

Decomposition Process of Nonoxidative Microwave Radiation Roasting of a Mixed Rare Earth Concentrate with Sodium Carbonate

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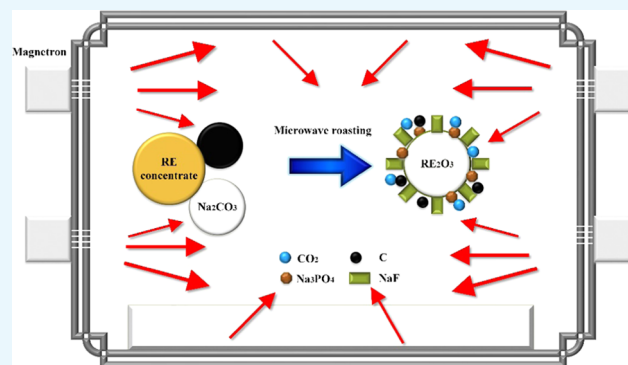
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ABSTRACT: This article introduces an efficient decomposition process that uses sodium carbonate (Na_2CO_3) and activated carbon (C) as additives to decompose Bayan Obo mixed rare earth concentrate (hereinafter to be referred to as RE concentrate) by nonoxidative microwave radiation roasting. The roasting temperature, holding time, and contents of Na_2CO_3 and activated carbon are investigated. The optimum process parameters for decomposition are 800 °C and 30 min. The ratio of $m(\text{Na}_2\text{CO}_3)/m(\text{RE concentrate})$ is 0.5, and the ratio of $m(\text{C})/m(\text{ER concentrate and Na}_2\text{CO}_3)$ is 0.2 based on experimental data. Under the above conditions, the decomposition rate (shortened to DR) of RE concentrate is 98.58%, and the removal rates (shortened to CRs) of fluorine (F) and phosphorus (P) reached 80.35 and 46.75%, respectively. These rates are higher than traditional oxidation roasting under the same conditions. The three reasons for the result are the unique microwave heating characteristics, the overall efficient reaction of the mixture (RE concentrate, Na_2CO_3 , and activated carbon), and the high nonoxidation rate of cerium. For these reasons and large experimental data, the reaction rate of the mixture is improved, and the efficiency of dilute hydrochloric acid for leaching rare earth elements is enhanced. In this article, the valence of rare earth elements in the roasted ore is all in the form of trivalence. Importantly, this nonoxidative roasted product can avoid the generation of chlorine in hydrochloric acid leaching. Moreover, such a short holding time is scarce in traditional roasting. When the mixture was roasted by utilizing microwave heating, the sinter phenomenon of the roasted product was avoided at high-temperature roasting. Finally, the surface morphology of RE concentrate at different conditions was observed by scanning electron microscopy (SEM) analysis, which can be used to compare the specific differences of roasting methods. According to these results, this process is beneficial for the decomposition of RE concentrate in terms of Na_2CO_3 roasting and is helpful for improving the clean and green technology method of hydrometallurgy.



INTRODUCTION

Bayan Obo rare earth mineral deposits are unique massive REE mines in the world. They are mainly composed of bastnaesite (REFCO_3) and monazite (REPO_4) in a ratio ranging from 8:2 to 6:4, and they also have rich light rare earth elements.¹ Therefore, cerium oxide accounts for approximately 50 wt % REO in RE concentrate. Due to the improvement of mineral processing technology, the grade of REO can reach as high as 65% in RE concentrate.^{2,3} At present, the primary method of an industrial process for Bayan Obo rare earth concentrate is sulfuric acid roasting, in which hydrogen fluoride gas is produced, and the equipment is corroded seriously in this process.⁴ With the ever strict regulation on environmental protection, the green ecological extraction process is an inevitable trend. Consequently, researchers continue to explore more green rare earth extraction processes. A series of roasting processes, such as the NaOH low-temperature decomposition method,^{5,6} CaO–NaCl–CaCl₂ decomposition method,⁷ and Na_2CO_3 roasting decomposition method,^{8–10} have been

reported. In addition, an important process is the oxidation roasting-hydrochloric acid leaching process.^{11,12} In this process, the acid leaching residue is mainly composed of REF_3 and monazite mainly. It needs to be decomposed again using sodium hydroxide. In all of the above processes, Ce(III) is inevitably oxidized to Ce(IV), in which the oxidation rate of cerium can reach as high as 96%. However, the stable complex ion $[\text{CeF}_x]^{4-x}$ can easily be generated in the hydrochloric acid leaching solution with Ce^{4+} and F^- .^{13,14} In this case, F can enter the acidic leaching solution during the leaching process. It has an impact on the subsequent extraction process of rare

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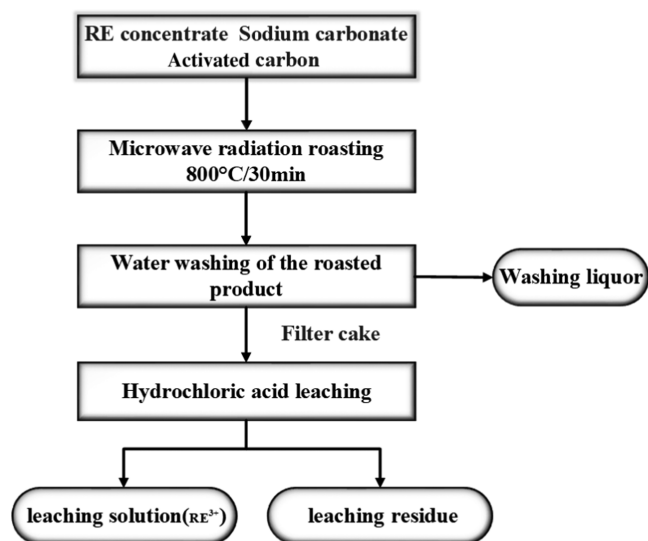


Figure 1. Flowsheet of processing RE concentrate by adding Na_2CO_3 and activated carbon by the microwave roasting method.

earth elements. Many studies have shown that it is difficult to leach Ce(IV) by dilute hydrochloric acid alone,¹⁵ which reduces the leaching rate of rare earth elements. While Ce(IV) is reduced to Ce(III) in the hydrochloric acid leaching solution, the stable complex ion $[\text{CeF}_x]^{4-x}$ causes the conversion of Cl^- to Cl_2 . Nevertheless, a large volume of chlorine can pollute the natural environment seriously and damage personal safety. The traditional treatment method is to add a reducing agent to prevent the generation of chlorine, such as thiourea. Although this method is feasible, it consumes many reducing agents and introduces other impurity ions into the system.^{16,17}

If Ce(III) in RE concentrate can be protected from the calcination process and F can be removed before hydrochloric acid leaching, the perfect acid leaching efficiency of rare earth concentrates can be gained. In this case, a small amount of an reducing agent needs to be added in the hydrochloric acid leaching process, which reduces the cost of the reducing agent.¹⁸ So, nonoxidative microwave radiation roasting is an excellent roasting method to decompose rare earth concen-

trates using sodium carbonate and activated carbon as additives. At the same time, it is necessary for processing RE concentrate to develop a new technique under nonoxidative microwave radiation roasting. In the past three decades, microwave radiation roasting as an effective metallurgy route has been used and investigated to improve the yield of extracted metals.^{19,20} Especially, compared with traditional muffle furnace roasting, microwave roasting has lower power consumption to reach the same effect.^{21,22} Microwave radiation has unique characteristics: rapid internal heating and higher thermal efficiency, which reduce heating time and energy consumption.²³ It only takes a few minutes for experiment samples to reach a settled temperature, and the roasting temperature is maintained by convenient automatization during the insulation stage. Moreover, the other advantages of microwave roasting are selective heating and several nonthermal effects of the microwave.²⁴ In our laboratory, the nonoxidative microwave roasting process of bastnasite concentrate has been reported.²⁵ However, there is no report about decomposition of RE concentrate with Na_2CO_3 at a high temperature by nonoxidative microwave radiation roasting. It is reported that bastnaesite, monazite, and Na_2CO_3 are all weak polarity substances,²⁶ which means they cannot absorb microwave radiation. Fortunately, activated carbon exhibits an effective absorbing characteristic of microwave energy and has a nonoxidative effect.

Based on these facts, an efficient, cleaner, and environmentally friendly hydrometallurgical process is proposed, as shown in Figure 1. This research aims to provide theoretical support for the decomposition process of RE concentrate under microwave radiation roasting and help us optimize the roasting conditions.

RESULTS AND DISCUSSION

Thermogravimetric (TG)–Differential Thermal Analysis. The thermogravimetric (TG)–differential scanning calorimetry (DSC) curves of RE concentrate in the presence or absence of Na_2CO_3 are shown in Figure 2. To simulate more realistic nonoxidative roasting conditions, TG–DSC analysis was performed from room temperature to 1200 °C at a heating rate of 10 °C/min under an argon atmosphere. As shown in Figure 2a, there is no addition of Na_2CO_3 in RE

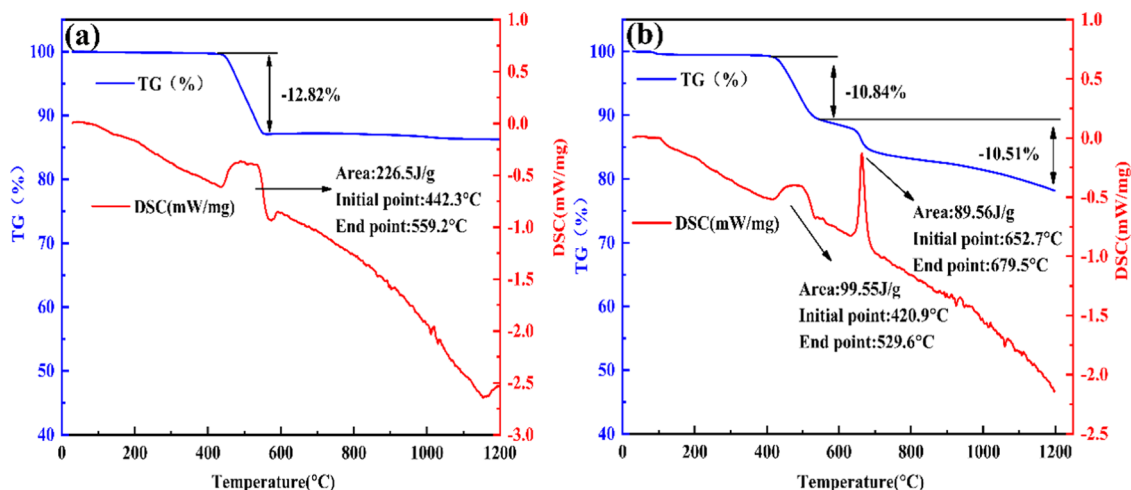


Figure 2. Thermogravimetric (TG)–differential scanning calorimetry (DSC) curves of RE concentrate in the absence (a) and presence (b) of Na_2CO_3 .

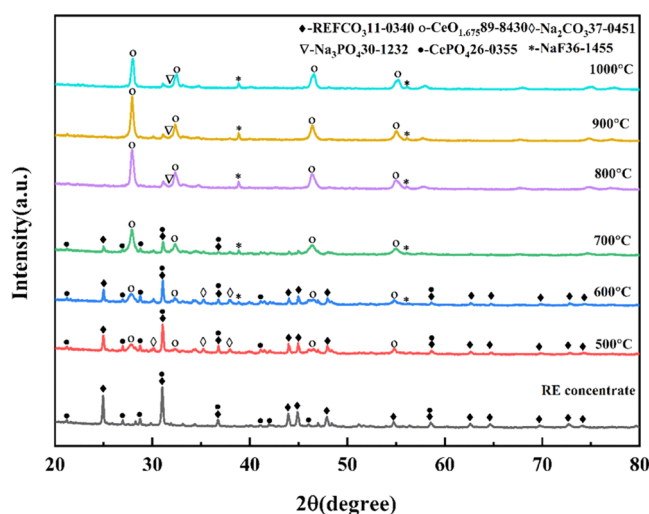


Figure 3. XRD patterns of RE concentrate and the microwave-roasted product at different temperatures (holding time: 30 min, [m(C)/m(ER concentrate and Na₂CO₃)]: 0.2, [m(Na₂CO₃)/m(RE concentrate)]: 0.5, 1200 W).

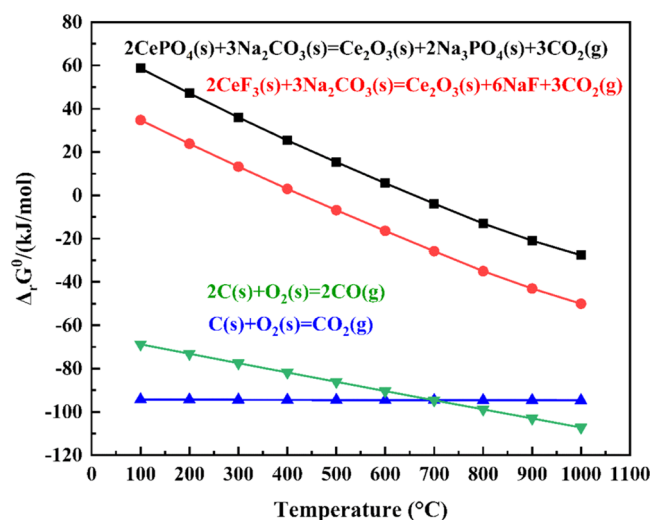


Figure 4. Changes of Gibbs free energy at different temperatures.

concentrate. A significant weight loss process was observed within 442.3–559.2 °C because the decomposition of bastnaesite in RE concentrate is an endothermic reaction. In addition, there are no other endothermic peaks in Figure 2a.

With regard to the mixture of RE concentrate and Na₂CO₃, there are two weight loss processes for the TG curve within a temperature range of 420–700 °C, as shown in Figure 2b. The mass loss was 10.84% within 420–530 °C during the first weight loss process. Furthermore, a prominent endothermic peak appeared in the DSC curve from 420.9 to 529.6 °C. This phenomenon could be due to the decomposition of bastnaesite. The second weight loss process was in a temperature range of 560–700 °C, in which the mass loss was 10.51%. Then, a crucial endothermic peak appeared in the DSC curve from 652.7 to 679.5 °C. This peak should be ascribed to the reaction between monazite and Na₂CO₃. By comparing TG–DSC curves shown in Figure 2a,b, it is evident that the decomposition temperature of bastnaesite decreases by adding Na₂CO₃, which proves that sodium carbonate can improve the RE concentrate decomposition. In summary, these

results indicate that different phase transition stages during the decomposition of RE concentrate occur mainly in the range of 500–700 °C, and the decomposition of RE concentrate at a high temperature is an endothermic reaction. So, microwave roasting temperatures from 500 to 1000 °C are optimal.

Decomposition and Phase Transformation Mechanism. According to the analysis result of TG–DSC, the microwave roasting experiments were performed from 500 to 1000 °C. The X-ray diffraction (XRD) patterns of the microwave-roasted ore at different temperatures were obtained, as shown in Figure 3. It could be seen that apparent phase transformations occurred for the roasted ore after microwave roasting through the X-ray diffraction patterns. The characteristic peaks of bastnaesite and monazite weakened and disappeared gradually with the increase of temperature. When roasting temperatures reached 500 and 600 °C, respectively, the bastnaesite and monazite characteristic peaks decreased slightly.

Further, a new diffraction peak appeared at 38.8° after 600 °C, which was ascribed to NaF (JCPDS No. 36-1455). The characteristic peak of monazite remains unchanged. This situation demonstrated that bastnaesite only reacted with Na₂CO₃ within a temperature range of 500–600 °C, which was consistent with the temperature of the complete reaction shown in Figure 2b. Fluorine was converted to NaF with the decomposition of RE₂F₃ or REOF by sodium carbonate, as shown in reactions 1–4. When the mixture sample was roasted at 700 °C, the characteristic peaks of monazite began to weaken. On the contrary, a new diffraction peak appeared at 32.2°, which is attributed to Na₃PO₄ (JCPDS No. 30-1232), when monazite reacted with Na₂CO₃, as shown in reaction 5. Then, it was constant for the diffraction peak of Na₃PO₄ when the roasting temperature was increased from 800 to 1000 °C. However, when the roasting temperature reached 800 °C, almost all of the bastnaesite and monazite characteristic peaks disappeared, indicating that the RE concentrate decomposed completely. In particular, the new diffraction peaks of the roasted product appeared at 27.9, 32.3, 46.3, and 54.9°, which can match well with CeO_{1.675} (JCPDS No. 89-8430) within a temperature range of 800–1000 °C. It is worth noting that the cerium element was trivalent in the form of CeO_{1.675} after the microwave roasting process instead of cerium dioxide. The reason why Ce(III) was not oxidized to Ce(IV) was explained in detail by our lab's pre-experiment study that activated carbon reacted with O₂ to generate CO₂ and CO,²⁵ and some pertinent studies are refs 28, 29. Since activated carbon consumed oxygen on the surface of mineral particles, the heating cavity of the microwave equipment was sealed with no air flow. As shown in reactions 6 and 7, the surface of the mixture particles was a CO₂ atmosphere because $\rho(\text{CO}_2) > \rho(\text{O}_2) > \rho(\text{CO})$ under the microwave roasting process. To elucidate the higher efficiencies of the reactions, the thermodynamic theoretical calculation was carried out for reactions 4–7, as shown in Figure 4. For the analysis of Gibbs free energy calculation (Figure 4), the decomposition reactions 4 and 5 can be in good agreement with the DSC results (i.e., the initial point of the reaction) shown in Figure 2b. Therefore, the phase transformation mechanism obtained better theoretical support. Finally, the main phases of the roasted ore were identified as rare earth oxides (CeO_{1.675}), sodium phosphate (Na₃PO₄), and sodium fluoride (NaF).

Therefore, the results of the XRD pattern indicated that the transformation process of the mineral phases revealed the

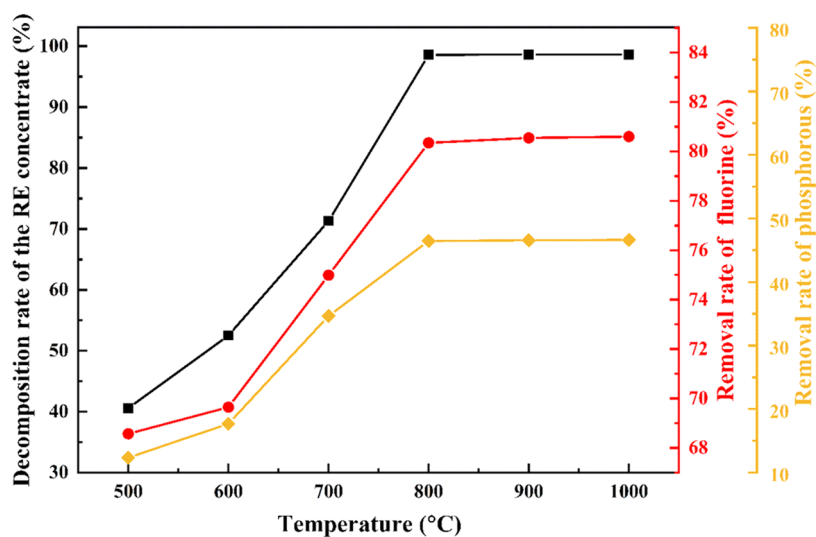


Figure 5. Effect of temperature on the DR of RE concentrate, the CR of fluorine, and the CR of phosphorus (holding time: 30 min, $[m(\text{Na}_2\text{CO}_3)/m(\text{RE concentrate})]$: 0.5, $[m(\text{C})/m(\text{ER concentrate and Na}_2\text{CO}_3)]$: 0.2, 1200 W).

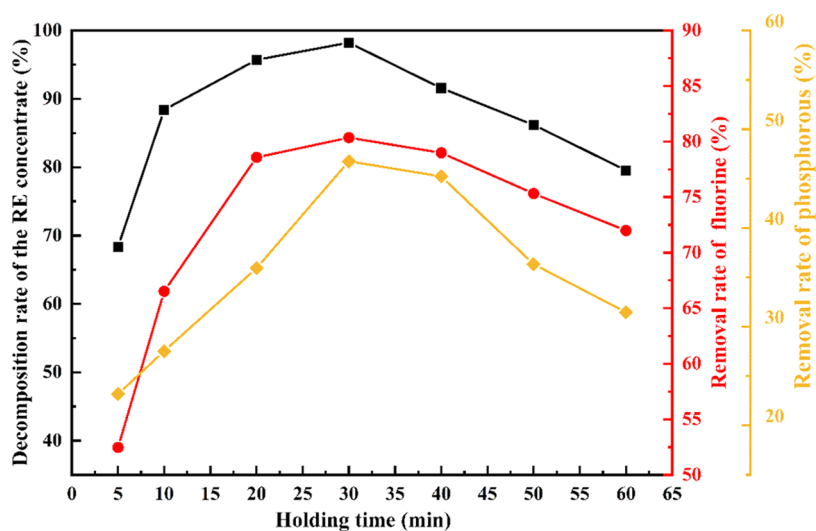


Figure 6. Effect of holding time on the DR of RE concentrate, the CR of fluorine, and the CR of phosphorus (roasting temperature: 800 °C, $[m(\text{Na}_2\text{CO}_3)/m(\text{RE concentrate})]$: 0.5, $[m(\text{C})/m(\text{ER concentrate and Na}_2\text{CO}_3)]$: 0.2, 1200 W).

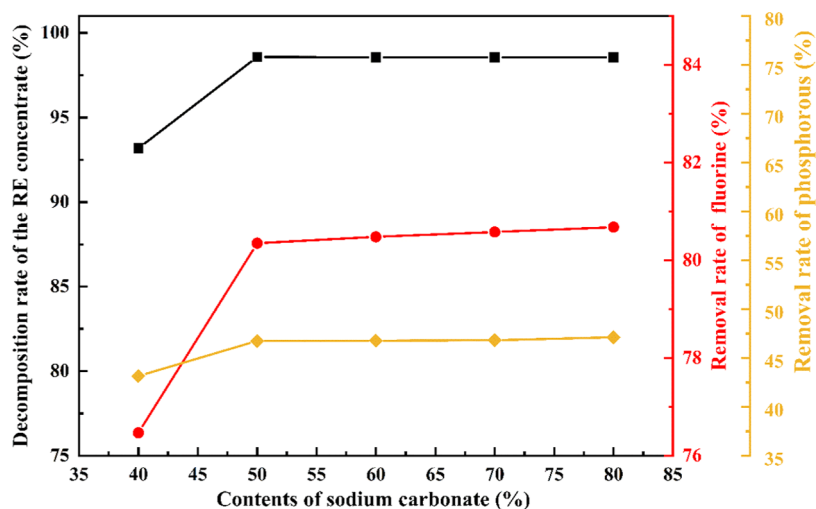


Figure 7. Effect of the Na_2CO_3 content on the DR of the mixed concentrate, the CR of fluorine, and the CR of phosphorus (roasting temperature: 800 °C, holding time: 30 min, $[m(\text{C})/m(\text{ER concentrate and Na}_2\text{CO}_3)]$: 0.2, 1200 W).

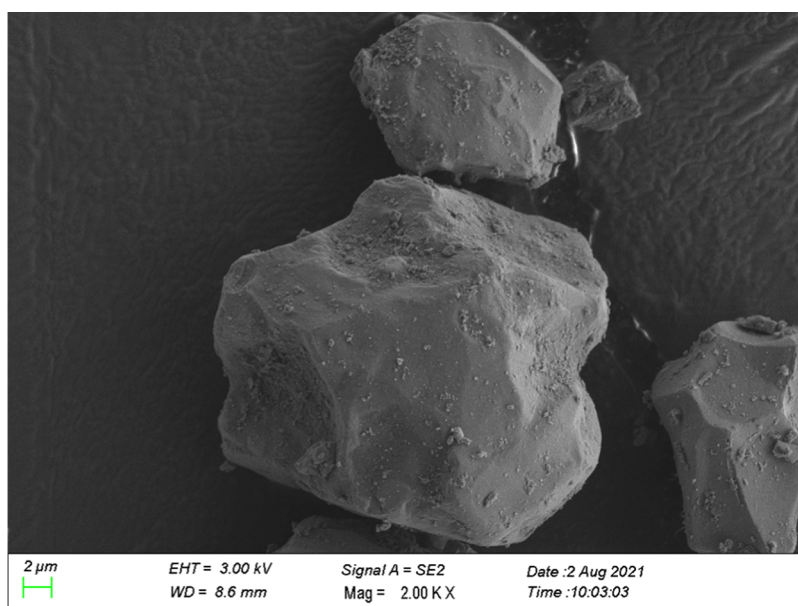


Figure 8. SEM micrograph of RE concentrate.

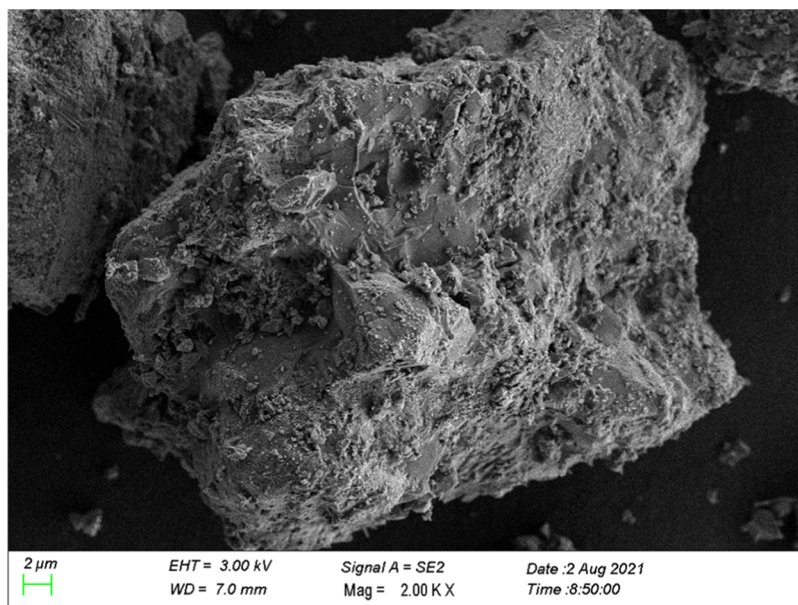
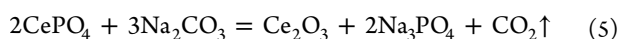
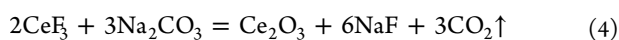
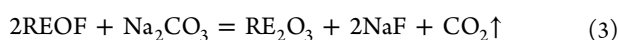
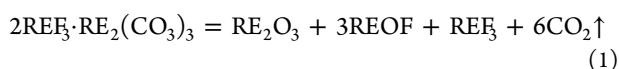


Figure 9. SEM micrograph of the traditional roasted ore (roasting temperature: 800 °C, [m(Na₂CO₃)/m(RE concentrate)]: 0.5, [m(C)/m(ER concentrate and Na₂CO₃)]: 0.2, holding time: 30 min, in a muffle furnace).

decomposition mechanism during the microwave nonoxidative roasting process. Its field can be summarized as follows



Effect of Microwave Roasting on the Decomposition of RE Concentrate. Temperature of Microwave Roasting.

As mentioned above, the roasting temperature played a crucial role in the decomposition of RE concentrate, which was investigated by conducting experiments of microwave roasting from 500 to 1000 °C. As shown in Figure 5, the DR increased gradually from 40.81 to 98.78% with the increase of the temperature of microwave heating from 500 to 1000 °C, and it reached as high as 98.58% at 800 °C. In other words, RE concentrate was decomposed completely at 800 °C in the microwave field. With the increase of calcination temperature, the DR remained almost unchanged. At the same time, the CR of F displayed a similar situation to the DR, in which the CR of F increased from 68.57 to 81.56%, with the temperature of microwave heating ranging from 500 to 1000 °C. Especially, it

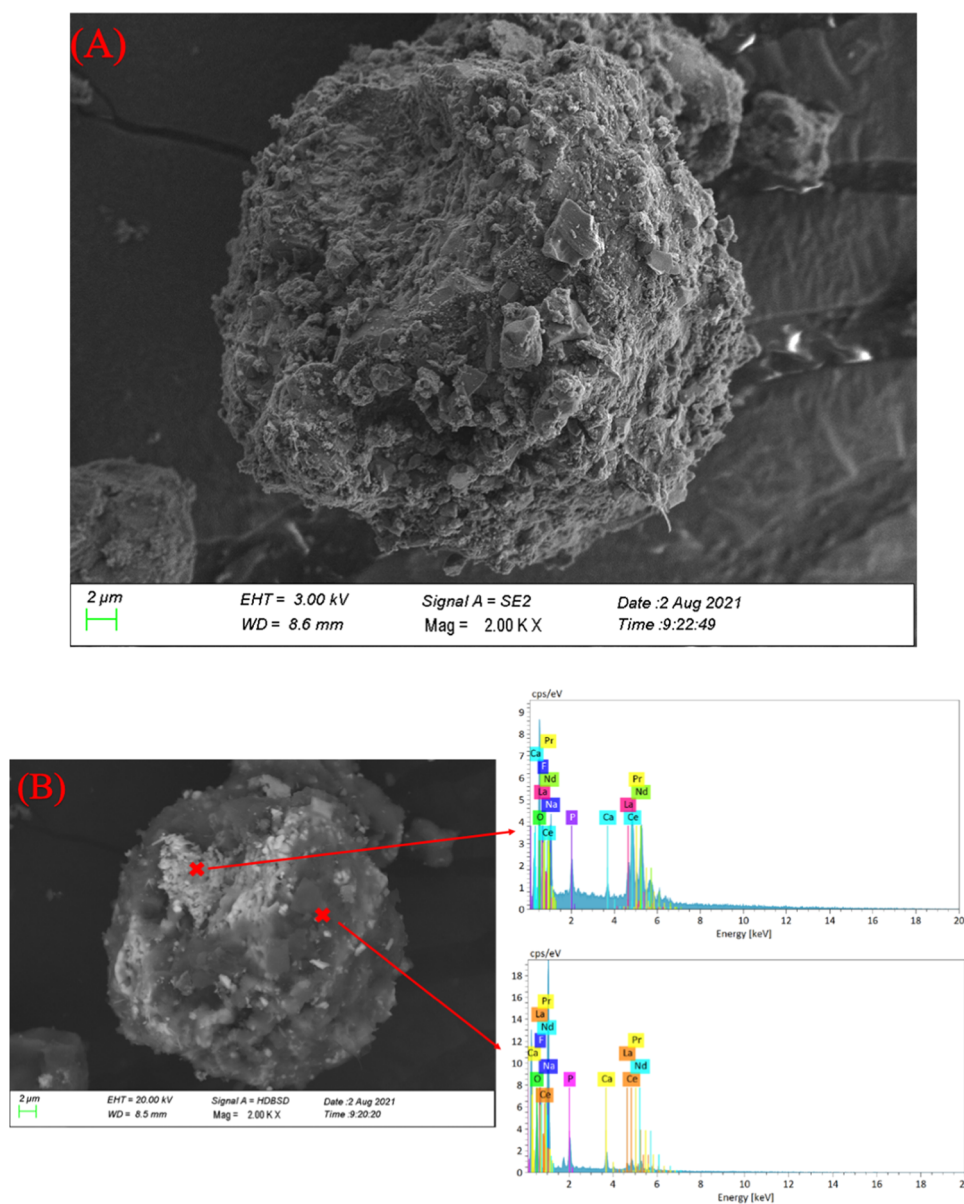
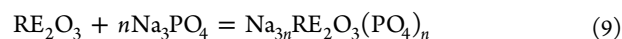
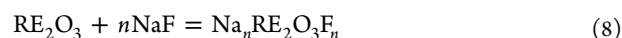


Figure 10. SEM micrograph (A) and energy-dispersive spectroscopy (B) of the microwave-roasted ore (roasting temperature: 800 °C, $[m(\text{Na}_2\text{CO}_3)/m(\text{RE concentrate})]: 0.5$, $[m(\text{C})/m(\text{ER concentrate and Na}_2\text{CO}_3)]: 0.2$, holding time: 30 min, 1200 W).

reached 80.35% at 800 °C. In addition, the experiment showed that the RC of P was 12.34% at 500 °C, 17.68% at 600 °C, and 46.75% at 800 °C.

As noted above, the reason for the increase of DR was that the decomposition of RE concentrate was more favorable with the increase of calcination temperature. According to chemical thermodynamic calculations, the decomposition reaction was in accord with the tendency of the thermodynamic calculation with the increase of temperature in the microwave field. However, as the roasting temperature continued to increase, DR and CR showed a slight increase. Even if the roasting temperature was increased to 1000 °C, the CR could not reach 100%, which can be ascribed to the formation of $\text{Na}_n\text{RE}_2\text{O}_3\text{F}_n$ and $\text{Na}_{3n}\text{RE}_2\text{O}_3(\text{PO}_4)_n$ ³⁰ as shown in reactions 8 and 9. $\text{Na}_n\text{RE}_2\text{O}_3\text{F}_n$ and $\text{Na}_{3n}\text{RE}_2\text{O}_3$ are soluble in dilute hydrochloric acid but are insoluble in water. Finally, based on the experiment results, the best microwave roasting temperature was 800 °C.

The possible chemical reactions for the formation of $\text{Na}_n\text{RE}_2\text{O}_3\text{F}_n$ and $\text{Na}_{3n}\text{RE}_2\text{O}_3(\text{PO}_4)_n$ are as follows



Effect of Holding Time. An appropriate holding time is crucial for ensuring the complete decomposition of RE concentrate. The holding time was investigated from 5 to 60 min in the microwave heating process, and the experimental results are shown in Figure 6. With holding times from 5 to 30 min, the DR increased from 68.34 to 98.58%. On the one hand, the decomposition process of RE concentrate in the microwave field can increase the porosity of the roasted ore. The reasons for the formation of pores are as follows: [1] It is attributed to the microfracturing of particles induced by thermal stress.³¹ [2] Microwave energy is converted into heat after being absorbed by the sample, causing the roasted ore to expand.^{32,33} After 30 min, the decomposition rate drops

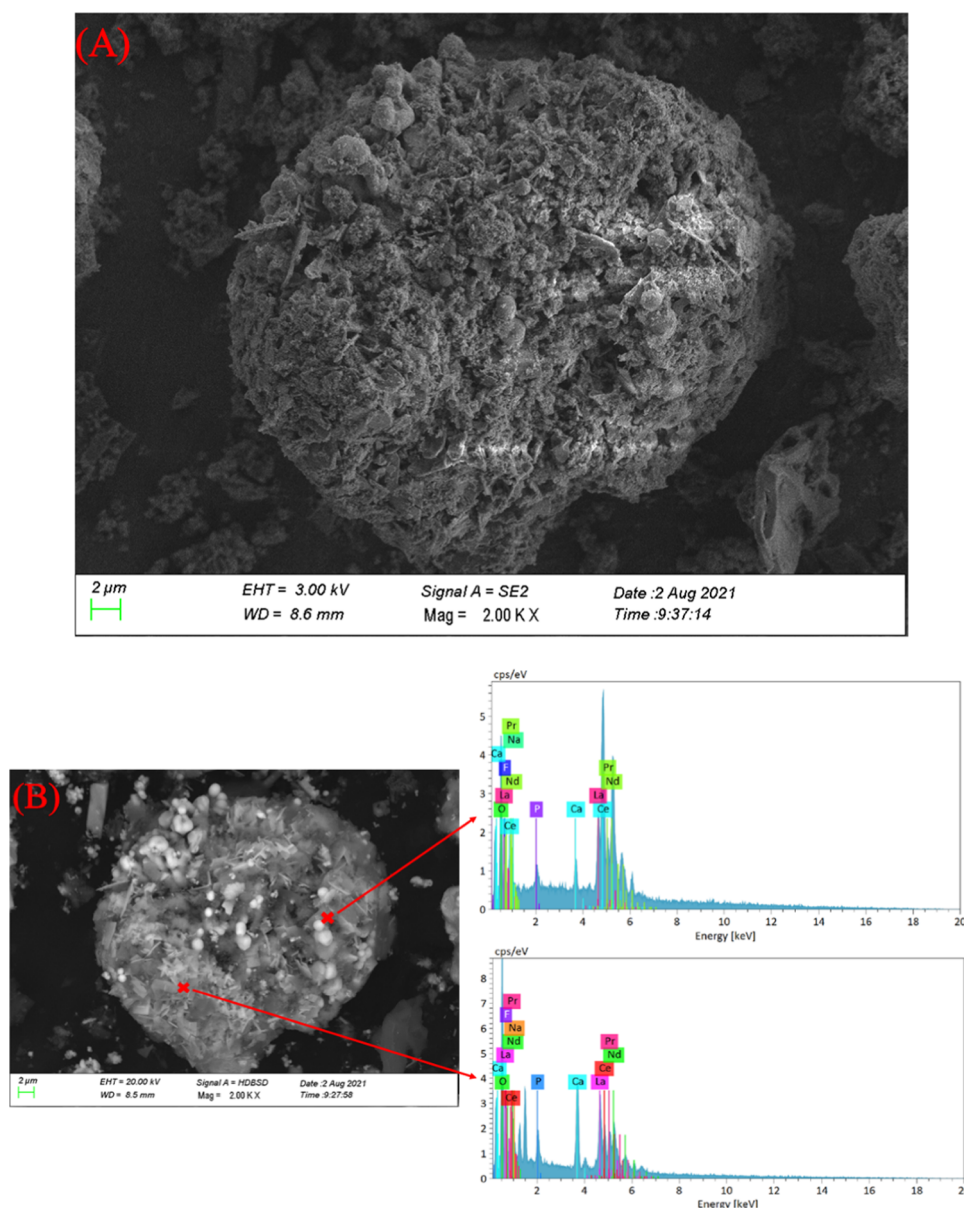


Figure 11. SEM micrograph (A) and energy-dispersive spectroscopy (B) of the water-washed residue.

sharply. The DR decreased due to the following two mechanisms: [1] It was attributed to the sintering degree of the roasted ore under microwave heating, which was due to the depletion of activated carbon with the increase of the REO oxidation rate. [2] The eutectic point was formed between fluorite and sodium carbonate.³⁴ As the holding time increases, the calcined product becomes dense. Hence, it was difficult for REO to leach out in the following acid leaching step.

Moreover, there was a similar situation for the CR of F and P. Within 5–30 min, the CR of F increased from 52.47 to 80.35%. When the holding time was prolonged to 60 min, it decreased to 75% drastically. In the microwave roasting process, the change of CR was similar to that of DR for the same reasons. That is to say, the sintering phenomenon of the roasted ore became more severe with the extension of time, which was not conducive to the subsequent water washing for the fluoride and phosphide removal process. Therefore, the optimum holding time for RE concentrate under microwave roasting was selected to be 30 min.

Content of Sodium Carbonate in the Microwave Roasting Process.

The mixed reaction of RE concentrate and Na_2CO_3 belonged to a solid–liquid reaction at a high temperature, involving many chemical reactions in the microwave field. Therefore, the content of Na_2CO_3 was an important indicator to determine the decomposition process. It was reported that the complete decomposition of RE concentrate and fluorite corresponded to a theoretical dosage of approximately 40% for Na_2CO_3 .⁹ So, the mass ratio of Na_2CO_3 was selected from 40 to 80%. Figure 7 shows that the DR and CR increased slightly with the increase of the content of Na_2CO_3 . When the Na_2CO_3 content increases up to 50%, the DR could reach as high as 98.58%, the CR of F was 80.53%, and the CR of P was 46.75%. When the Na_2CO_3 content was more than 50%, the DR and CR became steady. In summary, the optimal $m(\text{Na}_2\text{CO}_3)/m(\text{RE concentrate})$ ratio is 0.5.

Morphological Analysis. To better compare the extent of decomposition under different conditions, the morphology of

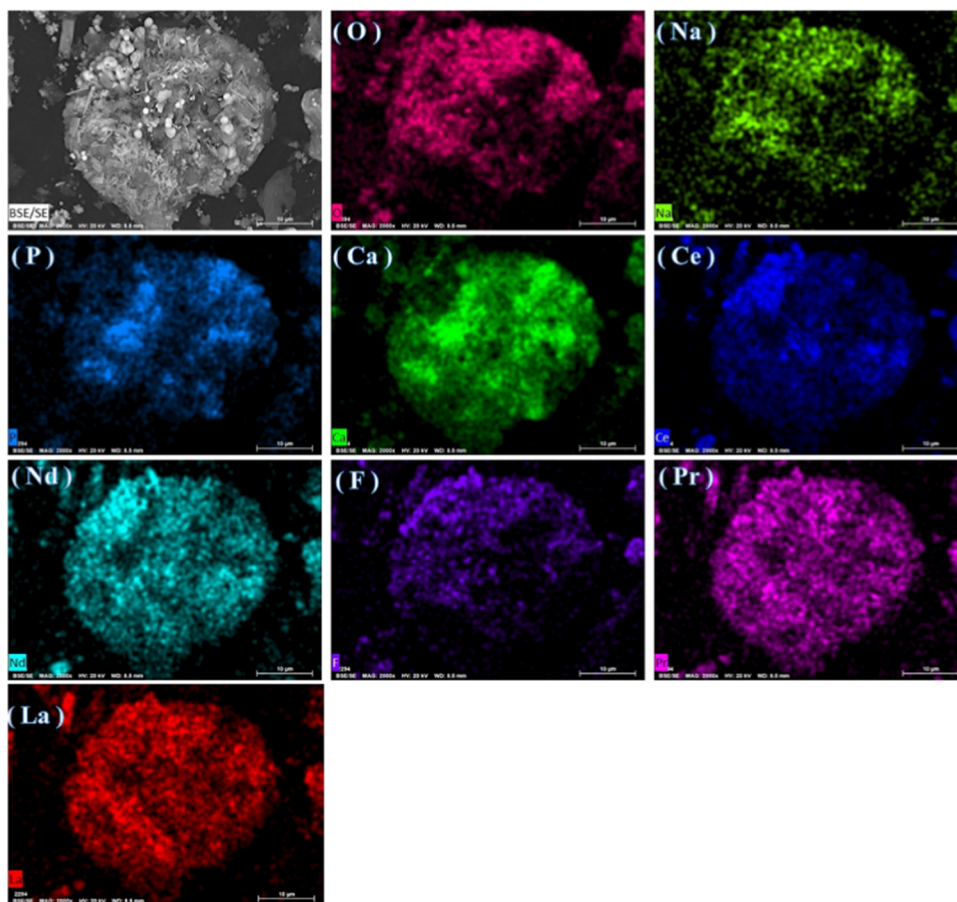


Figure 12. SEM mapping of the water-washed residue.

RE concentrate and the roasted ore under different roasting methods was examined by scanning electron microscopy (SEM) and energy-dispersive spectroscopy (EDS). As shown in Figure 8, the mineral particles of RE concentrate were mainly irregular in shape and smooth on the surface.

However, by comparing the morphologies of RE concentrate (Figure 8), the roasted ore (Figure 9) after traditional roasting, and the roasted ore (Figure 10A) after microwave roasting, the surface morphology of the roasted ore after microwave roasting (Figure 10A) became the loosest. Moreover, numerous rodlike particles and other particles could be observed on its surface, as shown in Figure 10A. The sample was also examined by EDS analysis to identify its chemical composition, as shown in Figure 10B. The results indicated that the rodlike particles and irregular particles mainly contained O, F, Na, P, and Ca and were composed of sodium phosphate and sodium fluoride. Under this circumstance, sodium phosphate and sodium fluoride were easily separated from the rare earth oxides via water leaching, which was beneficial for the efficient extraction of rare earth elements.

When the microwave-roasted ore was washed with water, rare earth oxides were exposed to the roasted ore surface because of the dissolution of sodium phosphate and sodium fluoride, as shown in Figure 11A. This further implied that the roasted ore became loose after microwave heating. It was deduced that NaF and Na_3PO_4 covered the roasted ore in the microwave roasting process. $\text{Na}_n\text{RE}_2\text{O}_3\text{F}_n$ and $\text{Na}_{3n}\text{RE}_2\text{O}_3(\text{PO}_4)_n$ were indicated by SEM and EDS mapping of the water-washed residue, as shown in Figures 11B and 12.

Figure 13A,B shows the morphology of the water-washed residue after hydrochloric acid leaching.

Comparison of Microwave Roasting and Traditional Roasting. By comparing Figures 9 and 10, the roasted ore by the traditional roasting method could not achieve the same effect. The surface transformation from smooth to loose during the roasting process indicated the decomposing of RE concentrate. Thus, this process indicated that the traditional roasted ore was not wholly decomposed. To further investigate the influence of the roasting method under the same roasting condition with the same leaching condition, the following two experiments were conducted: [1] the mixture (RE concentrate, Na_2CO_3 , and C) was roasted by traditional roasting using a muffle furnace (hereinafter to be referred to as experiment A). [2] the mixture was roasted by nonoxidative microwave radiation roasting (hereinafter to be referred to as experiment B). In addition, it has been reported that RE concentrate could be decomposed completely with Na_2CO_3 at around $600\text{ }^\circ\text{C}$ for 3 h in the muffle furnace (hereinafter to be referred to as experiment C).⁸ Three experiments were compared, as shown in Table 1. Obviously, the DR and CR of experiment B were both higher than those of experiment A, which can be due to the unique heating mechanism in molecules of the microwave.³³ To prove the energy saving of the microwave equipment, the electricity consumption of contrast experiments was measured, as shown in Table 2. So, the results clearly evidenced that microwave heating had a positive effect and was better energy saving than traditional roasting.

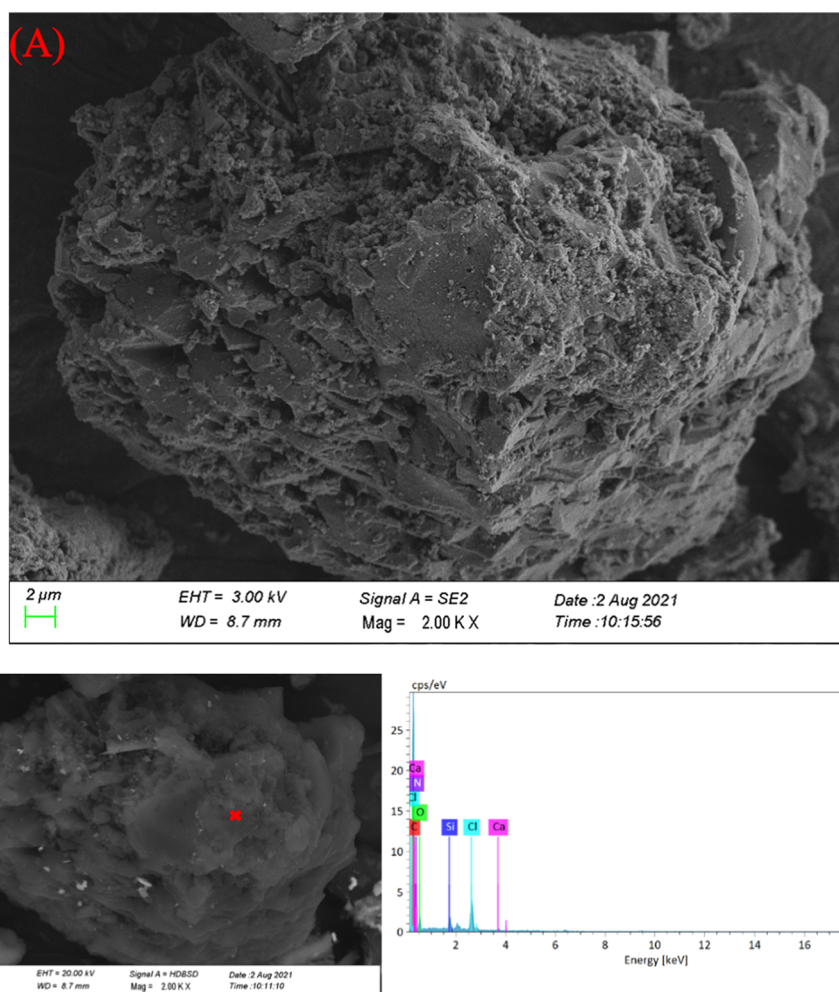


Figure 13. SEM micrograph (A) and energy-dispersive spectroscopy (B) of the acid-leached residue (4 mol/L HCl, stirring speed: 300 rpm, L/S: 20 mL/g, leaching temperature: 80 °C, time: 90 min).

Table 1. Comparison of Microwave Heating and Traditional Heating

experiment	DR (%)	CR of F (%)	CR of P (%)	roasting temperature (°C)	holding time (min)
experiment A	68.56	47.48	14.94	800	30
experiment B furnace	98.58	80.35	46.73	800	30
experiment C roasting	98.78	81.45	44.62	600	180

Table 2. Comparison of Microwave Heating and Traditional Heating on Energy Saving

contrast experiments	roasting temperature (°C)	holding time (min)	electricity consumption (kW·h)
experiment A	800	30	1.39
experiment B	800	30	0.87
experiment C	600	180	7.28

CONCLUSIONS

This research reveals a new decomposition process of nonoxidative roasting for RE concentrate by adding sodium carbonate and activated carbon in the microwave field. During the calcination process, RE concentrate was completely decomposed and converted into NaF, Na₃PO₄, and

RE₂O₃(CeO_{1.675}), where the cerium element is trivalent in the form of CeO_{1.675} instead of tetravalent (CeO₂). Moreover, this nonoxidative roasting process solves the difficulty that the traditional oxidative roasting in the dilute hydrochloric acid leaching process cannot achieve the DR and CR at the same time. Due to the unique microwave heating characteristics, the roasted ore is crisp and loose, and this method overcomes the sintering problem of the eutectic point between fluorite and sodium carbonate at a high temperature. In addition, the microwave roasting process is rapid and more energy saving in comparison with traditional roasting. According to our study's results, a green and low-energy consumption technique of the decomposition of RE concentrate is proposed by microwave roasting with Na₂CO₃. Thus, it sheds light on a potential application value for RE concentrate.

EXPERIMENTAL SECTION

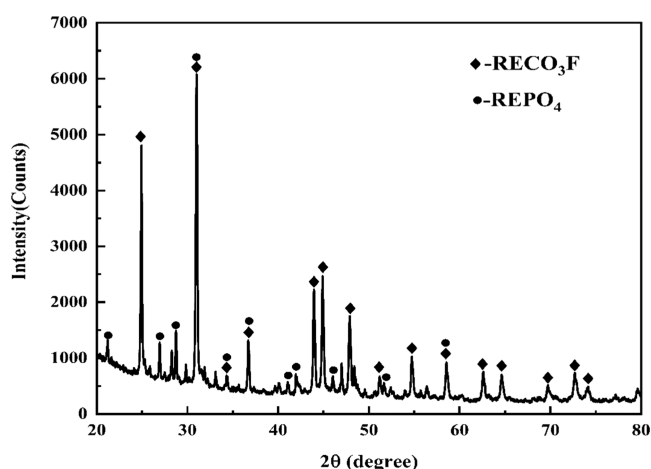
Materials and Chemical Composition. The mixed rare earth concentrate used in this research was Bayan Obo mixed concentrate (RE concentrate), provided by the Mining Research Institute of Baotou Iron and Steel Group (Co., Ltd.), Inner Mongolia, China. The particle size of the all-out RE concentrate was less than 86 μm. RE concentrate was desiccated in a drying box at 100 °C for 8 h, in which the free moisture was removed by the experimental procedure.

Table 3. Mineral Phase Components of RE Concentrate (Mass Fraction, %)

bastnaesite	monazite	fluorite	fergusonite	magnetite	apatite	barite
75.26	17.29	1.65	0.02	1.27	2.07	0.25
dolomite	calcite	amphibole	feldspar	phlogopite	quartz	others
0.32	0.30	0.10	0.05	0.12	0.19	1.12

Table 4. Chemical Composition of RE Concentrate (Mass Fraction, %)

composition	RE _x O _y	CaO	ThO ₂	F	P	Fe ₂ O ₃
content (%)	66.68	4.28	0.25	6.54	3.42	1.89
composition	PbO	ZnO	Al ₂ O ₃	Na ₂ O	MgO	BaO
content (%)	0.11	0.17	0.083	0.077	0.18	0.66

**Figure 14.** XRD patterns of the RE concentrate microwave heating equipment and parameter selection.

The mineralogical components of the raw material were analyzed and are listed in Table 3. It can be seen that bastnaesite (REFCO₃) and monazite (REPO₄) were the two main mineral phases of RE concentrate. The chemical composition of RE concentrate was analyzed, as shown in Table 4. Sodium carbonate (Na₂CO₃, purity >99.8%, molecular weight = 105.99) was from Tianjin Dingshengxin Chemical Industry Co., Ltd., activated carbon (C, purity >99.8%, molecular weight = 12) was from Tianjin Chemical Reagent No. 3 Factory, and hydrochloric acid (HCl, 36–38 wt %, molecular weight = 36.46) was from Tianjin Zhengcheng Chemical Products Co., Ltd., and all were of analytical grade. All of the aqueous solutions were prepared with distilled water. The X-ray diffraction (XRD) pattern of RE concentrate is shown in Figure 14. Two main mineralogical phases, bastnaesite (REFCO₃) and monazite (REPO₄), were identified by the XRD pattern.

The microwave equipment in this experiment was from the Key Laboratory of Untraditional Metallurgy, Ministry of Education, Kunming University of Science and Technology, China. Its microwave frequency was 2450 ± 50 MHz. The roasting experiment of RE concentrate was carried out at a power level of 1200 W, which was optimum for raw materials. The real-time temperature of the sample in the microwave equipment was measured endlessly using a corundum-sheathed B-type thermocouple, which can prevent making a spark. The adequate reaction dimensions of the furnace chamber were 26 cm in length, 18 cm in width, and 16 cm in height. During the

nonoxidative microwave roasting process, the crucible was placed on an asbestos insulation platform, and the heating furnace chamber of the microwave equipment was sealed with no air flow.

Sample Preparation and Processing. Sample Preparation. First, 20 g of dried RE concentrate was weighed. Then, it was mixed and ground with 10 g of Na₂CO₃, in which the weight ratio was certain of RE concentrate. Moreover, according to the mass ratio (10:5:3), 6 g of activated carbon was determined to ensure that all of the experiments were conducted without oxidation. In addition, the well-mixed samples were put into a corundum crucible and placed on an asbestos insulation platform in the center of the microwave furnace chamber. Meanwhile, the thermocouple was inserted into the center of the ceramic crucible to detect the sample's real-time temperature. The optimum holding time can ensure the roasted reaction ultimately. When the microwave roasting process ended, the roasted ore was cooled with stochastic cooling in the microwave chamber. Then, the roasted ore was crushed and ground for further analysis.

Water Washing Experiment. The roasted products were washed several times with deionized water in a beaker, heated to 90 °C with a magnetic heating stirrer, and continuously stirred until the pH value of the washing solution was near 7–8. Then, the washing solution was separated in time by filtering, and the filter cake was leached by dilute hydrochloric acid. The obtained water leaching liquor was used to analyze the concentrations of F and P.

Hydrochloric Acid Leaching Process. The leaching process was carried out under the following conditions: a hydrochloric acid concentration of 4.0 mol/L, a liquid/solid ratio of 20 (mL/g), and a stirring rate of 300 r/min. When the acid solution in a conical flask attained 80 °C, the nonoxidative roasted ore was leached, and then the stirring was started and maintained at around 80 °C for 90 min.

Analytical Methods. The concentrations of REO, F, and P in the liquid samples were analyzed. The total REO content of the solution was determined by the standard oxalate gravimetric method. The solution fluoride content is analyzed by Lanthanum–Alizarin complexone spectrophotometry. Inductively coupled plasma-optical emission spectrometry (ICP-OES, Optima 8300, Perkin-Elmer) determined the contents of P. The content of Ce⁴⁺ in the roasted ore was analyzed using ferrous ammonium sulfate titration without the addition of perchloric acid.²⁷ Fluoride and phosphide were detected in the water leaching liquid of the roasted product and the water residue for calculating the removal rate.

The thermogravimetric (TG)–differential scanning calorimetry (DSC) curves of the mixture were determined by an STA-449C type thermal analyzer (Nexus, Germany). A Sigma-500 field emission scanning electron microscope (SEM, Zeiss, Germany) was used to analyze the morphology of the minerals, and an XFlash-6160 spectrometer (Brook) was used to analyze the mineral composition. The mineral phase composition of the calcined sample was measured by XRD (Dmax-RB X-ray diffractometer, Rigaku, Japan).

The decomposition rate of RE concentrate was calculated as follows

$$DR = \frac{C_1 \times V_1}{\omega_1 \times m} \times 100\%$$

where C_1 is for the concentration of REO in hydrochloric acid liquor (g/L), V_1 is the filtrate volume of hydrochloric acid liquor (L), ω_1 is for the mass fraction of REO in the roasted product (%), and m is the weight of the roasted ore (g).

The removal rate of fluorine and phosphorus (shortened to CR) was calculated as follows

$$CR = \frac{C_{F,P} \times V_2}{\omega_{F,P} \times m} \times 100\%$$

where $C_{F,P}$ represents the concentration of F or P in the water washing liquor, V_2 refers to the volume of the water washing liquor (L), and $\omega_{F,P}$ is the mass fraction of F or P in the roasted product (%).

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Notes

The authors declare no competing financial interest.

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