

Article

An Environmentally Friendly Sulfuric Acid Decomposition Strategy for Mixed Rare Earth Concentrate

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Abstract: A novel environmentally friendly one-step decomposition strategy for mixed rare earth concentrate of Bayan Obo in sulfuric acid solution was proposed in this work. In this process, more than 84% of bastnasite and monazite were decomposed in the leaching step at a temperature lower than the boiling point of sulfuric acid solution. So, the dilapidation of sulfuric acid in this current proposed process will be reduced to a large extent. The stability region of rare earth ion in the RE(La, Ce, Nd)-F-P-SO₄-H₂O system at 170 °C has been proven through Eh-pH diagrams. The factors influencing decomposition of rare earth concentrate in this process were also investigated and the optimal leaching conditions were determined to be a leaching temperature of 170 °C with an ore/acid ratio of 1:5 (g/mL), a sulfuric acid concentrate of 75% and a leaching time of 80 min. The mineralogical changes occurring during the H₂SO₄ leaching process were investigated by X-ray diffraction and SEM-EDS. The analysis results showed that bastnasite and most of monazite had been decomposed, leaving only a small amount of monazite in the leaching residue.

Keywords: mixed rare earth concentrate; one-step decomposition strategy; Eh-pH diagrams; RE(La, Ce, Nd)-F-P-SO₄-H₂O system; H₂SO₄ leaching



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1. Introduction

Bayan Obo deposit is a rare polymetallic deposit containing iron, rare earths and niobium across the world [1–3]. The Bayan Obo mine has four characteristics: low element content, complex mineral types, multiple element and mineral components and fine mineral crystal size [4,5]. In all of the beneficiation and smelting processes developed for the Bayan Obo mine, only the beneficiation and smelting processes of iron minerals and rare earth minerals have been industrialized [6–9]. In the current beneficiation process, iron minerals enter the iron concentrate through magnetic separation, and then, the rare earth minerals are recovered from the iron tailings by flotation with hydroxyvaleric acid-based reagents. A mixed rare earth concentrate with a grade of 60% can be obtained. Due to the characteristics of poverty, impurity, abundance and fineness mentioned above, gangue minerals such as fluorite, barite, pyrite, apatite and calcite would inevitably enter the rare earth concentrate during the rare earth mineral processing stage. This brings challenges to the treatment of solid waste, liquid waste and gas waste in the smelting process of rare earth concentrate [10].

In response to the smelting technical problem of Baotou mixed rare earth concentrate, Chinese rare earth researchers have successively developed various decomposition methods for rare earth minerals, such as sulfuric acid roasting, caustic soda decomposition, sodium carbonate roasting, calcification roasting and high-temperature (600~800 °C) chlorination [11]. Currently, only the sulfuric acid method and caustic soda method have been applied in industrial production. According to statistics, 90% of the mixed rare earth

concentrate is smelted using the sulfuric acid high-temperature roasting technology [12]. During the high-temperature sulfuric acid roasting process, HF generated by the decomposition of fluorinated minerals (bastnasite, fluorite and fluorapatite), SO₂ and SO₃ generated by sulfuric acid decomposition form complex flue gas. Additionally, PO₄³⁻ combines with Fe³⁺ and then enters the smelting slag in the form of FePO₄. The accompanying element Th in rare earth minerals ultimately enters the tailings in the form of Th₂P₂O₇ under the action of PO₄³⁻ [13,14]. Overall, although the high-temperature sulfuric acid roasting method has the advantage of an ideal mineral decomposition result, it also has disadvantages of high energy consumption, the generation of harmful gases and solid waste during the production process, and the stacking of radioactive residue [15]. This process not only fails to achieve the comprehensive utilization of coexisting resources such as P and Th, but also reduces the processing efficiency of roasting equipment for rare earth concentrate due to the addition of Fe³⁺ [16,17]. In the alkaline treatment process, a mixed slag of CaCO₃-CaF₂-Ca₃(PO₄)₂ is produced through CaO alkali-conversion of Na₂CO₃-NaF-NaPO₄ mixed salinity wastewater. The F and P resources entering the mixed slag are difficult to effectively recover and utilize [18]. The first three papers mainly study the leaching of rare earths from bastnasite, although the leaching process and mechanism of bastnasite, monazite and other rare earth-containing minerals in the sulfuric acid system have been reported in some related studies. However, the leaching process of each rare earth mineral were investigated separately [19,20]. The mixed rare earth concentrate was composed of bastnasite and monazite. These two rare earth minerals and other impurity minerals were leached in sulfuric acid together. This would form a new complex leaching systems of RE-F-P-SO₄-H₂O. The related research on that has never been reported.

In this work, a novel environmentally friendly one-step strategy for the decomposition of Bayan Obo mixed RE concentrate was designed through leaching rare earth minerals in sulfuric acid at a lower temperature. In this process, bastnasite and monazite are decomposed, and rare earth elements are dissolved in a sulfuric acid solution as rare earth sulfate. Most of the F and P are transferred into the H₂SO₄ leaching liquid. Moreover, the technology of separating and extracting H₂SO₄ from H₂SO₄-H₂O mixed acid has already become mature and stable in the phosphorus chemical industry, which can be a reference for further recovery of P resources. Because the experimental leaching temperature is lower than the boiling point of the sulfuric acid solution, S-containing flue gas will not be generated, which greatly reduces the sulfuric acid consumption. The sulfuric acid leaching solution can be used for cyclic leaching of rare earth minerals and can repeatedly make rare earth rich. The element content would be concentrated. Hence, it can be expected that the novel one-step decomposition strategy for the mixed RE concentrate is an environmentally friendly process due to the absence of waste gas generation and the convenience of recycling associated resources.

2. Experimental

2.1. Materials

The rare earth concentrate used as raw material is provided by Baotou Iron and Steel, North Rare Earth High Teach Co., Ltd. (Baotou, China). The concentrate was dried to a water content lower than 2% and was riffled to choose representative samples for chemical analysis, XRD and leaching experiments.

Tables 1 and 2, respectively, show the chemical composition and rare earth element distribution of the rare earth concentrate. Generally, the rare earth concentrate mainly contains 59.05% REO, 8.59% CaO, 12.92% P₂O₅ and 5.88% F (Table 1). It includes 59.05% REOs, and the partitioning of La₂O₃, Ce₂O₃, Pr₆O₁₁ and Nd₂O₃ is 98.04% (Table 2). The rare earth elements were mainly light ones. The XRD analysis of the sample performed shows various diffraction peaks of (Ce, La, Nd)PO₄, Ce(CO₃)F, CaF₂ and Ca₅F(PO₄)₃ (Figure 1).

The chemical reagents such as sulfuric acid used for the experiment were of laboratory grade. The supplier is Tianjin Jingdongtianzheng Precision Chemical Reagent Factory

(Tianjin, China). The diluted sulfuric acid was obtained by diluting concentrated sulfuric acid with distilled water.

Table 1. Chemical composition of rare earth concentrate (mass fraction, %).

Composition	Na ₂ O	K ₂ O	MgO	CaO	BaO	MnO ₂	SiO ₂	TiO ₂	ThO ₂
Wt.%	0.29	0.010	0.18	8.59	0.94	0.13	0.69	0.11	0.21
	Al ₂ O ₃	Sc ₂ O ₃	REO	P ₂ O ₅	Nb ₂ O ₅	F	S	TFe	/
Wt.%	0.074	<0.0050	59.05	12.92	0.054	5.88	1.66	2.77	/

Table 2. Rare earth element distribution of rare earth concentrate (mass fraction, %).

Y ₂ O ₃	La ₂ O ₃	Ce ₂ O ₃	Pr ₆ O ₁₁	Nd ₂ O ₃	Sm ₂ O ₃	Eu ₂ O ₃	Gd ₂ O ₃
0.24	28.16	50.93	4.76	14.19	1.03	0.20	0.36
Tb ₄ O ₇	Dy ₂ O ₃	Ho ₂ O ₃	Er ₂ O ₃	Tm ₂ O ₃	Yb ₂ O ₃	Lu ₂ O ₃	/
<0.10	0.10	<0.10	<0.10	<0.10	<0.10	<0.10	/

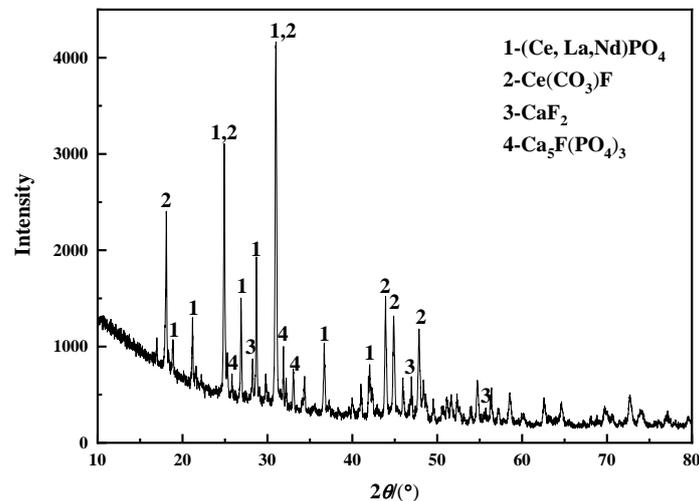


Figure 1. XRD analysis of rare earth concentrate.

2.2. Methods

REEs were obtained by H₂SO₄ solution dissolution of Bayan Obo mixed rare earth concentrate in a beaker using H₂SO₄ solution. The samples with a mesh size of −200 mesh were leached in an H₂SO₄ solution (45%~75%wt) which was heated in an oil bath to the desired temperature and time. The leaching liquid and residue were separated through filtrating. After completing the filtration experiment, the leaching residue was washed with distilled water repeatedly to ensure the transfer of rare earth ions to the leaching liquid. The remaining leaching liquid was then dried for further analysis.

The concentration of the REO was determined by chemical analysis or inductively coupled plasma (ICP-OES). Meanwhile, the mineral and element composition of the leaching residue were determined using SEM-EDS analysis. The mineral constituents of the residues were identified by X-ray diffraction with the step of 0.005° at 10° min^{−1}, covering a range from 10° to 90°.

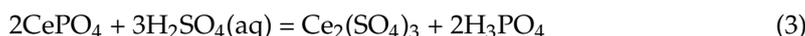
The calculation formula of the rare earth leaching rate is shown in Equation (1). And the meaning of each symbol in the equation is illustrated as follows.

$$\eta = \frac{cV}{wm} \times 100\% \quad (1)$$

where is the leaching rate of rare earth (REO); c is the rare earth concentration of leaching liquid, g/L; V is the volume of leaching liquid, L; w is the rare earth concentrate grade, %; m is the mass of rare earth concentrate, g.

2.3. Thermodynamic Theory of Ce-, F-, PO₄⁻ and SO₄-H₂O Systems

Some of the reactions occurred during the leaching procedure can be expressed as follows [21–23]:



It is well known that the reaction between rare earth carbonate and sulfuric acid is easy to happen, so the thermodynamics condition of the reaction in Equation (1) will not be discussed further. The computed Gibbs energy of the more serve reaction in Equation (3) is shown in Figure 2. From the plot, it is evident that the reaction between monazite and sulfuric acid solution is thermodynamically favorable at a temperature higher than 50 °C.

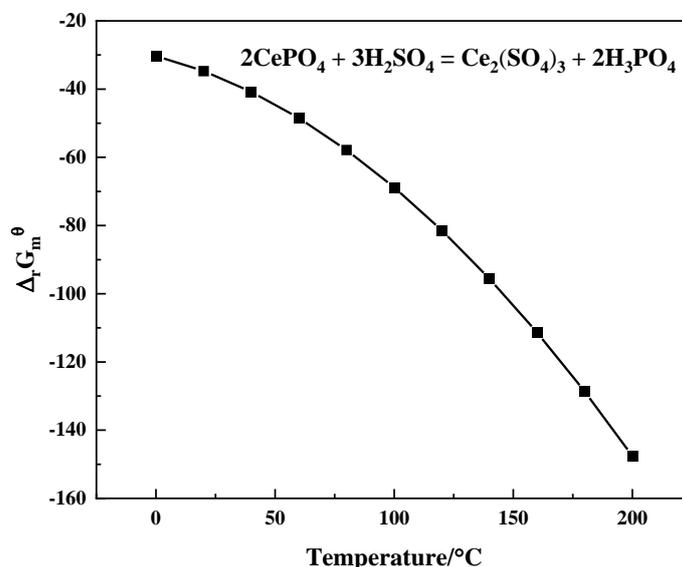


Figure 2. $\Delta_r G_m^\theta$ versus temperature plot of reaction in Equation (3). (The symbol in figure respectively represent $\Delta_r G_m^\theta$ of the reaction at different temperatures).

Rare earth sulfate, rare earth hydroxide and rare earth fluoride are encountered as possible decomposition products of bastnasite and monazite in sulfuric acid. The systems of RE-, F-, PO₄⁻ and SO₄-H₂O were considered to predict the existing forms of rare earth ions. The distribution of La, Ce and Nd in rare earth of Bayan Obo is about 93%. Therefore, these three elements were selected as representative elements to study the theoretical occurrence forms of rare earth elements in the RE-, F-, PO₄⁻, SO₄-H₂O system. Figures 3a, 3b and 3c, respectively, represent the Eh-pH diagrams for the La-, F-, PO₄⁻, SO₄-H₂O system, Ce-, F-, PO₄⁻, SO₄-H₂O system and Nd-, F-, PO₄⁻, SO₄-H₂O system at 170 °C. As can be seen from Figure 3, La, Ce and Pr may exist in a stable ionic state in the interval of the solution Eh “−1.1 V < Eh < 0.1 V” and “Eh > −1.1 V”, “−1.2 V < Eh < 0 V”, respectively, in an acid solution. In addition, SO₄²⁻ belongs to free radicals with high redox potential, and the pH of sulfuric acid solution with high concentration is less than 0. Therefore, rare earths can be stabilized in the ionic state in sulfuric acid solution. Thus, the La, Ce and Nd resulting from the decomposition product of rare earth minerals (REFCO₃ and REPO₄) could dissolve in sulfuric acid solution as RE³⁺ ions, leaving the impurity element in a CaSO₄ form.

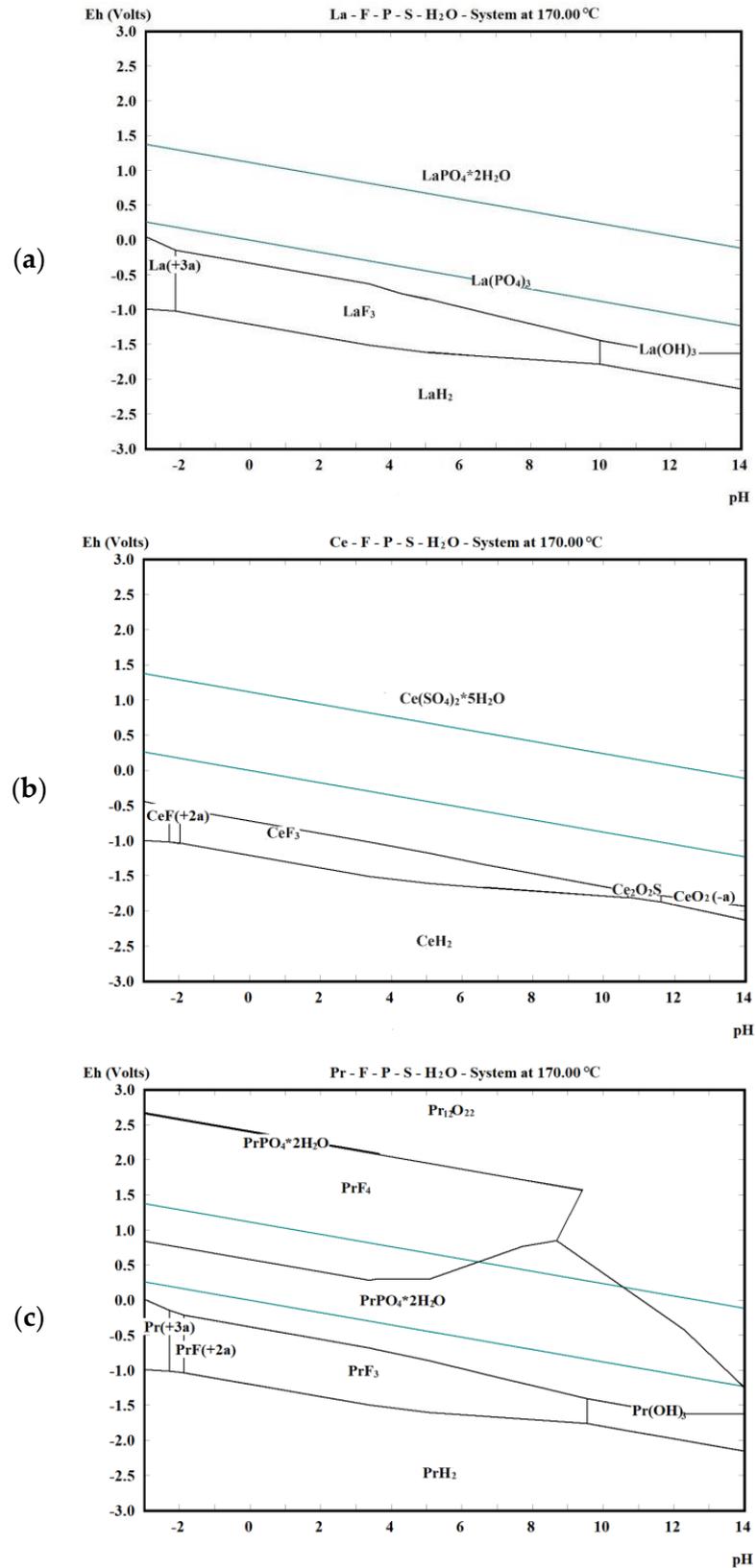


Figure 3. Eh-pH diagrams for the RE(La, Ce, Nd)-F-PO₄-SO₄-H₂O system at 170 °C: (a) [La³⁺] = 1 M, [SO₄²⁻] = 1 M; (b) [Ce³⁺] = 1 M, [SO₄²⁻] = 1 M; (c) [Nd³⁺] = 1 M, [SO₄²⁻] = 1 M. (Diagonal lines represent reactions that are involved with both electrons and H⁺ and OH⁻ ions. (The chemical formula containing “*” represent crystalline water-containing compounds).

3. Results and Discussion

3.1. Effect of Sulfuric Acid Concentration on Leaching

The rare earth concentrate was leached in sulfuric acid solutions with concentrations of 65%, 75% and 85% at 170 °C. The sulfuric acid to rare earth concentrate ratio was fixed at 5:1 (mL/g). And the leaching time was 60 min. Figure 4 illustrates the variation in rare earth leaching rate with temperature in different concentrations of sulfuric acid. As can be seen from the figure, the rare earth leaching rate tends to increase with increasing temperature. Under the same experimental conditions, the rare earth leaching rate shows a trend of first increasing and then decreasing with increasing sulfuric acid concentration. XRD patterns of the leaching residue obtained in different sulfuric acid concentrations are shown in Figure 5. At a sulfuric acid concentration of 65%, there is no diffraction peak of bastnaesite in the XRD pattern of the leaching residue, indicating that the bastnaesite almost has completely decomposed. However, the diffraction peaks of monazite can still be observed. The bastnaesite has decomposed completely, and only a small amount of monazite remains in the leaching residue. As the sulfuric acid concentration increases to 75%, monazite can still be observed in the leaching residue. Continuing to increase the sulfuric acid concentration to 85%, the diffraction peaks of monazite almost disappear, while the bastnaesite diffraction peaks appear in the pattern. Comparing the energy spectrum analysis data of different sulfuric acid leaching residues in Figure 6, it is evident that the P content of the 75% (points 3 and 4) sulfuric acid leaching residue is significantly lower than that of the 65% (points 1 and 2) acid leaching residue. At a sulfuric acid concentrate of 85%, no monazite minerals were found in the leaching residue (points 5 and 6) by SEM-EDS, but the unreacted bastnaesite can be detected. This also confirms that increasing sulfuric acid concentration exacerbates the decomposition of monazite, which is in agreement with the experiments and XRD analysis shown above. Sulfuric acid with a high concentration is not conducive to the decomposition reaction of bastnaesite, while a low concentration sulfuric acid solution is not conducive to the decomposition reaction of monazite [24]. According to rare earth phase analysis of Bayan Obo rare earth concentrate, approximately 70% of rare earth occurs in bastnaesite. That means that the incomplete decomposition of bastnaesite greatly affects the overall leaching rate of the rare earth. The optimal sulfuric acid concentration for leaching is 75%.

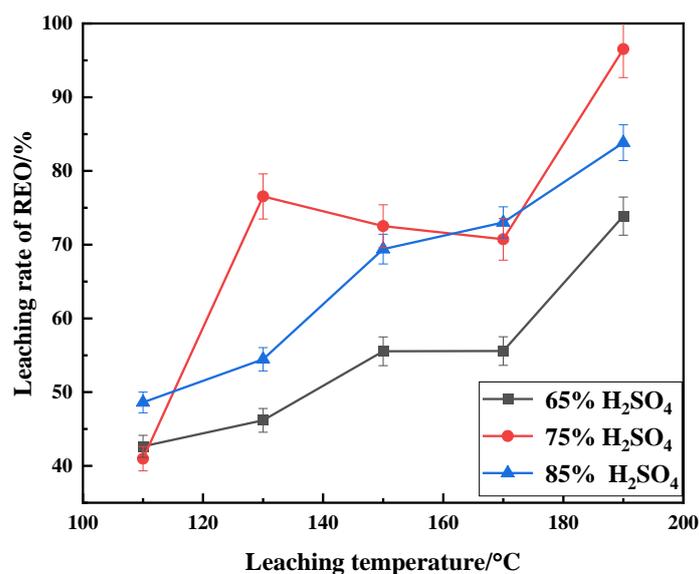


Figure 4. Variation in rare earth leaching rate with temperature in different concentrations of sulfuric acid.

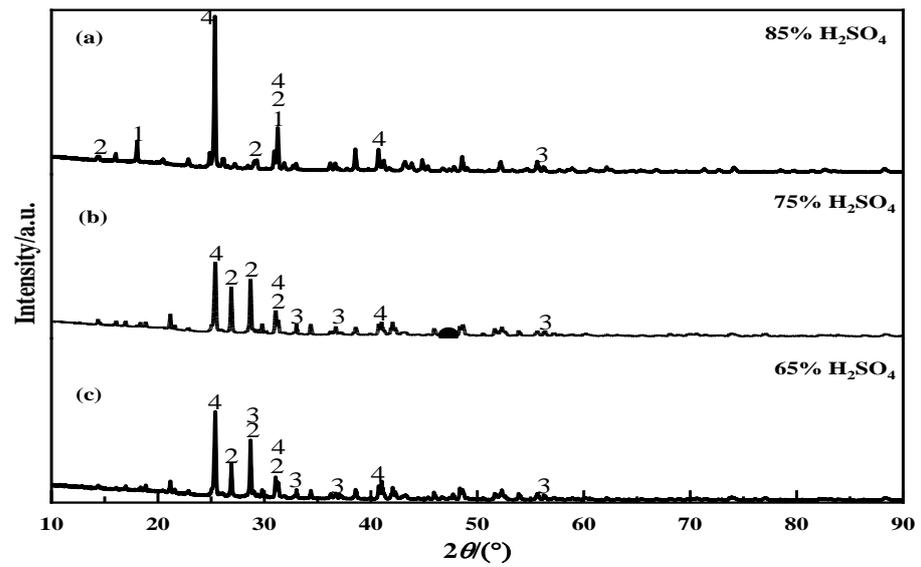


Figure 5. XRD pattern of leaching residues. (a) At 85% H₂SO₄; (b) at 75% H₂SO₄; (c) at 65% H₂SO₄. 1-CeFCO₃; 2-CePO₄; 3-FeS₂; 4-CaSO₄.

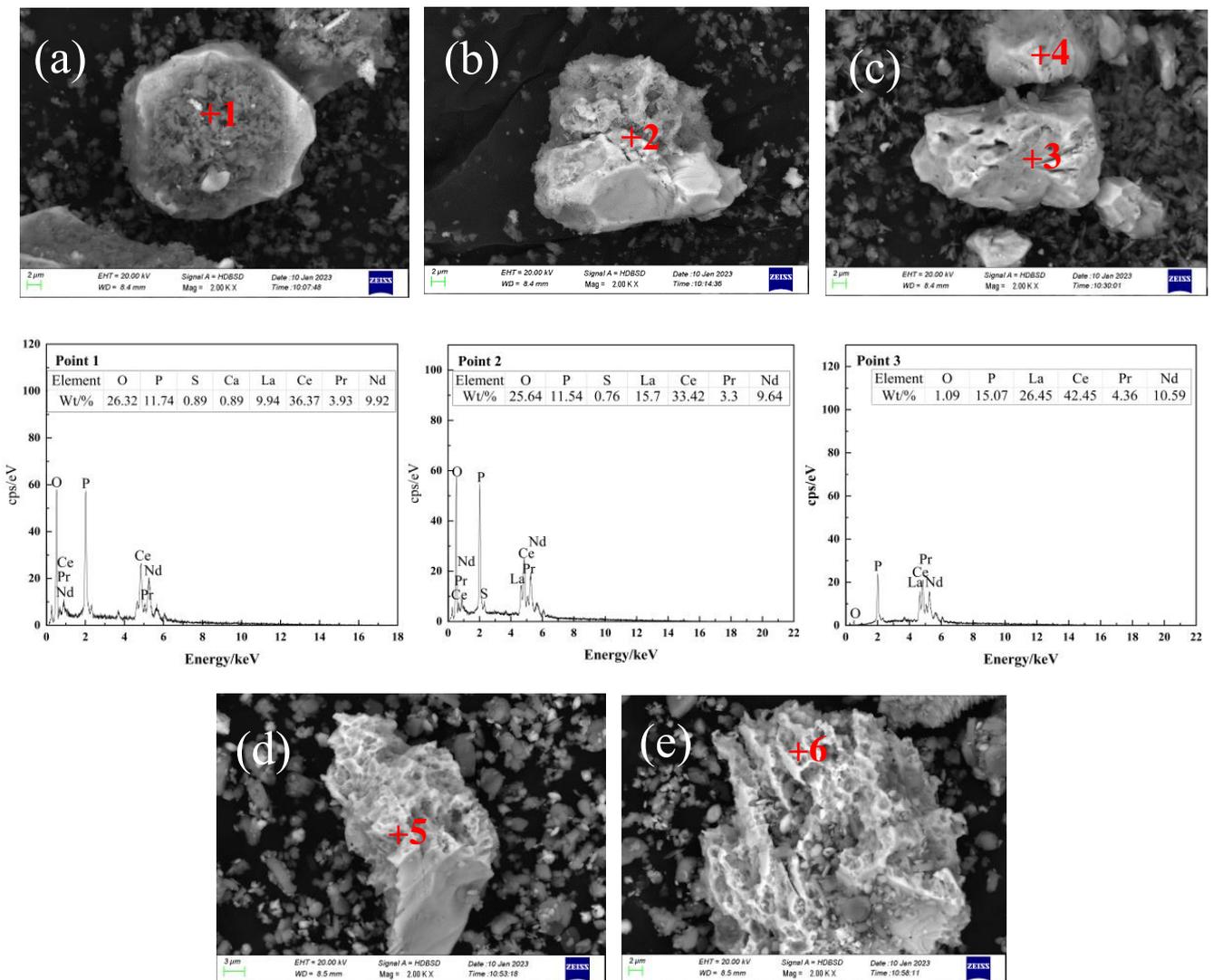


Figure 6. Cont.

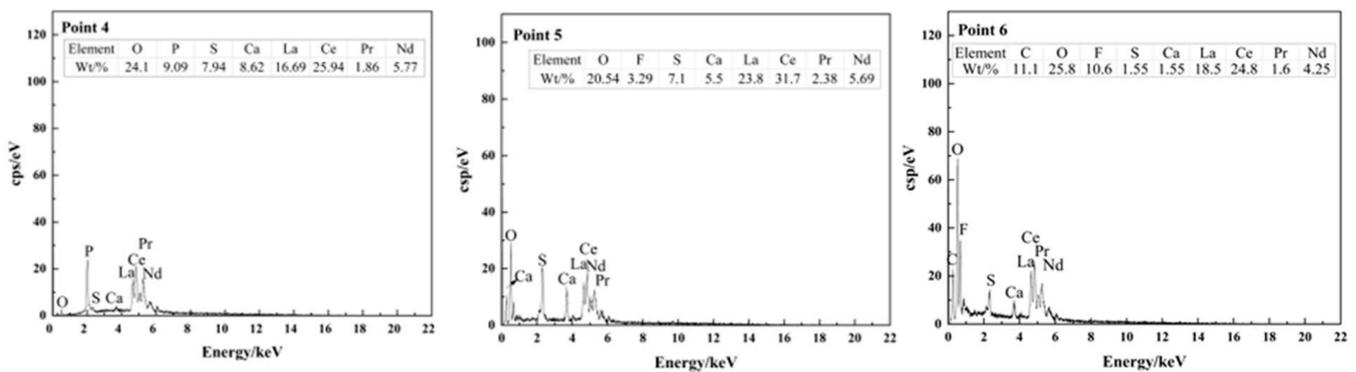


Figure 6. SEM-EDS analysis of leaching residue of rare earth concentrate. (a,b) At 65% H₂SO₄; (c) at 75% H₂SO₄; (d,e) at 85% H₂SO₄.

3.2. Effect of Temperature on Leaching

Leaching experiments were conducted at different temperature with 75% sulfuric acid for rare earth concentrate. Other experimental conditions were the same as those in Section 3.1. In Figure 7, the leaching rate of REO increases with the increase in leaching temperature. When the temperature is lower than 150 °C, bastnaesite and monazite are not decomposed completely. The XRD pattern of the leaching residue at 110 °C and 150 °C in Figure 8, as well as the EDS analysis data in Figure 9, also confirmed the existence of these two kinds of rare earth minerals. The surface of the monazite particle does not show any obvious changes at 110 °C, indicating that monazite has not reacted with sulfuric acid completely in this condition. However, corrosion spots appears on the surface of monazite particles at 150 °C, and energy spectrum scanning also detects characteristic peak of the sulfur element, indicating that a slight chemical reaction between monazite and sulfuric acid has occurred at 150 °C. Additionally, some obvious holes resulting from sulfuric acid corrosion appear on the surface of monazite particles, as shown in Figure 8c. The decomposition degree of monazite tends to complete with increasing temperature. The optimal leaching temperature was chosen as 170 °C because the boiling point of 75% sulfuric acid solution is lower than 190 °C.

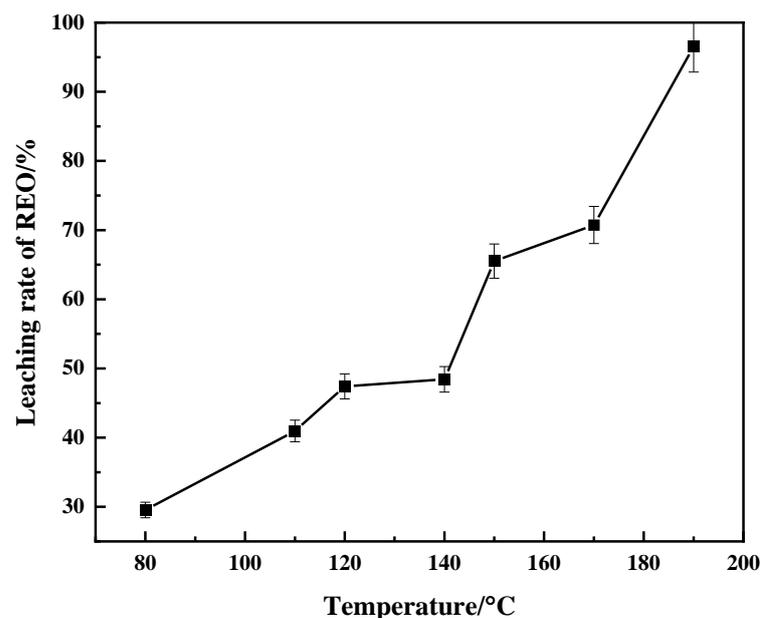


Figure 7. Variation in rare earth leaching rate with temperature (At 80 °C, 110 °C, 120 °C, 140 °C, 150 °C, 170 °C and 190 °C).

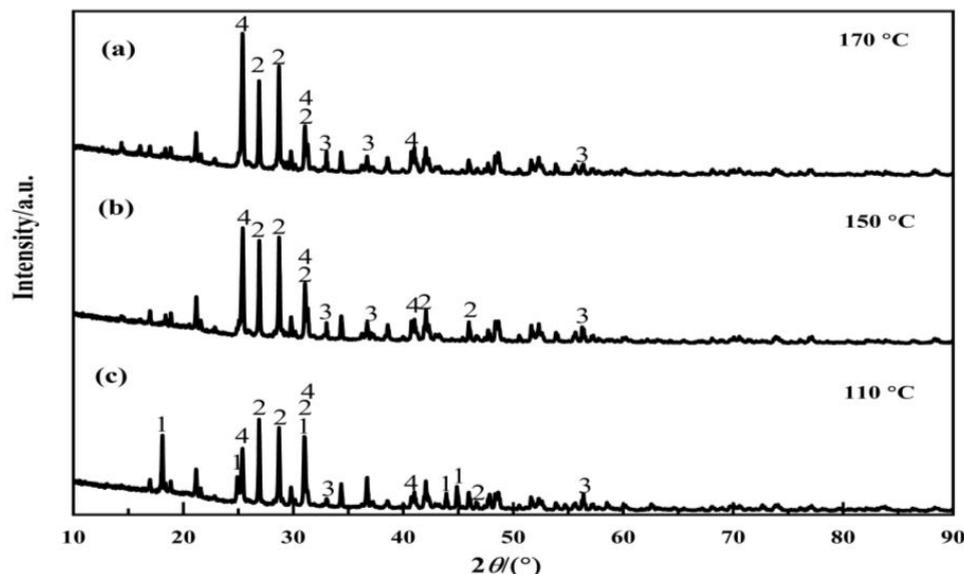


Figure 8. XRD pattern of leaching residue. (a) at 110 °C; (b) at 150 °C; (c) at 170 °C. 1-CeFCO₃; 2-CePO₄; 3-FeS₂; 4-CaSO₄.

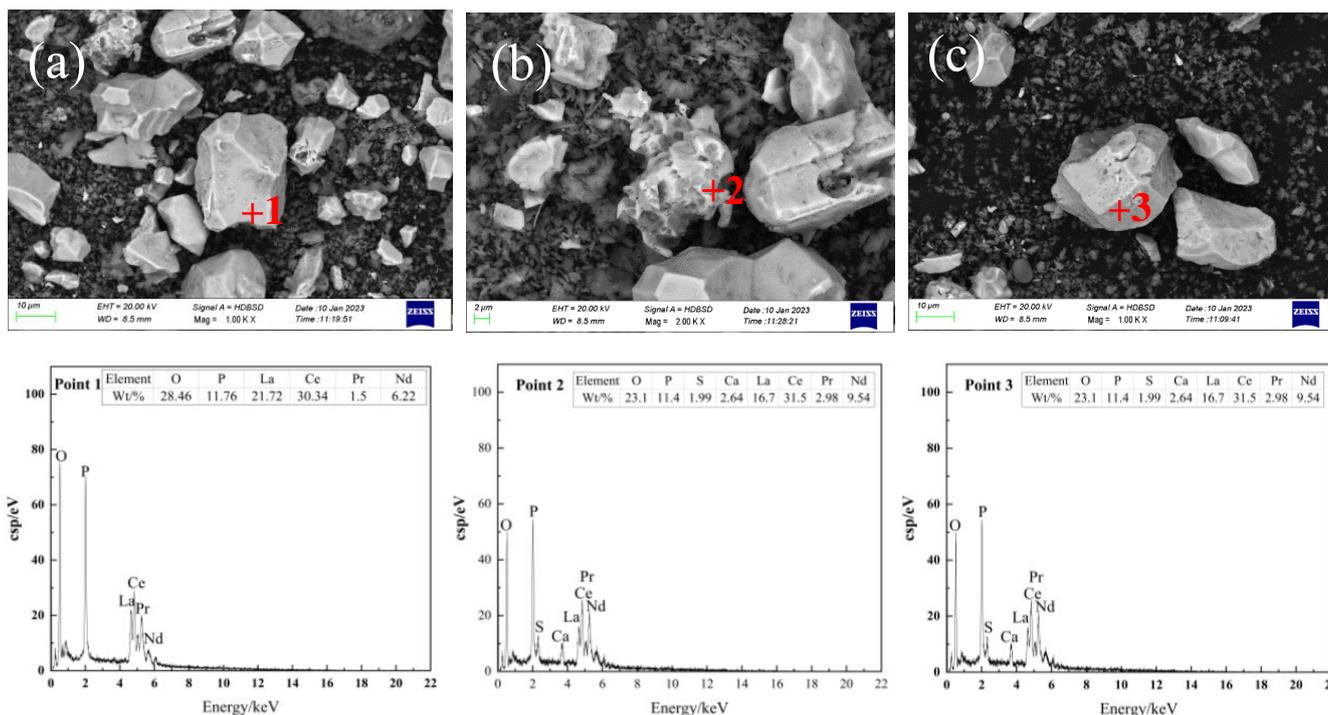


Figure 9. SEM-EDS analysis of leaching residue. (a,b) 110 °C, 60 min, 75% H₂SO₄; (c) 150 °C, 60 min, 75% H₂SO₄.

3.3. Effect of Leaching Time on Leaching Rate

Sulfuric acid leaching experiments were carried out by varying the leaching time from 20 to 100 min at 170 °C using 65%, 75% and 85% sulfuric acid solution. Figure 10 shows the variation in rare earth leaching rate with time. Leaching time shows a noticeable effect on rare earth dissolution. The increase in leaching time greatly intensifies the reaction, leading to an increased leaching rate of rare earth. However, the leaching rates of rare earth all begin to decrease when the leaching time exceeds 80 min. The acidity of the sulfuric acid solution gradually increases due to water evaporation, which may cause a decrease in rare earth sulfate solubility in the sulfuric acid solution. In view of this, excessive reaction time

is not conducive to rare earth leaching. As can be seen from Figure 11, all of the diffraction peaks of bastnaesite disappear, leaving only a small amount of monazite diffraction peaks at a roasting time of 40 min. When the roasting time is 80 min, the diffraction peaks of monazite are obviously weakened, and the content of monazite in the filter residue is reduced. At 100 min, all of the diffraction peaks of monazite disappear and monazite minerals are decomposed completely. From this perspective, the precipitation of rare earth sulfate is the main reason for the decrease in rare earth leaching rate [25]. Figure 12a–c are SEM-EDS analysis of leaching residue at 40 min, 80 min and 100 min. The rare earth concentrate has decomposed evidently at 80 min and 100 min from the EDS data. The optimal leaching time was determined to be 80 min.

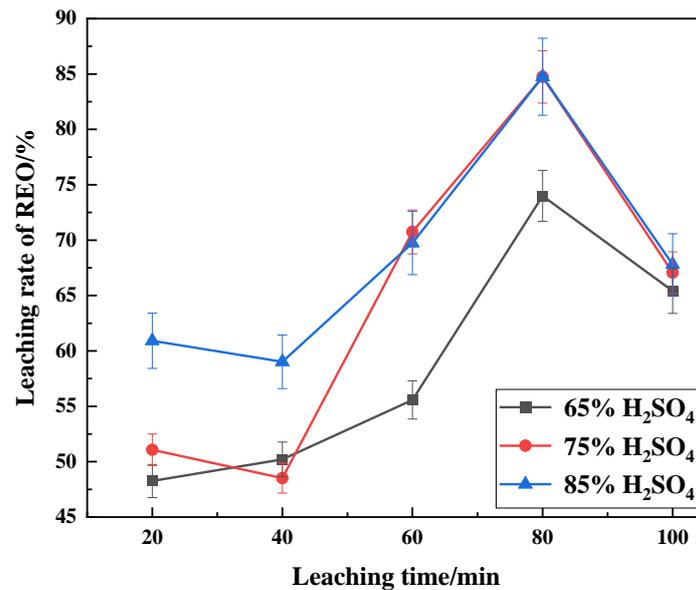


Figure 10. Variation in rare earth leaching rate with time.

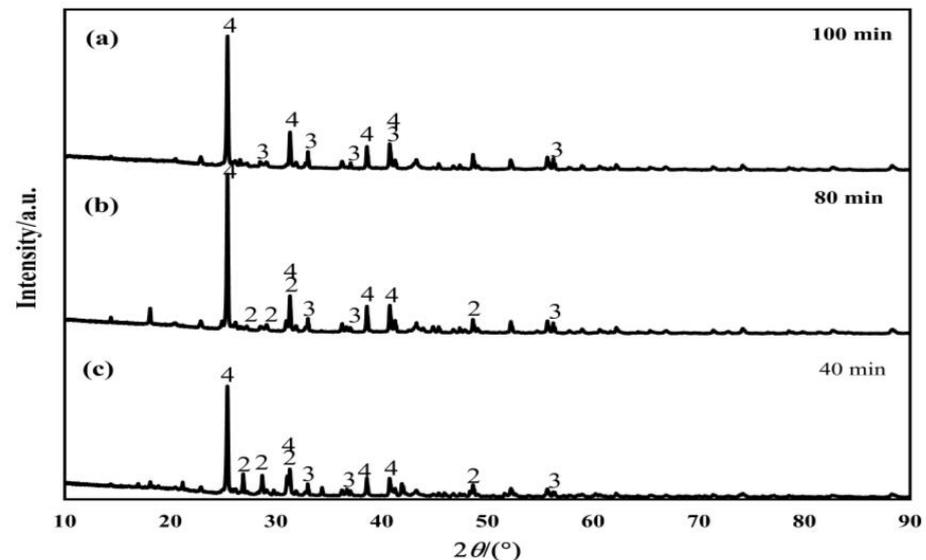


Figure 11. XRD pattern of leaching residue. (a) 100 min; (b) 80 min; (c) 40 min. 1-CePO₄; 2-FeS₂; 3-CaSO₄.

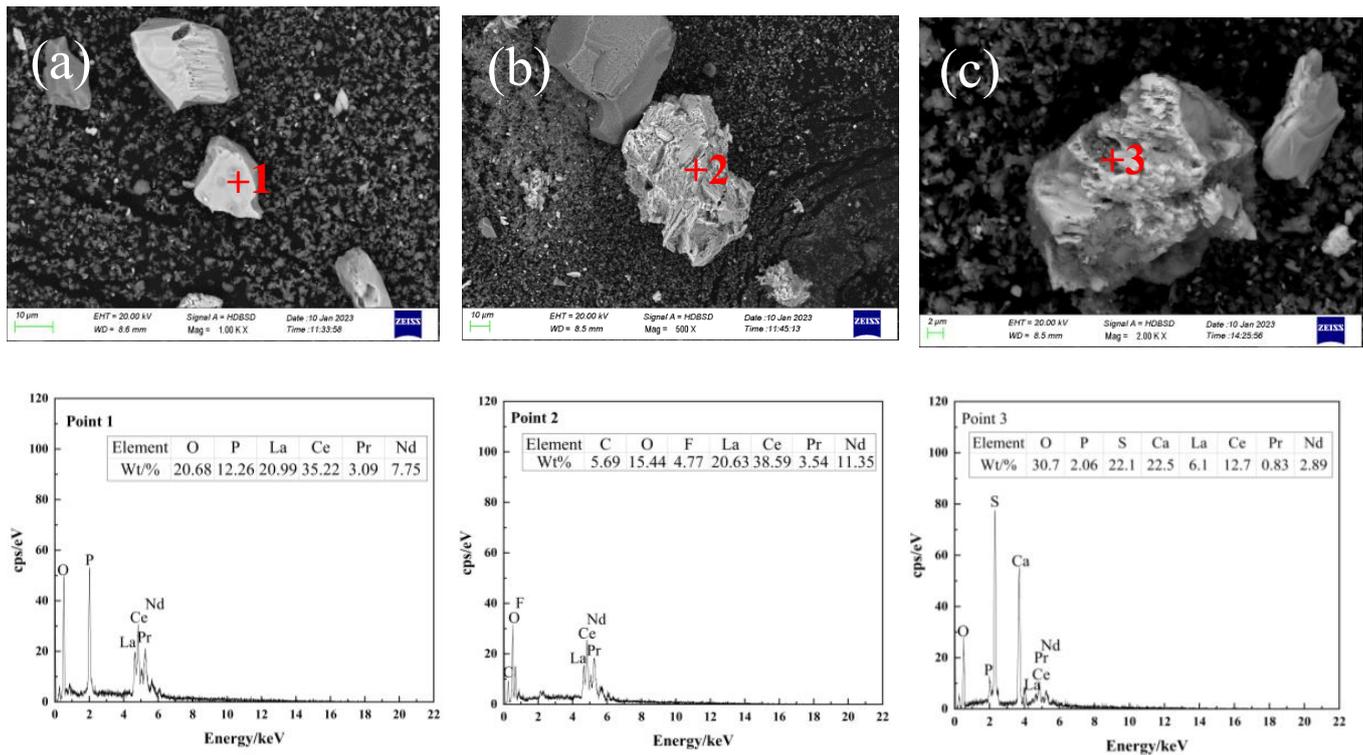


Figure 12. SEM-EDS analysis of leaching residue. (a) 100 min; (b) 80 min; (c) 40 min.

3.4. Kinetics of H_2SO_4 Leaching Process

The shrinking particle model and the shrinking nucleus model are usually applied to reactions between non-porous particles and other reactants, where the unreacted nucleus gradually shrinks as the leaching reaction proceeds. However, the shrinking particle model is only applicable to the reaction with a solid product layer around the unreacted particles, and the shrinking nucleus model is applicable to the reaction without a product layer around the reacted particles [12,26–28].

From the experimental study in Section 2, it can be observed that there is no product formation wrapping around the solid reactants. Therefore, the shrinking nucleus model is chosen to describe the leaching process of mixed rare earth concentrate.

According to the shrinkage model, the leaching process of mixed rare earth concentrate can be divided into three steps: diffusion of the leaching agent to the surface of the mineral grains through the diffusion layer, further inward diffusion of the leaching agent through the solid product layer, chemical reaction between the leaching agent and the solid reactants at the phase interface [29,30].

When the leaching process is controlled by the chemical reaction at the phase interface, the rate of the reaction can be expressed by Equation (4).

$$1 - (1 - x)^{1/3} = k_1 t \quad (4)$$

When the leaching rate is controlled by internal diffusion of the leaching agent or through the solid product layer, the rate of the reaction can be expressed by Equation (5).

$$1 - 3(1 - x)^{2/3} + 2(1 - x) = k_2 t \quad (5)$$

When the leaching rate is controlled by both interfacial mass transfer and diffusion through the product layer, the rate of the reaction can be expressed by Equation (6).

$$1/3 \ln(1 - x) - 1 + (1 - x)^{-1/3} = k_3 t \quad (6)$$

where k_1 , k_2 and k_3 represent the rate constants for different control steps; x is the rare earth leaching rate, %; t denotes the leaching time, min.

Figure 13 shows the change law of the rare earth leaching rate with time at different reaction temperatures. The data in the figure were respectively substituted into Equations (4)–(6) to obtain the reaction rate constant and determine the rate-controlled part of the leaching reaction through linear fitting. The fitted curves are shown in Figures 14–16. From the fitting results, the highest correlation coefficient of the fitted curves in Figure 16 indicates that the sulfuric acid leaching process of mixed rare earth concentrates is controlled by interfacial mass transfer and diffusion through the product layer.

The apparent rate constants of the leaching reaction at different temperatures were calculated based on the mixed control model, and the points of $\ln k$ vs. $1/T$ were calculated and fitted on a curve (Figure 17). The apparent activation energy (E_a) of the reaction was calculated to be 35.45 kJ/mol according to the Arrhenius equation, with an indexing factor determined as 2.72.

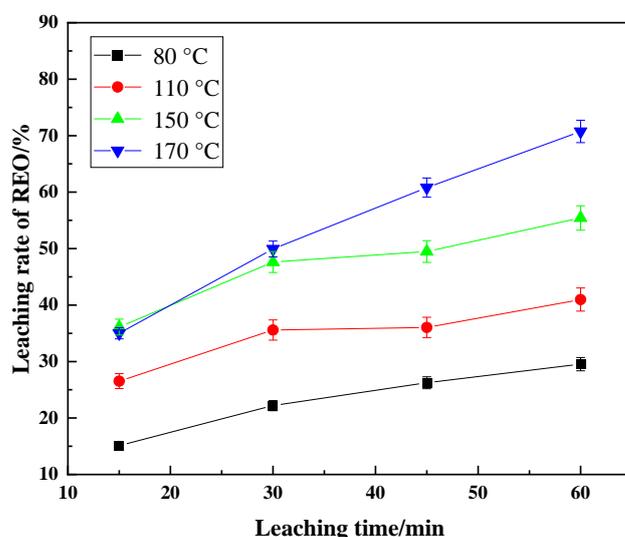


Figure 13. Change curve of rare earth leaching rate with time at different temperatures.

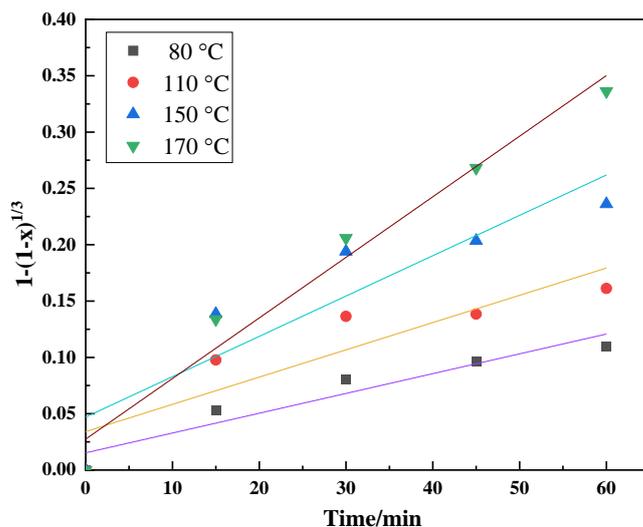


Figure 14. Plots of $1 - (1 - x)^{1/3}$ vs. time for different reaction temperatures.

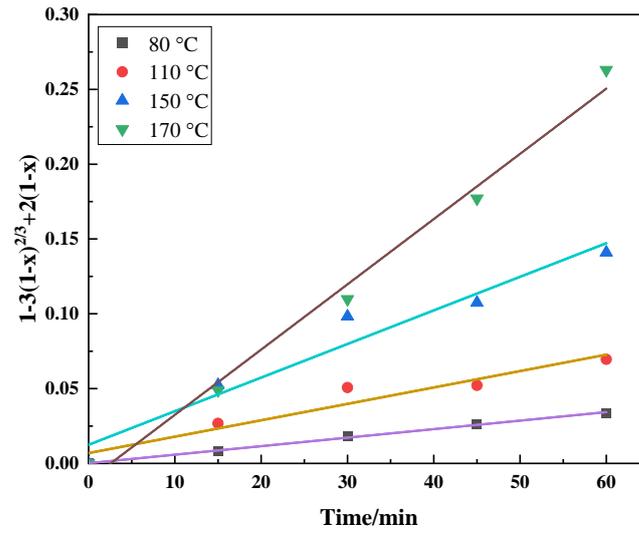


Figure 15. Plots of $1 - 3(1 - x)^{2/3} + 2(1 - x)$ vs. time for different reaction temperatures.

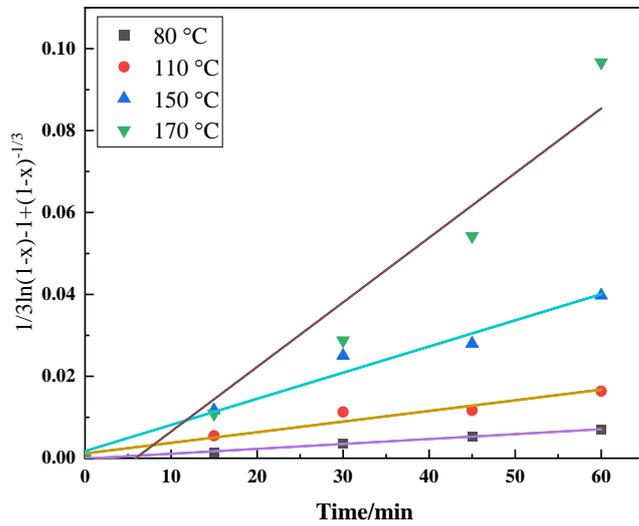


Figure 16. Plots of $1/3 \ln(1 - x) - 1 + (1 - x)^{-1/3}$ vs. time for different reaction temperatures.

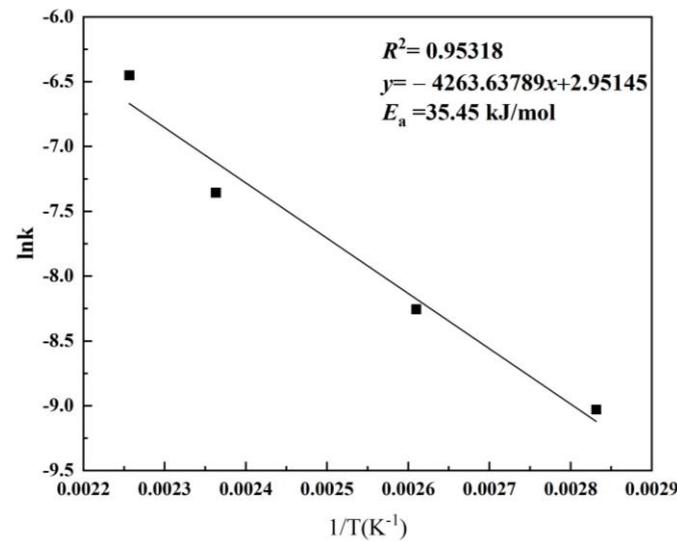


Figure 17. Arrhenius plot of leaching reaction. (Symbols in figure respectively represent values of $1/T$ and $\ln k$ t under 80 °C, 110 °C, 150 °C and 170 °C).

4. Conclusions

The current proposed one-step strategy for the decomposition of mixed rare earth concentrate, which involves sulfuric acid solution leaching minerals, has been shown to be effective in breaking down mixed rare earth concentrates. The leaching conditions were chosen as follows: a concentration of 75% for sulfuric acid, a leaching temperature of 170 °C, a leaching time of 80 min and a ratio of 5:1 for the H₂SO₄/rare earth concentrate. In the strategy described above, about 84% of rare earth could be leached out from mixed rare earth concentrate. The leaching rate of rare earths increased with the increase in leaching temperature and showed a tendency to increase and then decrease with increasing sulfuric acid solution concentration. This was mainly due to the fact that the sulfuric acid with a concentration higher than 85% was unfavorable for the decomposition of bastnasite in the mixed rare earth concentrates. In the initial stage of the leaching reaction, the rare earth leaching rate increased with the increase in sulfuric acid concentration. And in the later stage of the leaching reaction, the rare earth leaching rate increased with the increase in sulfuric acid concentration and then tended to stabilize. Additionally, the amount of sulfuric acid was significantly reduced compared to the traditional high-temperature sulfuric acid roasting process. Under the low-temperature leaching conditions, no sulfur-containing waste gas was generated, and the escape of HF can be effectively controlled. The subsequent extraction of RE and recovery of P and F in the solution will be carried out in future studies. Compared with the sulfuric acid leaching process reported in the literature for bastnasite, monazite and other rare earth-containing minerals, the decomposition process of REFCO₃-REPO₄ mixed rare earth minerals in sulfuric acid solution was interconnected through theoretical calculation and condition optimization. The study on the sulfuric acid leaching kinetics of mixed rare earth concentrates shows that the control link of the leaching reaction is controlled by interfacial mass transfer and diffusion through the product layer. This study will provide new ideas for the green smelting of Bayan Obo, special rare earth ore.

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