12] such as sodium carbonate, magnesium oxide, and calcium oxide, have been widely studied. Among these, a green Mg−Ca salt extraction process of the ion-adsorption-type rare earth ore has been performed,[13,14] as shown in Figure 1. In this process, the use of a magnesium salt compound leaching agent can realize a rare earth leaching efficiency of more than 94%, and it can modify the content and ratio of ion-exchangeable calcium and ion-exchangeable magnesium in red soil.[5,13] The use of a calcium oxide precipitant can reduce the production costs and
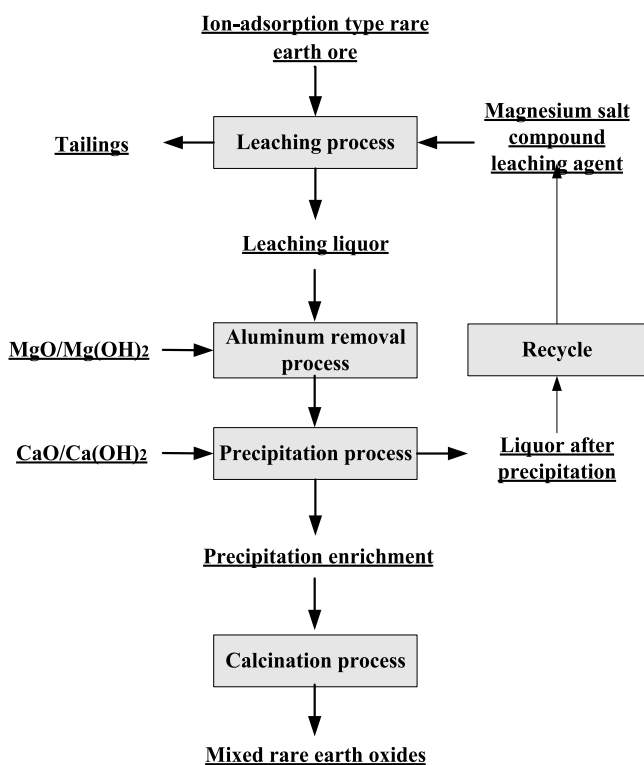
Figure 1. Flow chart of the green Mg−Ca salt extraction process for the ion-adsorption-type rare earth ore.

obtain rare earth hydroxide with a low calcination temperature, thus reducing energy consumption.[14,15] More importantly, the green Mg−Ca salt extraction process can realize the effective recycling of calcium and magnesium, and finally solve the ammonia−nitrogen problem in the whole extraction process of the ion-adsorption-type rare earth ore.

In the CaO precipitation process, calcium sulfate precipitation would not occur, which was shown by the solubility behavior of calcium sulfate in the above system, as previously determined by our team.[16] However, in addition to the formation of rare earth hydroxides, a part of the rare earth forms alkaline rare earth sulfate in the CaO precipitation process, resulting in an excessive SO_4^{2-} content in the mixed rare earth oxides.[10,14,17] Under these circumstances, the purity of the mixed rare earth oxides obtained from the green Mg−Ca salt extraction process was only approximately 82%. The above results cannot meet the national standard of mixed rare earth oxides, which requires the purity to be over 92%.[18] Moreover, excessive SO_4^{2-} content in the mixed rare earth oxides increases the operating load of the follow-up rare earth extraction−separation process. Therefore, it is necessary to develop a method to reduce SO_4^{2-} in the mixed rare earth oxides and improve the green Mg−Ca salt extraction process. For this purpose, a series of studies were conducted. Meng[19] proposed precipitating rare earth from low-concentration rare earth liquor using a CaO−Na_2CO_3 progressive precipitation method, namely, a certain amount of calcium oxide slurry was first added to the rare earth liquor and then sodium carbonate was added to enrich the rare earth. When the doses of calcium oxide and sodium carbonate were 60% and 50% of the theoretical amount, respectively, the SO_4^{2-} content in the mixed rare earth oxides decreased to 8.66%, and the purity of the rare earth can increase to 88.99%. However, the problem of

the low purity of mixed rare earth oxides cannot be essentially solved by the progressive precipitation method. Based on an alkaline rare earth sulfate being able to decompose to SO_3 at high temperatures, Huang[10] proposed a method of reducing the SO_4^{2-} content in mixed rare earth oxides by high-temperature calcination. When the rare earth precipitation enrichment was calcined at 1300 °C for 2 h, the SO_4^{2-} content in the mixed rare earth oxides decreased to 0.55%. However, a high calcination temperature greatly increases energy consumption. Considering that the use of sodium hydroxide can transform the rare earth sulfate and its complex salt into rare earth hydroxides,[1,2] a new method to reduce SO_4^{2-} in mixed rare earth oxides by stirring washing the precipitation enrichment with sulfate-removal reagents was presented by our team.[14,15,20] An anion that had a strong coordination ability with rare earth was introduced into the sulfate-removal agent to compete with the sulfate ions in the stirring washing process; thus, the sulfate ions could be exchanged and enter the solution, and the SO_4^{2-} content in the mixed rare earth oxides would be decreased. In addition, the coordination ability between the anion and the rare earth elements should be lower than that between hydroxyl ions and rare earth elements, which would prevent the formation of soluble rare earth complexes and the loss of rare earth elements in the stirring washing process. Preliminary exploration experiments showed that the purity of the mixed rare earth oxides could be increased to 89.45%, 88.76%, and 88.03%,[14] when the precipitation enrichment was washed with 100 mL of 0.05 mol/L sodium succinate, sodium malonate, and sodium hydroxide, respectively. However, the price of sodium succinate and other organic substances is relatively high, which is not suitable for industrial applications. As a result, sodium hydroxide could be the first choice for use as a sulfate-removal reagent.

In this paper, a precipitation enrichment, which was obtained by calcium oxide precipitation, was studied with sodium hydroxide in a stirring washing process. First, the Gibbs free energy of the stirring washing reaction was calculated by a group contribution method to verify the feasibility of the washing reaction with NaOH. Then, the effects of the sodium hydroxide feed ratio, liquid−solid ratio, reaction time, reaction temperature, and recyclability of sodium hydroxide during the stirring washing process were investigated; the washing product was analyzed using thermogravimetry-differential thermal analysis (TG-DTA), X-ray diffraction (XRD), and scanning electron microscopy-energy-dispersive spectrometry (SEM-EDS) to verify the stirring washing reaction process with sodium hydroxide. Moreover, considering the amphoteric properties of aluminum hydroxide, a new extraction process of the ion-adsorption-type rare earth ore by magnesium salt leaching, calcium oxide precipitation, and sodium hydroxide stirring washing was suggested and explored. The new process can eliminate the rare earth loss caused by the traditional aluminum-removal process and solve the problem of excessive SO_4^{2-} content in the mixed rare earth oxides caused by the calcium oxide precipitation process. Hence, a feasible operation is provided for nonammonia enrichment of rare earth from a rare earth leaching liquor, which has great significance for green, efficient extraction of the ion-adsorption-type rare earth ore and the improvement of resource utilization.

Table 1. ΔG_i Values of RE^{3+}, $\Delta_f G^{\theta}(RE(OH)_3)$, $\Delta_f G^{\theta}(RE_2(OH)_4SO_4)$, and $\Delta_f G^{\theta}(1)$ Corresponding to Different Rare Earth Elements

rare earth element	ΔG_i values of RE^{3+} (kJ/mol)	$\Delta_f G^{\theta}(RE_2(OH)_4SO_4)$ (kJ/mol)	$\Delta_f G^{\theta}(RE(OH)_3)$ (kJ/mol)	$\Delta_f G^{\theta}(1)$ (kJ/mol)
La	−559.23	−2835.21	−1262.21	−119.16
Ce	−569.97	−2856.69	−1254.97	−83.19
Pr	−562.90	−2842.56	−1257.60	−102.57
Nd	−566.49	−2849.74	−1265.96	−112.12
Sm	−537.93	−2792.62	−1264.31	−165.93
Eu	−466.03	−2648.82	−1177.34	−135.80
Gd	−543.85	−2804.45	−1262.59	−150.68
Tb	−544.37	−2805.50	−1247.53	−119.50
Dy	−554.97	−2826.69	−1261.51	−126.27
Ho	−565.86	−2848.48	−1272.76	−126.99
Er	−568.56	−2853.88	−1274.36	−124.78
Tm	−455.38	−2627.52	−1267.70	−337.82
Yb	−520.71	−2758.18	−1250.39	−172.53
Lu	−555.91	−2828.58	−1235.17	−71.69
Y	−614.97	−2946.70	−1291.60	−66.44
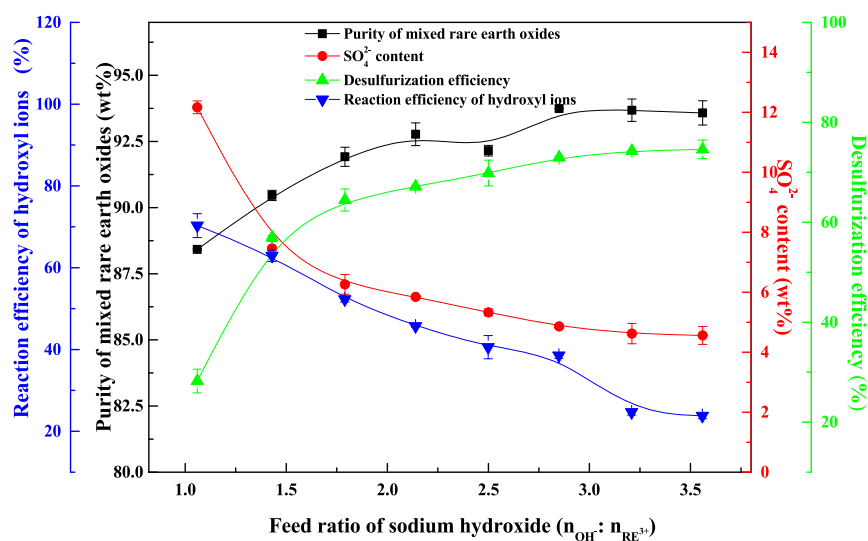
Figure 2. Effect of the feed ratio of NaOH on the stirring washing process (L/S = 9.5 mL/g, T = 35 °C, t = 40 min).

2. RESULTS AND DISCUSSION

2.1. Thermodynamic Analysis of the Stirring Washing Reaction with NaOH. Due to a lack of thermodynamic data on alkaline rare earth sulfates, a group contribution method was used to calculate the Gibbs free energy of formation ($\Delta_f G^{\theta}$, kJ/mol) for the alkaline rare earth sulfate in this paper. The group contribution method was first applied to the calculation of the thermodynamic properties of organic compounds.[22] Subsequently, due to its simplicity and accuracy, the group contribution method was widely used in the thermodynamic calculation of inorganic salts.[23−25] For example, the group contribution method was applied to calculate the $\Delta_f G^{\theta}$ and $\Delta_f H^{\theta}$ values of calcium sulfoaluminate,[25] and the obtained thermodynamic data were applied to the analysis of the reaction process. It was shown that the analytical results were in good agreement with the experimental results. In the group contribution method, the inorganic salts were considered to be composed of cations, anions, and ligands (e.g., water of hydration); therefore, the $\Delta_f G^{\theta}$ of the inorganic salts was equal to the sum of the products of the group contribution values (ΔG_i, kJ/mol) and the number of groups, as shown in eq 1. To calculate the group contribution values (ΔG_i, kJ/mol), the

$\Delta_f G^{\theta}$ values of a large number of compounds were used to establish many linear equations. Therefore, the values of the group contributions (ΔG_i, kJ/mol) to the Gibbs free energy of formation were determined by a multiple linear regression.[26] The ΔG_i values of RE^{3+} have been calculated in reports in the literature,[23,27] shown in Table 1, and the ΔG_i value of OH^- and SO_4^{2-} is −230.43 and −795.05 kJ/mol,[27] respectively.

$$\Delta_f G^{\theta} = \sum (n_i \times \Delta G_i) \tag{1}$$

where n_i is the number of groups of the ith type and ΔG_i is the contribution for the ith atomic or molecular group.

According to eq 1 and the ΔG_i values, the $\Delta_f G^{\theta}(RE_2(OH)_4SO_4)$ of alkaline rare earth sulfate was calculated according to eq 2, and the results are shown in Table 1. It was determined in Table 1 that the $\Delta_f G^{\theta}(RE_2(OH)_4SO_4)$ ranged from −2600 to −3000 kJ/mol. Moreover, the Gibbs free energy values of the rare earth hydroxides $\Delta_f G^{\theta}(RE(OH)_3)$ in Table 1 were collected from Lange's Handbook of Chemistry,[28] and $\Delta_f G^{\theta}(OH^-)$ and $\Delta_f G^{\theta}(SO_4^{2-})$ were reported to be −157.28 and −744.50 kJ/mol,[29] respectively. Then, the Gibbs free energy of the stirring washing reaction ($\Delta_r G^{\theta}(1)$, kJ/mol) was calculated by eq 3,
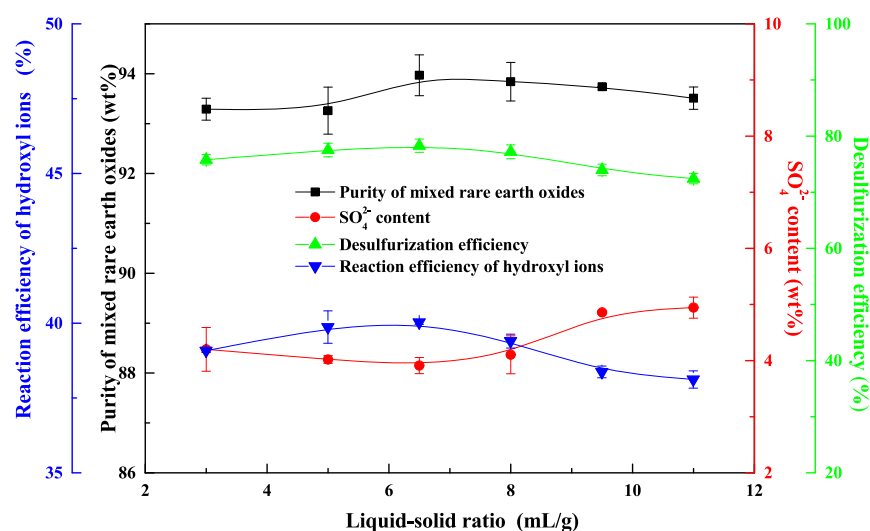
Figure 3. Effect of the liquid−solid ratio on the stirring washing process ($n(OH^-)/n(RE^{3+})$ = 2.85, T = 35 °C, t = 40 min).

and the results are also shown in Table 1. The $\Delta_r G^\theta(1)$ was negative for any rare earth element, which indicated that the stirring washing reaction with sodium hydroxide was thermodynamically feasible. For instance, the $\Delta_r G^\theta(1)$ of alkaline yttrium sulfate was −66.44 kJ/mol; therefore, sodium hydroxide may remove sulfate radicals in the precipitation enrichment and convert alkaline yttrium sulfate into yttrium hydroxide.

$$\Delta_f G^\theta(RE_2(OH)_4SO_4)$$
$$= 2 \times \Delta G_{RE^{3+}} + 4 \times \Delta G_{OH^-} + \Delta G_{SO_4^{2-}} \quad (2)$$

$$\Delta_r G^\theta(1) = 2 \times \Delta_f G^\theta(RE(OH)_3) + \Delta_f G^\theta(SO_4^{2-})$$
$$- 2 \times \Delta_f G^\theta(OH^-) - \Delta_f G^\theta(RE_2(OH)_4SO_4) \quad (3)$$

2.2. Study on the Stirring Washing Process. *2.2.1. Effect of the Feed Ratio of NaOH on the Stirring Washing Process.* For a chemical reaction, the concentration and dose of reactants have a great influence on the reaction equilibrium. In the stirring washing process, the molar amount of rare earth in the rare earth precipitation enrichment was fixed at approximately 0.0078 mol. Therefore, to study the effect of the feed ratio of NaOH on the stirring washing process, 60 mL of a sodium hydroxide solution with different concentrations was used to wash the precipitation enrichment. The feed ratio of NaOH ($n_{OH^-}/n_{RE^{3+}}$) was calculated by the mole ratio of hydroxyl ions to rare earth ions. The results are shown in Figure 2. Because the reaction time was long enough, the stirring washing process was mainly related to thermodynamics rather than kinetics. With the increase in the feed ratio of sodium hydroxide, the concentration of sodium hydroxide increased, which could promote the remainder of the reaction (eq 7) to move to the right. Therefore, an increasing amount of alkaline rare earth sulfate was converted into rare earth hydroxide, and there was an increasing number of SO_4^{2-} ions in the liquor. At this time, the purity of the mixed rare earth oxides increased rapidly. When the concentration of sodium hydroxide was increased to a certain extent, the reactant (OH^-) and the product (SO_4^{2-}) could reach thermodynamic equilibrium, and the reaction (eq 7) no longer shifted to the right; therefore, the rare earth purity increased slowly until it

was stable. Therefore, as shown in Figure 2, when the feed ratio of NaOH increased to 1.79, the purity of the mixed rare earth oxides increased rapidly to 91.92%. As the feed ratio was increased to 2.85, the purity of the mixed rare earth oxides increased slowly to 93.74% and finally tended to be stable with a further increase in the feed ratio. For the SO_4^{2-} content in the mixed rare earth oxides, the change law was opposite to that of the purity in the mixed rare earth oxides. With the increase in the feed ratio of NaOH, the SO_4^{2-} content in mixed rare earth oxides first decreased rapidly to 6.26%, then decreased slowly to approximately 4.86%, and finally remained unchanged. The behavior of the desulfurization efficiency was in good agreement with the change trend of rare earth purity. Moreover, when the feed ratio of NaOH was low, more sodium hydroxide was involved in the sulfate-removal process, and the reaction efficiency of the hydroxyl ions was high. However, with an increase in the feed ratio, sodium hydroxide became increasingly excessive, and the reaction efficiency of the hydroxyl ions decreased. Finally, considering the purity of the mixed rare earth oxides and the concentration of residual hydroxyl ions in the filtrate, 2.85 was chosen as the feed ratio for the subsequent study.

2.2.2. Effect of the Liquid−Solid Ratio on the Stirring Washing Process. To study the effect of the liquid−solid ratio on the stirring washing process, stirring washing experiments were carried out under different liquid−solid ratio conditions. The results are shown in Figure 3. It was shown in Figure 3 that under the condition of a feed ratio of 2.85, the stirring washing reaction was sufficiently carried out; therefore, the purity of the mixed rare earth oxides in different experiments was basically higher than 93% and slightly changed under different liquid−solid ratio conditions. When the liquid−solid ratio was increased to 6.5 mL/g, the purity of the mixed rare earth oxides increased slowly to 93.97% and then decreased to 93.51% with continuing increase in the liquid−solid ratio. The above result was consistent with the change trend in the desulfurization efficiency and reaction efficiency of hydroxyl ions. The main reasons for this trend were as follows: as the total amount of hydroxide ions in the experiments was the same, with an increase in the liquid−solid ratio, the concentration of sodium hydroxide solution decreased. When the liquid−solid ratio was small, the concentration of the
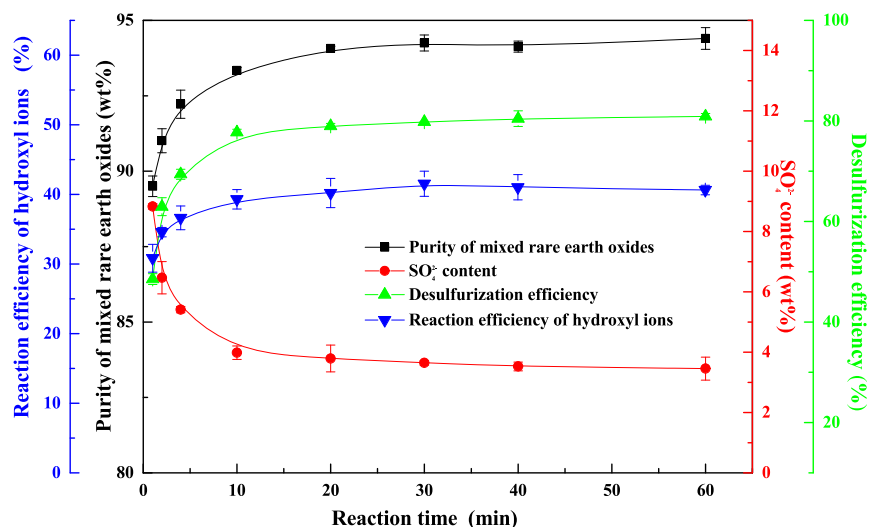
Figure 4. Effect of the reaction time on the stirring washing process $(n(OH^-)/n(RE^{3+}) = 2.85$, L/S = 6.5 mL/g, $T = 35$ °C).

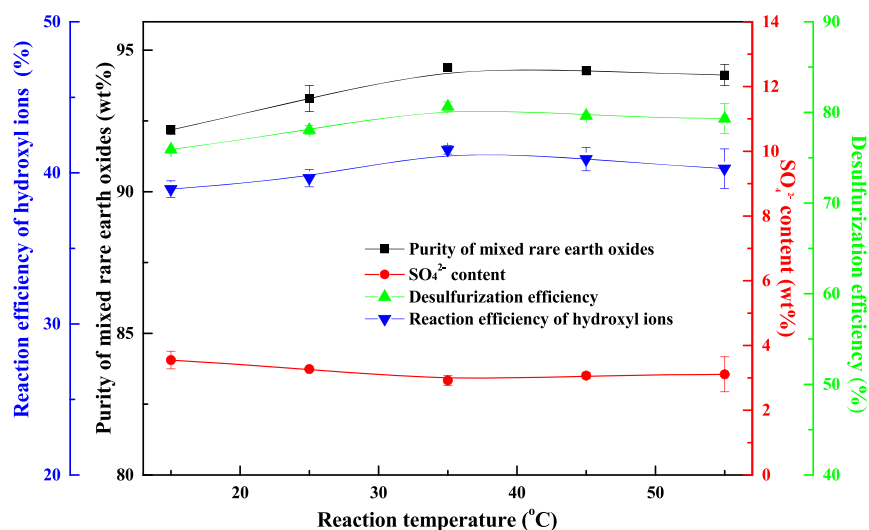**Figure 5.** Effect of the reaction temperature on the stirring washing process $(n(OH^-)/n(RE^{3+}) = 2.85$, L/S = 6.5 mL/g, $t = 20$ min).

sodium hydroxide solution was high, but there was insufficient liquid−solid contact in the stirring washing process. With an increase in the liquid−solid ratio, the liquid−solid contact would be sufficient; therefore, the reaction efficiency of the hydroxyl ions increased with the increase in the liquid−solid ratio. However, when the liquid−solid ratio increased to 6.5 mL/g, the liquid−solid contact was sufficient, and the concentration of sodium hydroxide was the main factor affecting the sulfate-removal reaction. At this time, with a decrease in the sodium hydroxide concentration, the trend of the reaction moving to the right was weakened, resulting in the reduction of the reaction efficiency of the hydroxyl ions. Therefore, the desulfurization efficiency and reaction efficiency of the hydroxyl ions first increased first and then decreased with an increasing liquid−solid ratio, and the change trend of the SO_4^{2-} content in the mixed rare earth oxides was the opposite. Considering the SO_4^{2-} content and the purity of the mixed rare earth oxides, a liquid−solid ratio of 6.5 mL/g was chosen.

2.2.3. Effect of the Reaction Time on the Stirring Washing Process. The length of the reaction time has an important influence on the reaction efficiency; therefore, it is necessary to

study the effect of the reaction time on the stirring washing process. The results are shown in Figure 4. The stirring washing reaction with sodium hydroxide was a typical liquid−solid reaction, which was controlled by kinetics in the early stage, and then approached equilibrium. With increasing reaction time, the mass transfer in the solid−liquid phase became increasingly sufficient, and the stirring washing reaction became increasingly thorough. Therefore, the purity of the mixed rare earth oxides, the desulfurization efficiency, and the reaction efficiency of the hydroxyl ions increased with increasing reaction time. On continuing to increase the reaction time, the stirring washing reaction tended to reach equilibrium and was controlled by thermodynamics. In this way, the purity of the mixed rare earth oxides, the desulfurization efficiency, and the reaction efficiency of the hydroxyl ions became stable. As demonstrated in Figure 4, the purity of the mixed rare earth oxides increased rapidly to approximately 93% in the first 10 min, then slowed over time, and finally remained stable at approximately 94.00% when the stirring washing time exceeded 20 min. This result indicated that the stirring washing process was controlled by kinetics in the first 10 min and approached equilibrium. Moreover, the
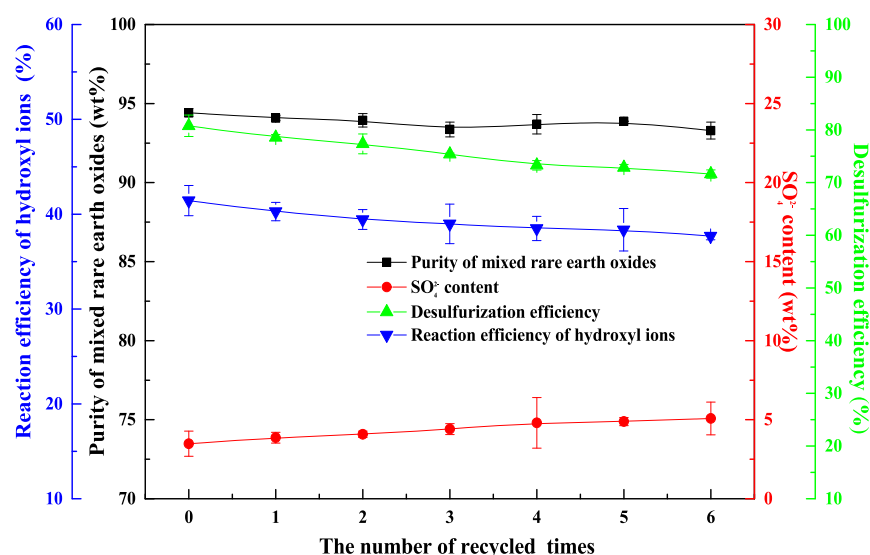
Figure 6. Effect of recyclability on the stirring washing process ($n(OH^-)/n(RE^{3+})$ = 2.85, L/S = 6.5 mL/g, T = 35 °C, t = 20 min).

desulfurization efficiency and the reaction efficiency of the hydroxyl ions had the same change trend as the purity of the mixed rare earth oxides and were approximately 80.5% and 40.5%, respectively. Accordingly, the content of SO_4^{2-} increased with increasing reaction time and then stabilized at approximately 3.46%. To ensure that the stirring washing reaction proceeded adequately, 20 min was chosen as the stirring washing time for the subsequent experiments. In this case, the purity of mixed rare earth oxides and the SO_4^{2-} content were 94.07% and 3.79%, respectively; the desulfurization efficiency was 79.0%, and the reaction efficiency of the hydroxyl ions was 40.5%.

2.2.4. Effect of the Reaction Temperature on the Stirring Washing Process. Temperature has an important influence on the kinetics and thermodynamics of a reaction. Therefore, the effect of the reaction temperature on the stirring washing process was investigated. The results are shown in Figure 5. Figure 5 shows that the purity of the mixed rare earth oxides first increased with increasing reaction temperature. When the temperature reached 35 °C, the purity of the mixed rare earth oxides was approximately 94.40% and then remained unchanged with increasing temperature. In addition, the desulfurization efficiency, the SO_4^{2-} content in the mixed rare earth oxides, and the reaction efficiency of the hydroxyl ions were consistent with the rare earth purity data. Considering that the purity of the mixed rare earth oxides changes slightly after 35 °C, the reaction temperature was determined to be 35 °C.

In summary, the following optimum conditions were chosen for the stirring washing process with the sodium hydroxide solution for precipitation enrichment, which was obtained from calcium oxide precipitation: a feed ratio of 2.85, a liquid–solid ratio of 6.5 mL/g (40 mL, 0.48 mol/L NaOH), a reaction temperature of 35 °C, and a reaction time of 20 min. Under the optimal conditions, the purity and the SO_4^{2-} content of the mixed rare earth oxides were 94.38% and 3.48%, respectively. The desulfurization efficiency was 80.6%, and the reaction efficiency of the hydroxyl ions was 41.5%.

2.2.5. Effect of Recyclability on the Stirring Washing Process. Under the optimum conditions, the reaction efficiency of the hydroxyl ions was only 41.5%, and a large amount of hydroxyl ions remained in the filtrate after the
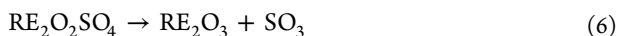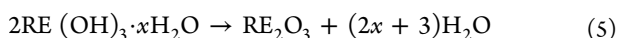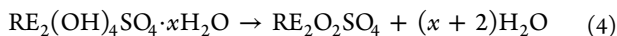
stirring washing process. If these hydroxyl ions could be recycled, not only could the sodium hydroxide consumption be reduced but also the production of wastewater could be reduced and water resources would be saved. Therefore, the effect of recyclability on the stirring washing process was investigated. The results are shown in Figure 6. In every recyclability experiment, the volume of the filtrate was stable at 40 mL, and the concentration of hydroxide ions in the filtrate was set to 0.48 mol/L (which was consistent with the optimum conditions for the stirring washing process) by adding a quantitative amount of sodium hydroxide. Then, it was used to wash the fresh precipitation enrichment. However, with an increase in the number of times the filtrate was recycled, more SO_4^{2-} entered into the filtrate, leading to an increasing concentration of sulfate ions in the filtrate. Every time the concentration of sulfate ions increased, the equilibrium of the stirring washing reaction shifted to the left. Therefore, as the number of recycle times increased, the reaction efficiency of the hydroxyl ions, desulfurization efficiency, and purity of the mixed rare earth oxides decreased slowly, while the SO_4^{2-} content in the mixed rare earth oxides increased gradually. When the filtrate was recycled for the sixth time, the purity of the mixed rare earth oxides decreased only from 94.42% to 93.29%, and the SO_4^{2-} content increased from 3.48% to 5.08%. The cyclic sulfate-removal effect of the filtrate was relatively stable, but when sulfate ions accumulate to a certain extent, some methods should be used to remove the sulfate ions from the filtrate before recycling could be continued.

2.2.6. Characterization of the Washing Product. To verify the stirring washing reaction process with sodium hydroxide, a thermodecomposition process of the washing product obtained under optimum conditions was developed using TG-DTA. The results are shown in Figure 7. As shown in Figure 7, there were two weight-loss stages from 40 to 1400 °C. In the first stage, the washing product continued to lose weight and was accompanied by an endothermic peak when the temperature rose to 950 °C. The weight-loss ratio was 27.68%, and the reactions involved in this stage might include the dehydration of the rare earth hydroxides and alkaline rare earth sulfates, as shown in eqs 4 and 5. In the second stage, as the temperature increased from 950 to 1300 °C, the washing product continued to lose weight, which was accompanied by
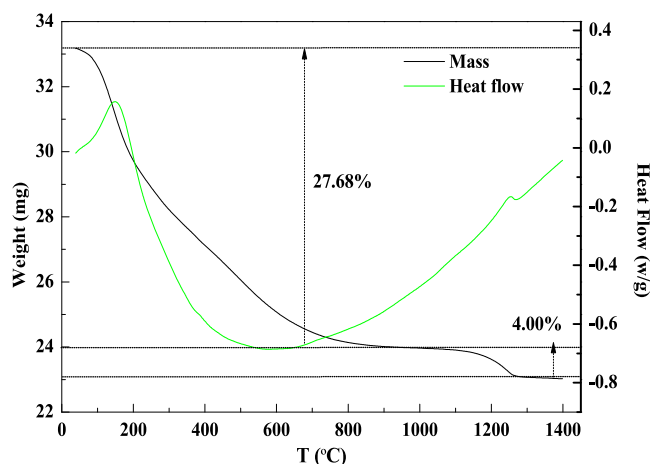
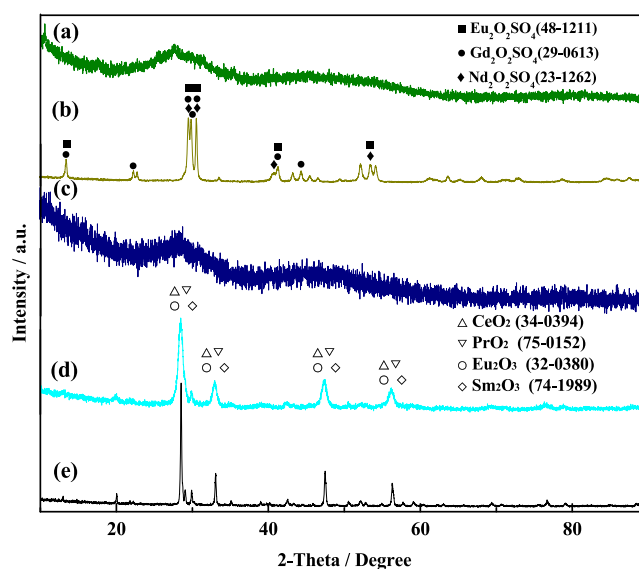**Figure 7.** TG-DTA curves of the washing product obtained under the optimum conditions.

Figure 8. XRD patterns of the solid samples. Sample obtained after the precipitation enrichment was (a) dried and (b) calcined at 950 °C. Sample obtained after the washing product was (c) dried, (d) calcined at 950 °C, and (e) calcined at 1400 °C.

an endothermic peak; the above weight loss was due to the decomposition of the washing product to release SO_3, as shown in eq 6.[10,30] Clearly, the weight-loss rate in this stage should be consistent with the SO_4^{2-} content in the mixed rare earth oxides. As shown in Figure 7, the weight-loss rate of the washing product in the second stage was only 4.00%, which was close to the SO_4^{2-} content in the mixed rare earth oxides obtained under optimum conditions of the stirring washing process. Therefore, most of the sulfate in the precipitation enrichment had been removed after the stirring washing process with sodium hydroxide.

$$RE_2(OH)_4SO_4 \cdot xH_2O \rightarrow RE_2O_2SO_4 + (x + 2)H_2O \quad (4)$$

$$2RE\,(OH)_3 \cdot xH_2O \rightarrow RE_2O_3 + (2x + 3)H_2O \quad (5)$$

$$RE_2O_2SO_4 \rightarrow RE_2O_3 + SO_3 \quad (6)$$

To further study the thermal decomposition process of the washing product, three types of treatments were carried out for the precipitation enrichment and the washing product, namely, drying, calcination at 950 °C for 2 h, and calcination at 1400 °C for 2 h. All of the solid samples of these treatments were analyzed using XRD, and the results are shown in Figure 8. As shown in Figure 8, both the washing product and the precipitation enrichment were amorphous (samples (a) and (c)). The phase composition of sample (b) was a rare earth oxysulfate, such as $Nd_2O_2SO_4$ and $Eu_2O_2SO_4$. However, the phase composition of sample (d) consisted of rare earth oxides, such as CeO_2 and Eu_2O_3, and there was no diffraction peak for the rare earth oxysulfate. This indicated that most of the alkaline rare earth sulfate was converted to rare earth hydroxide after the stirring washing process. Moreover, the phase composition of sample (e) was also rare earth oxide, but the intensity of the diffraction peak was enhanced. This was because, after calcination at 1400 °C, the small amount of $RE_2O_2SO_4$ would be further decomposed into RE_2O_3, which was consistent with the analysis of the thermal decomposition process of the washing product.

Furthermore, the precipitation enrichment and the washing product were further analyzed using SEM-EDS, as shown in Figure 9 and Table 2. As can be seen from Figure 9, the morphologies of the precipitation enrichment and the washing product were the same, being amorphous agglomerates, which was consistent with the XRD. An energy spectrum analysis was

carried out on different sites of the precipitation enrichment and the washing product. The atomic content of each site is shown in Table 2. In the precipitation enrichment, most sites had sulfur atoms, and the content of sulfur atoms in the sites was more than 8%. However, some sites had no sulfur atoms. This result to some extent indicated that both rare earth hydroxide and alkaline rare earth sulfates could be formed in the precipitation process by CaO. In the stirring washing process, the chemical reaction that is described by eq 7 occurs so that the SO_4^{2-} in the precipitation enrichment was exchanged by the hydroxyl ions. Therefore, in the washing product, sulfur atoms were not detected at all sites (because of the detection limit of EDS), as shown in Table 2. Moreover, comparing the atomic content of different sites in the precipitation enrichment and the washing product, it was found that the content of oxygen atoms in the precipitation enrichment was greater than that in the washing product and the content of rare earth atoms was less than that in the washing product.

Through the above testing and analyses, it was further confirmed that sulfate in the precipitation enrichment was effectively removed by stirring washing with sodium hydroxide.

2.3. Exploratory Experiment for the Stirring Washing Process of the New Extraction Process of the Ion-Adsorption-Type Rare Earth Ore. Although the stirring washing process with NaOH could effectively remove SO_4^{2-} from the precipitation enrichment into solution and solve the problem of excessive SO_4^{2-} content in the mixed rare earth oxides caused by the calcium oxide precipitation process, the addition of the stirring washing process with NaOH causes the extraction process of ion-adsorption-type rare earth ore to be longer. In the conventional extraction process of ion-adsorption rare earth ore, the aluminum ions in the rare earth ore are leached into the leaching liquor and they are removed from the leaching liquor by adjusting the system pH value with NH_4HCO_3 or CaO/MgO. However, because aluminum hydroxide is not easy to crystallize and the separation coefficients of rare earth and aluminum are not
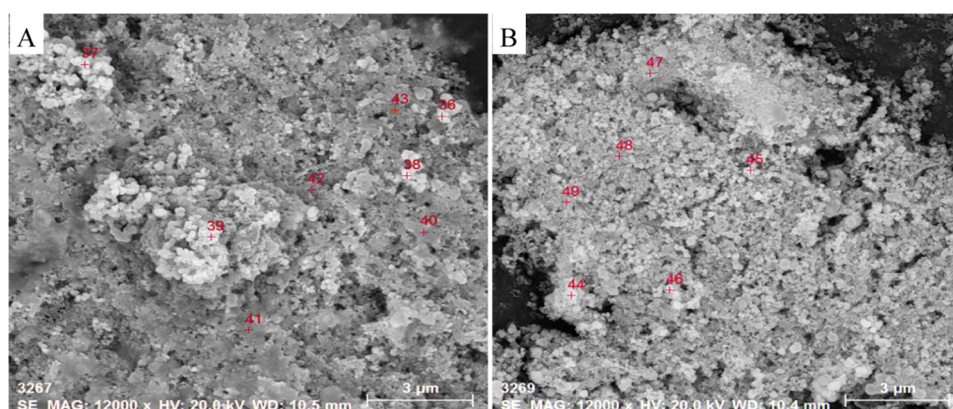
Figure 9. SEM photographs of the precipitation enrichment (A) and the washing product (B).

Table 2. Atomic Contents of Different Sites in the Precipitation Enrichment and the Washing Product (%)

| samples	site	O	Al	S	Y	La	Nd
precipitation enrichment	36	52.74		8.55	11.68	13.67	12
	37	55.99			16.38	13.64	12.1
	38	52.53		8.61	14.96	12.3	10.02
	39	58.61			14.43	13.21	12.39
	40	41.76		9.71	14.89	18.96	14.42
	41	36.06		10.1	17.28	18.18	17.43
	42	36.04	0.27	10.01	16.01	19.1	17.34
	43	41.7	0.1	9.61	13.48	18.13	15.05
	average	46.93			14.88	15.89	13.84
washing product	44	50.75			16.49	16.73	16.03
	45	51.92			16.83	16.85	14.40
	46	49.38	0.14		17.24	17.49	15.74
	47	40.11			18.59	21.58	19.72
	48	36.79			18.50	23.73	18.64
	49	42.37			17.32	22.58	17.73
	average	45.22			17.49	19.82	17.043

large enough in this system, more than 5% of rare earth is lost in the aluminum-removal process. In view of the amphoteric properties of aluminum, aluminum hydroxide can be introduced into the solution by stirring washing with sodium hydroxide. Therefore, a new extraction process of the ion-adsorption-type rare earth ore was proposed, and the flow chart of the new process is shown in Figure 10. In the new process, the rare earth ore is leached by a Mg salt compound leaching agent, the rare earth and aluminum elements in the leaching liquor are precipitated by CaO, and then the precipitation enrichment was washed with NaOH. The new process can get rid of ammonia−nitrogen pollution, eliminate the rare earth loss caused by the traditional aluminum-removal process, and solve the problem of excessive SO_4^{2-} content in the mixed rare earth oxides caused by the calcium oxide precipitation process.

In the early stage, extensive research on the magnesium salt leaching process and calcium oxide precipitation process had been performed by our research group, and good results had been achieved.[5,13−15] Therefore, to verify the feasibility of the new process, exploratory experiments were developed for the stirring washing process. In the exploratory experiment of the new process, a certain amount of aluminum sulfate was added to the simulated rare earth leaching liquor in a magnesium salt system to adjust the concentration of aluminum ions in the liquor to 200 mg/L. The precipitation process by CaO was developed as described in Section 2.1, and then the

precipitation enrichment including aluminum and rare earth was obtained and washed with 40 mL of sodium hydroxide solution. The contents of RE_2O_3, Al_2O_3, and SO_4^{2-} in the mixed rare earth oxides were tested to study the effect of removing aluminum and sulfur. The experimental results are shown in Figure 11. As can be seen from Figure 11, in the mixed rare earth oxides without the stirring washing process, the purity of the rare earth was 52.35% and the contents of Al_2O_3 and SO_4^{2-} were 24.74% and 17.94%, respectively.

When the precipitation enrichment was washed with 2.0 mol/L sodium hydroxide solution, the rare earth purity and the contents of Al_2O_3 and SO_4^{2-} in the mixed rare earth oxides were 73.88%, 16.43%, and 3.44%, respectively. Ulteriorly, when the concentration of sodium hydroxide was increased to 2.5 mol/L and the reaction temperature was increased to 60 °C, the Al_2O_3 content continued to decrease to 9.46%, the SO_4^{2-} content decreased to 2.99%, and the purity in the mixed rare earth oxides reached 80.75%. This is because increasing the concentration of sodium hydroxide and the temperature is beneficial to increase the solubility of aluminum hydroxide.[31,32] Therefore, more aluminum hydroxide in the precipitation enrichment reacts to form sodium aluminate and enters into the solution. It can be seen that the stirring washing process with NaOH can remove aluminum and sulfur from the precipitation enrichment, which provides a solid foundation for the proposal and implementation of the new extraction process of the ion-adsorption-type rare earth ore. In the future, a
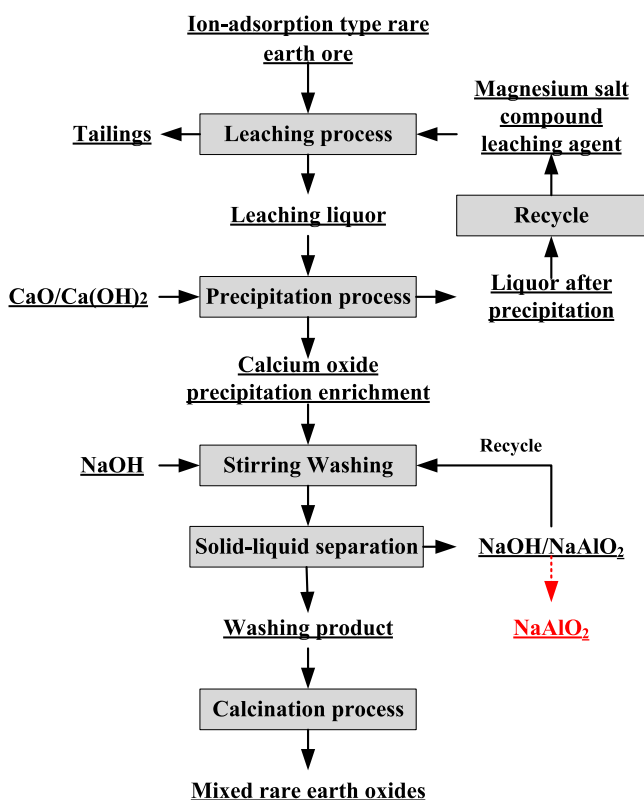
Figure 10. New extraction process of the ion-adsorption-type rare earth ore by magnesium salt leaching−calcium oxide precipitation−sodium hydroxide stirring washing.
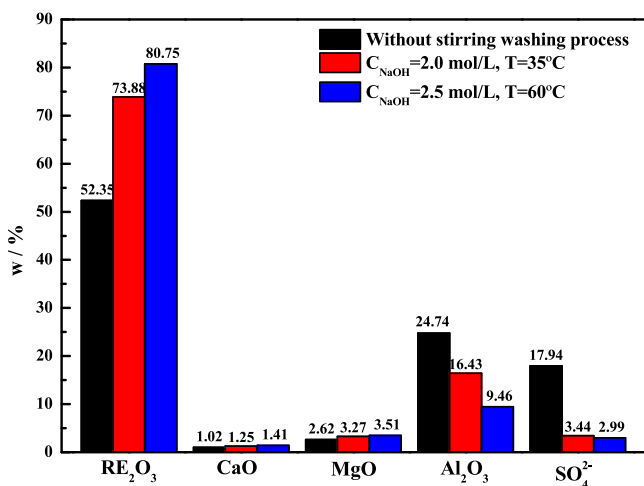
Figure 11. Relevant conditions and results of the exploratory experiment for the new process.

detailed study will be developed for the stirring washing process to improve the new extraction process and solve the problems existing in the traditional process of the ion-adsorption-type rare earth ore.

3. CONCLUSIONS

1. According to a group contribution method, the $\Delta_f G^\theta(\mathrm{RE}_2(\mathrm{OH})_4\mathrm{SO}_4)$ of alkaline rare earth sulfate and the $\Delta_r G^\theta(1)$ of the stirring washing reaction with NaOH were calculated. The $\Delta_f G^\theta(\mathrm{RE}_2(\mathrm{OH})_4\mathrm{SO}_4)$ of alkaline rare earth sulfate ranged from −2600 to −3000 kJ/mol. The $\Delta_r G^\theta(1)$ was negative; for instance, the $\Delta_r G^\theta$ of the stirring washing reaction of alkaline yttrium sulfate was −66.44 kJ/mol, which indicated that the stirring washing reaction with sodium hydroxide was thermodynamically feasible.

2. Optimum conditions for the stirring washing were chosen as follows: a feed ratio of 2.85, a liquid−solid ratio of 6.5 mL/g, a stirring washing temperature of 35 °C, and a stirring washing time of 20 min. Under the optimal conditions, the purity and the SO_4^{2-} content of the mixed rare earth oxides were 94.38% and 3.48%, respectively. When the sodium hydroxide solution was recycled for the sixth time, the purity of the mixed rare earth oxides could still reach 93.29%. By analyzing the washing product using TG-DTA, XRD, and SEM-EDS, it could be further confirmed that the alkaline rare earth sulfate would be effectively converted by sodium hydroxide into a rare earth hydroxide and sulfate ions in the calcium oxide precipitation enrichment could be removed by the stirring washing process.

3. Based on the above research and the solubility of aluminum hydroxide, a new extraction process of the ion-adsorption-type rare earth ore is proposed. The process can get rid of ammonia−nitrogen pollution and eliminate the rare earth loss caused by the traditional aluminum-removal process. The exploratory experiments for the stirring washing process with NaOH showed that aluminum and sulfur in the CaO precipitation enrichment can be removed, which provides a solid foundation for the new extraction process.

4. EXPERIMENTAL SECTION

4.1. Calcium Oxide Precipitation Enrichment of a Simulated Rare Earth Leaching Liquor. Mixed rare earth carbonate, which was obtained after an aluminum-removal and precipitation process by ammonium bicarbonate, was supplied by Chinalco Guangxi Chongzuo Rare Earth Development Co., Ltd. (Guangxi province, China). It was dissolved in dilute sulfuric acid to prepare a 20 g/L mixed rare earth solution (measured in rare earth oxide (REO), g/L). The rare earth partition and impurity concentrations in the solution were analyzed and are shown in Table 3. According to the rare earth partition, the average molar mass of the mixed rare earth (M_{REO}, g/mol) was calculated to be 154.54 g/mol.

A certain volume of the mixed rare earth solution was obtained, and a specific mass of magnesium sulfate was added to it. The solution was then diluted to 1500 mL. In this way,

Table 3. Rare Earth Partition and Impurity Concentration in the Mixed Rare Earth Solution of 20.0 g/L

elements	La	Ce	Pr	Nd	Sm	Eu	Gd	Tb	Dy
rare earth partition (%) or impurity concentration (mg/L)	23.18	7.28	5.56	16.46	4.36	0.57	4.93	0.66	4.25
elements	Ho	Er	Tm	Yb	Lu	Y	Al	Ca	Mg
rare earth partition (%) or impurity concentration (mg/L)	0.81	1.65	0.22	1.40	0.19	28.49	203.25	277.50	32.00

1500 mL of the simulated liquor with a rare earth concentration of 0.8 g/L (measured by REO) and a magnesium ion concentration of 1.0 g/L (measured by Mg^{2+}) was prepared. It was used to simulate the rare earth leaching liquor in a magnesium salt system after the aluminum-removal process. According to preliminary studies,[15] the optimum conditions for the calcium oxide precipitation process were determined to be a terminal pH of 9.18, a calcium oxide slurry feeding speed of 1.5 mL/min, a calcium oxide slurry concentration of 0.45 mol/L (measured by OH^-), and a precipitation temperature of 25 °C. Therefore, the simulated rare earth leaching liquor was precipitated by calcium oxide under the optimum precipitation conditions, and the calcium oxide precipitation enrichment (approximately 6.20 g) was acquired. In this case, the precipitation efficiency of rare earth was above 99%. The calcined product was obtained after the precipitation enrichment was calcined in a muffle furnace at 950 °C for 2 h. The weight of the calcined product was approximately 1.45 g. Moreover, both rare earth hydroxide and alkaline rare earth sulfate are formed in the calcium oxide precipitation process. Therefore, the rare earth purity of the calcined product was approximately 82.6%; the SO_4^{2-} content in the calcined product was approximately 15.84%; and the contents of Al_2O_3, MgO, and CaO were all less than 2.0%.[15]

4.2. Stirring Washing Experiment. Chemical reagents used in the experiments, such as calcium oxide, magnesium sulfate, and sodium hydroxide, were analytically pure and purchased from Sinopharm Chemical Reagent Co., Ltd. The experimental procedure is shown in Figure 12.

The wet calcium oxide precipitation enrichment, which was obtained by a CaO precipitation process under the optimum precipitation conditions, was used as the raw material. To reduce the content of SO_4^{2-}, the precipitation enrichment was added to a NaOH solution with a specific concentration (C_0,

mol/L) and volume (V_1, mL) for stirring washing, which proceeded in a beaker. The reaction equation is shown in eq 7. In the stirring washing process, the rare earth elements were not lost, and all of them entered into the washing products. The stirring washing temperature (T, °C) was maintained in a water bath. After a certain time (t, min) of stirring washing, all of the reaction slurry was filtered by suction filtration, and then the washing product and the filtrate were obtained. The washing product was then rinsed with deionized water. On the one hand, the mixed rare earth oxides, whose weight was m_1 (g), were obtained after calcination of the washing product in a muffle furnace at 950 °C for 2 h. On the other hand, to effectively utilize the residual sodium hydroxide in the filtrate, recyclability experiments were carried out with the filtrate. In the recyclability experiments, a certain amount of NaOH was added into the filtrate to ensure that the concentration of NaOH could reach the optimum concentration, and then it was used as a sulfate-removal reagent for another cycle of the stirring washing process.

$$RE_2(OH)_4SO_4 + 2OH^- = 2RE(OH)_3 + SO_4^{2-} \qquad (7)$$

4.3. Test and Analysis. To calculate the purity of the mixed rare earth oxides, 0.5 g of mixed rare earth oxides was dissolved with H_2O_2–HCl and then diluted with water to 100 mL. The concentrations of rare earth and nonrare earth impurities in the 100 mL solution were analyzed. The concentration of rare earth (measured in REO, C_{REO}, mol/L) in the solution was determined by an ethylenediaminetetra-acetic acid (EDTA) titration method, and the concentration of nonrare earth impurities (measured in oxides, C_{non-RE}, g/L) in the solution was tested using inductively coupled plasma-atomic emission spectroscopy (ICP-AES) (Ultima2, Horiba Co., Ltd.). Therefore, the purities of the mixed rare earth oxides (ω_{RE}, wt %) were calculated according to eq 8. The content of nonrare earth elements (ω_{non-RE}, wt %) in the mixed rare earth oxides was calculated by eq 9. Moreover, the concentration of residual hydroxyl ions in the filtrate (C_1, mol/L) was determined by an acid−base titration. The desulfuriza-tion efficiency ($\varnothing$, %) in the stirring washing process was calculated according to eq 10. Assuming that there was no loss of solution during the stirring washing process, the filtrate volume could be regarded as the same as that of the NaOH solution used for stirring washing. Therefore, the reaction efficiency of hydroxyl ions (η, %) in the stirring washing process was calculated according to eq 11.

$$\omega_{RE} = C_{REO} \times 0.1 \times M_{REO}/0.5 \times 100\% \qquad (8)$$

$$\omega_{non-RE} = C_{non-RE} \times 0.1 \times M_{non-RE}/0.5 \times 100\% \qquad (9)$$

$$\varnothing = (1.45 \times 15.84\% - \omega_{SO_4^{2-}} \times m_1)/(1.45 \times 15.84\%) \times 100\% \qquad (10)$$

$$\eta = (C_0 \times V_1 - C_1 \times V_1)/(C_0 \times V_1) \times 100\% \qquad (11)$$

where M_{non-RE} (g/mol) is measured in oxides and represents the molar mass of nonrare earth impurities and $\omega_{SO_4^{2-}}$ (%) is the SO_4^{2-} content in the mixed rare earth oxides.

Moreover, the sulfur element content of the solid samples was determined by a carbon−sulfur analyzer (CS744, LECO Co., Ltd.),[21] and the carbon and sulfur standards used were GBW 07285 and GBW 07241, respectively. The thermal decomposition behavior of the CaO precipitation enrichment
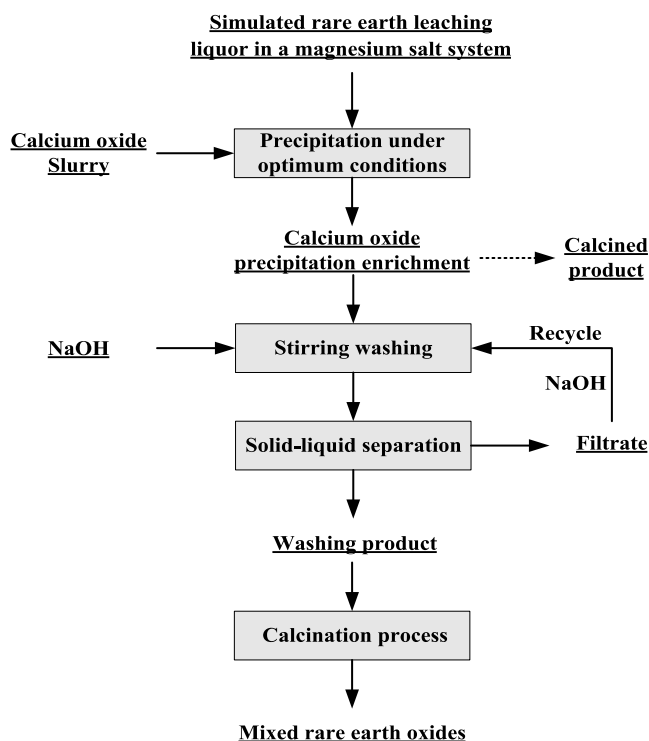

Figure 12. Schematic diagram of the experimental procedure.

Simulated rare earth leaching liquor in a magnesium salt system

Calcium oxide Slurry → Precipitation under optimum conditions

Calcium oxide precipitation enrichment ⇢ Calcined product

NaOH → Stirring washing ← Recycle / NaOH

Solid-liquid separation → Filtrate

Washing product

Calcination process

Mixed rare earth oxides

and the washing product was determined using TG-DTA (STA 449F5, NETZSCH Co., Ltd.). A phase analysis of the solid samples was obtained by X-ray diffraction (Axios max, PANalytic Co., Ltd.). The morphology and atomic content were measured using SEM-EDS (MLA650F, FEI Co., Ltd., and Bruker Co., Ltd.).

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Notes

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