Effect of Particle Size Refinement on the Leaching Behavior of Mixed Rare-Earth Concentrate Using Hydrochloric Acid

Zheng Ruan,†§ Mei Li,‡†‡§ Kai Gao,‡†‡ Dongliang Zhang,‡†‡ Lan Huang,‡ Wei Xu,‡ and Xingyu Liu‡

†School of Materials Science and Engineering, Beijing University of Chemical Technology, Beijing 100029, China
‡Key Laboratory of Green Extraction and Efficient Utilization of Light Rare Earth Resources and §Mining Research Institute, Inner Mongolia University of Science and Technology, Baotou 014010, China

ABSTRACT: The effects of particle size, temperature, and leaching time on the leaching behavior of rare-earth elements were studied. The leaching efficiency of the rare earth reached 39.24% under leaching conditions of hydrochloric acid concentration of 8.00 mol/L, particle size 95% distributed below 1.5 μm, leaching time of 120 min, and temperature of 90 °C. According to the scanning electron microscopy and X-ray diffraction analysis of the residue, the mechanism of the leaching process was also investigated. Actually, the phase of REFCO3 transformed into that of RECl3 and REF3, but there was an existing intermediate transition, where the phase of REFCO3 on reacting with hydrochloric acid generated that of REO2F3, and this process also released RE3+ into the solution. REO2F3 precipitated with hydrochloric acid to release a lot of F-, which on combining with RE3+ formed REF3 precipitation. The leaching kinetics of rare earths follows a shrinking core model that can be expressed as $1 - 3(1 - x)^{2/3} + 2(1 - x) = k_\text{f}t$. The activation energies are 62.1, 54.8, 35.1, and 34.9 kJ/mol, respectively.

INTRODUCTION

As an important strategic resource, rare earths are widely applied in phosphor light-emitting diodes and magnetic materials1-12 due to their unique physicochemical property. The majority of the rare-earth elements’ (REEs) production happens in China, which has a large number of rare-earth resources. As the world’s largest rare-earth element (REE) mineral deposits, the Bayan Obo ore deposit has a great variety of minerals and is especially abundant in iron, rare earth, and niobium, which have an extremely high comprehensive utilization value. Over the past years, China has begun to treat rare-earth elements as strategic and crucial materials13 due to their unique physicochemical property.3

In view of the disadvantages of the above smelting processes, a new green metallurgical process is proposed by our research group to treat the mixed rare-earth concentrate, the specific flow chart of which is shown in Figure 1.25 Bastnaesite in the mineral could be readily decomposed into REOF accompanied by release of CO2 during roasting;26,27 then, a large proportion of the concentrate of grade reaches 50%. Moreover, sulfuric acid is not only cheap but also easily available to solve the corrosion problem. However, a lot of industrial effluents and waste gas containing F and S are generated in the production process. In particular, the amount of solid waste is not only large but also its radioactive intensity exceeds the national standard, causing serious pollution to the surrounding environment. Furthermore, the treatment of these wastes also brings about a high cost of disposal. The alkali decomposition is only mainly applied in treating the concentrate, whose grades range from S5 to 60%. But there are some critical problems awaiting to be settled in the smelting process, for instance, expensive caustic soda price, rare-earth yield lower than that in the acid method, and the challenge of removing calcium with acid. Ca would also enter the rare-earth chloride solution in acid solution, affecting the quality of rare-earth chloride products.

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of the rare-earth elements could be extracted by HCl. Monazite, mainly consisting of rare-earth phosphates, is highly stable even at temperatures up to 1500 °C and do not undergo phase change. The slag containing monazite and REF 3 was stepwise decomposed to RE(OH)₃ by using NaOH. The product that is mainly composed of RE(OH)₃ continues to be combined with the leaching solution after washing several times so that rare-earth chloride solution could be finally obtained. In addition, the rinsing solution containing sodium hydroxide, sodium fluoride, and trisodium phosphate anhydrous could be, respectively, recovered due to the significant differences in solubility. This process effectively reduces the production of waste gas in the leaching process and has the advantages of low production cost and high recovery.

However, most of the rare-earth elements in the bastnaesite are inevitably oxidized whose valence state increases from trivalent to tetravalent during roasting. In the leaching process, by using hydrochloric acid, the tetravalent rare-earth elements will oxidize Cl⁻ into Cl₂, which releases into the air and causes severe environmental pollution so the high cost of a reducing agent must be added to avoid releasing chlorine in the leaching process, causing the introduction of impurities. In addition, the waste gas containing F will be also produced during the roasting process, which will increase the processing cost. Recently, with continuous upgradation of the grinding equipment, mineral particle size refinement has become possible and has been industrialized in some factories. For heterogeneous reactions, the migration rate of reactive molecules from one phase to another must be related to the area of the interface so fine particles react faster than coarse particles because of the larger surface area of the former. Unfortunately, few studies have been conducted on the effects of particle size refinement on the leaching of rare-earth elements in the concentrate. The effect of different particle sizes, temperature, and time on extraction for REEs and mechanism of RE leaching after refining the mineral is not yet clear.

In this paper, the method of mechanical activation is used to pretreat the concentrate instead of the roasting process. This mechanical activation method has the advantages of high activation efficiency and easy operation. It enables the efficient leaching of rare-earth elements under mild reaction conditions. Moreover, no other impurities were introduced in the process, which fundamentally solved the problem of waste gas pollution and waste residue treatment in the process of rare-earth smelting and roasting. Through increasing its specific surface area and causing its lattice defects, the activity of mineral is extremely increased to improve the leaching rate of rare-earth elements without adding a reducing agent and introducing impurities. The mixed rare-earth concentrate is finely ground into different particle sizes by a ball mill. All leaching experiments were done at different particle sizes, temperature, and time. By analyzing leaching rate and the phase structure of residue, the leaching regularities and mechanism of RE are clarified.

RESULTS AND DISCUSSION

Material Characteristics. Figure 2 shows the X-ray diffractogram (XRD) of the concentrate. The diffraction peak of REFCO₃ and REPO₃ could be observed evidently, which are
the main phases of the ore. Without the roasting process, the bastnaesite is not decomposed in the XRD patterns and all rare-earth elements in the concentrate are maintained in the trivalent state. The concentration of fluorine has also not been released into the atmosphere to cause environmental pollution. In the subsequent process of removing impurity, the concentration of fluorine will be used in the production of sodium fluoride, as an important by-product, which can be used as a pesticides and wood preservatives. This also increases the economic efficiency and improves the atom economy. Figure 3 shows the microstructure of the concentrate; it is obvious that the particle surface of bastnaesite is relatively dense and compact and reacts with difficulty with a solvent, which may lead to a low leaching rate.

Effect of Temperature and Reaction Time on the Leaching of Rare-Earth Elements. The effect of temperature and time on the extraction of rare earths was investigated at 30, 50, 70, and 90 °C for leaching time varied in the range 2–120 min. Figure 5 displays the changes in the leaching rate with temperature as a function of time. Figure 5a reflects the variation of the leaching rate of the unground concentrate, and Figure 5b–d, particle size of the concentrate 95% distributed below (b) 10 μm, (c) 5 μm, and (d) 1.5 μm. It can be seen from Figure 5 that the leaching rate of rare-earth elements increased gradually with the increasing temperature. When the temperature was 30 °C, the acid-leaching reaction was not fierce and the rare-earth leaching rate increased slowly, but when the temperature reached 90 °C, the reaction rate could greatly accelerate to make the bastnaesite come have a better contact with hydrochloric acid, which could increase significantly up to 39.24%. Within 2–10 min, the reaction between bastnaesite and hydrochloric acid was relatively severe and the rare-earth leaching rate improved fast. This situation was particularly obvious under the ground concentrate and the higher temperature; the extraction of rare-elements increased at different leaching temperatures from 10 to 60 min, as shown in Figure 5. However, the leaching rate of rare earth increased slowly within 10–60 min. Compared with the unground concentrate, the particle size refinement mitigates the downward trend. The extractions were nearly constant after 60 min. This phenomenon occurred because the recovery of La was maximum at room temperature. However, the rise in temperature promoted the dissolutions of Ce and Nd, whose recovery rates were low at room temperature. This variation in recovery rates of different rare-earth elements at different temperatures points that it is hard to extract rare-earth elements completely in one stage, thus causing this trend.35

Effect of Particle Size on the Leaching of REEs. As can be seen from Figure 4, the particle size $D_{50}$ of the mixed rare earth before fine grinding was 20.72 μm and the proportion of the particle diameter below 10 μm was small. Compared with the concentrate before fine grinding, the particle size below 10 μm of the finely ground concentrate was obviously predominant, which can extremely increase the specific surface area to more fully contact with the solvents and accelerate the reaction rate to improve the leaching rate of the rare-earth elements. Figure 5 shows that the ratio of rare-earth leaching can be improved significantly with the refinement of particle size. At 30 °C, bastnaesite of the mixed rare-earth concentrate without grinding was hard to be leached, whose leaching rate was only 7.04%; when the mineral particle size is finely ground from the particle size of 95% below 10 μm to 95% below 5 μm, the leaching rate of rare-earth elements was improved from 9.87 to 10.13%. In contrast, the leaching rate of the concentrate (the particle size distribution of 95% under 1.5 μm) reached 15.05% at 30 °C, increasing by 8.01%, even better than that of the concentrate without grinding at 90 °C. This may be because the surface of bastnaesite was relatively dense, leading to insufficient reaction, and the refinement of mineral particle size can increase the contact area of reactants, greatly accelerating the reaction between minerals and leaching agents. In the process of grinding, mineral particles under the action of impact friction and local high temperature will also lead to the increase of stress and energy in the lattice; thus, this greatly reduced the reaction activation energy. Compared with Figure 5a, it can be seen from Figure 5b–d that the variation range of the rare-earth leaching rate had been remarkably raised with increasing temperature with the refinement of particle size. For the concentration without grinding, when the temperature increased from 30 to 90 °C, the leaching rates were 7.04, 8.42, 9.45, and 10.41% and there was not much change between
them. However, when the mineral particle size is finely ground to 95% below 10 μm, the leaching rate changes significantly from 9.87 to 21.48%. With the refinement of the particle size, this situation obviously occurred, from Figure 5d. The leaching efficiency of REEs (the particle size distribution of 95% under 1.5 μm) reached 39.24%. It can be seen that the refinement of particle size and temperature have a great influence on the leaching rate of rare-earth elements.

Figure 4. Distribution of different particle sizes of the concentrate 95% distributed below (b) 10 μm, (c) 5 μm, and (d) 1.5 μm, respectively, and (a) unground concentrate.

Figure 5. Effect of temperature, time, and particle size on extraction of the rare earths in the rare-earth ore 95% distributed below (b) 10 μm, (c) 5 μm, and (d) 1.5 μm, respectively, and unground concentrate (a).
Mechanism of the Leaching Process. To further investigate the phase transformation of the mixed rare-earth concentrate without roasting during leaching, it is necessary to carry out XRD and SEM analysis of the leaching slag (the particle size of the concentrate is 95% distributed below 1.5 μm; leaching temperature, 90 °C; reaction time, 120 min). Considering that the leaching efficiency of the unground ore (unroasted) is low and the leaching time is longer than that of roasted ore, it is likely that intermediate products will be produced in the leaching reaction. Figures 6 and 7 show XRD patterns and SEM images of leaching residue-acquired raw concentrate without stirring, and the finely ground concentrate is heated at 90 °C for 2 h (particle size of 95% distributed below 1.5 μm).

In Figure 6a, the diffraction peaks of REFCO₃, REPO₄, and (Ce, La)F₃ are obvious. According to the intensity of the diffraction peaks, it can be concluded that the main phase of the leaching slag is bastnaesite, followed by monazite and (Ce, La)F₃ phase, with a small amount of (Ce, La)OF phase. This indicates that a large part of bastnaesite has not been leached for unground samples. In Figure 6b, the diffraction maximum of REPO₄ and (Ce, La)F₃ in the leaching residue of the fine grinding concentrate (particle size of 95% distributed below 1.5 μm) is obvious, accompanied by the appearance of the peak of REFCO₃. This indicates that the bastnaesite is basically fully leached, which is also in line with the high leaching rate of the fine grinding concentrate.

Figure 7a reveals the microstructure of the bastnaesite in the leaching slag for the unmilled sample. It can be seen from the figure that bastnaesite is often distributed in a granular manner, with obvious dissolution traces on the surface and often showing bumpy gullies. Within the bastnaesite, residual particles of the (Ce, La)OF phase are found. (Ce, La)OF phase was accidentally discovered in Figure 7b, and its existence was also confirmed by the X-ray energy spectrum. This is a new phase generated by the unground concentrate during acid leaching. Figure 7c showed that the (Ce, La)OF phase often retains the crystal shape of the bastnaesite and the interior of the new phase often contains the debris of bastnaesite. Therefore, it can be concluded that the (Ce, La)OF phase is formed by the original deposition of the bastnaesite during the acid leaching. X-ray energy spectrum analysis of the Figure 7c shows that (Ce, La)OF phase often contains a small amount of P⁵⁺ and Ca²⁺. These P⁵⁺ and Ca²⁺ are generated from fluorite and apatite in the ore dissolved during acid leaching and adsorbed on the surface of (Ce, La)OF phase. However, the (Ce, La)OF phase was not found in the SEM images of the milled sample.

(Ce, La)F₃ phase is also a newly formed material phase in slag leaching for both the milled sample and unmilled sample shown in the Figure 7d,e. In Figure 7d,e, P⁵⁺ and Ca²⁺ are also adsorbed on the surface of colloidal (Ce, La)F₃ phase. (Ce, La)F₃ phase presents the phenomenon of distant deposition. This explains that a part of bastnaesite will dissolve into the solution in the form of RE³⁺ and newly formed (Ce, La)OF phase retained in the surface. As the reaction continued further, (Ce, La)OF phase also gradually dissolved into the leaching solution. At the same time, a huge amount of fluoride ions was immersed into the solution and combined with RE³⁺, generating undissolved (Ce, La)F₃ precipitation into the leach residue. The leaching residue (Ce, La)OF as an intermediate, chemical property is very unstable, and its content is less, which explains why XRD analysis in Figure 6a did not show the characteristic peak of (Ce, La)OF but the X-ray energy spectrum analysis results showed the existence of the rare-earth oxide phase whose F:O ratio is between 3–5 to 1; so the rare-earth oxide phase is defined as (Ce, La O,F) (x = 0.20–0.33). Figure 7e shows the (Ce, La)F₃ phase in the fine grinding concentrate leaching slag, which is often dispersed with a large number of monazite and a small amount of bastnaesite due to its coarse particle size, as shown in Figure 7f.

Figure 7b,e of the SEM images showed that the surface of monazite in the two acid-leaching residues was relatively smooth and showed no signs of dissolution, indicating that monazite remained in the leaching residue without leaching.

According to the above results, the acid-leaching process of mixed rare-earth concentrate is as follows. Unlike the REOF in the roasting ore directly leached into the RECl₃ solution using HCl, the structure of bastnaesite in the ore (unroasted) was not decomposed and it would react with hydrochloric acid (8 mol/L) to form an intermediate product, REOF. Meanwhile, it also produced RECl₃ into the solution. The chemical properties of the intermediate product REOF are extremely unstable. It will continue to react with hydrochloric acid and eventually form RECl₃ into solution. At the same time, a large amount of fluoride ion was poured into the solution and then the reaction with RE³⁺ would generate insoluble (Ce, La)F₃ precipitations. REOF and REF₃ would concentrate on the mineral surface, preventing the hydrochloric acid from continuing to interact with the ore. This may be the reason why the leaching rate of the unroasted concentrate is lower than that of the roasted concentrate and the leaching time is longer. The monazite in the mineral is not basically leached. The equations of the leaching process are as follows:

\[(3 - 2x)\text{REFCO}_3 + 6(1 - x)\text{H}^+ = \text{REO}_x\text{F}_{3-2x} + 2(1 - x)\text{RE}^{3+} + 3(1 - x)\text{H}_2\text{O} + (3 - 2x)\text{CO}_2 \quad (1)\]

\[\text{RE}_x\text{O}_y\text{F}_{3-2x} + 2x\text{H}^+ = \text{RE}^{3+} + x\text{H}_2\text{O} + (3 - 2x)\text{F}^- \quad (2)\]

\[\text{RE}^{3+} + \text{F}^- = \text{REF}_3 \quad (3)\]

The X-ray energy spectrum analysis results in Figure 7d show that x = 0.20–0.33 in the equation.
Kinetics Study of Leaching Process. Because of the acid-leaching reaction leveling off after 60 min, the kinetics could be studied within 60 min. For the leaching process, the shrinking core model can usually be used to interpret the liquid–solid reaction.\textsuperscript{36} The shrinking core models are normally represented to be the diffusion, chemical, and mixed control models.\textsuperscript{37} One

Figure 7. SEM images of leaching residues acquired by acid leaching at 90 °C for 2 h (a–d) the raw concentrate without stirring, (e, f) the finely ground concentrate (particle size of 95% distributed below 1.5 μm), and EDS analysis (b–e).
Figure 8. Plots of $1 - 3(1 - x)^{2/3} + 2(1 - x)$ and $t$ at different temperatures for different particle sizes of the mixed rare-earth concentrate 95% distributed below (b) 10 μm, (c) 5 μm, and (d) 1.5 μm, respectively, and unground concentrate (a).

Figure 9. Arrhenius plots of ln $k_1$ and $T^{-1}$ under different particle sizes of the ore 95% distributed below (b) 10 μm, (c) 5 μm, and (d) 1.5 μm, respectively, and unground concentrate (a).
of these steps can control the leaching process. Considering that the leaching efficiency may be controlled by diffusion through the REO,F and REF layer remaining in the ore surface, the kinetic equation can be showed as follows

\[ 1 - 3(1 - x)^{2/3} + 2(1 - x) = k_at \]  

(4)

where \( x \) represents the extraction efficiency of rare-earth elements, \( t \) represents leaching time (min), and \( k_1 \) represents the rate constant.

To clarify the kinetics of the unground concentrate reacting with hydrochloric acid, data were fitted against the model. In Figure 9, the plots of \( 1 - 3(1 - x)^{2/3} + 2(1 - x) \) and \( t \) at different temperatures indicate that the kinetic data of the rare-earth elements (shown in Figure 5) was fitted well to the eq 4 due to high values of \( R^2 \). According to the eq 5, \( E_a \) could be obtained as follows

\[ A \exp \left( -\frac{E_a}{RT} \right) = k_1 \]  

(5)

where \( k_1 \) represents the rate constant (s\(^{-1}\)), \( T \) represents the temperature (K), \( R \) represents the universal gas constant, 8.314 J/(K·mol), and \( E_a \) represents the activation energy (kJ/mol).

Figure 9 presents that \( k_1 \) was plotted against \( T^{-1} \). The \( E_a \) of the rare-earth elements under different particle size distributions was calculated to be 62.1, 54.8, 35.1, and 34.9 kJ/mol, respectively.

The \( E_a \) of the reaction controlled by diffusion is relatively low, typically about 4-12 kJ/mol. Furthermore, the value of apparent activation energy (>41.8 kJ/mol) is one of the characteristics of chemical reaction control.\(^{38} \) From Figure 9, with the increase of the grinding degree, the reaction activation energy of the concentrate decreased from 62.1 to 34.9 kJ/mol. It can be seen from Figure 9 that the fine grinding process can greatly reduce the activation energy of the concentrate and increase the reaction rate. There is a great difference between the activation energy of the unground concentrate and fine ground concentrate. The activation energy of the unground concentrate is 62.1 kJ/mol, indicating that the influence of chemical reaction control is greater than that of diffusion control. But the surface of the unground concentrate was very dense, causing a low leaching rate from the images of SEM shown in Figure 3. However, the value of \( E_a \) (Figure 9b) (the particle size distribution is 95% under 10 \( \mu \)m) is 54.8 kJ/mol, because the degree of fine grinding may not be enough so that it is controlled by the surface chemical reaction. The value of \( E_a \) ((c) and (d) shown in Figure 9) is 35.1 and 34.9 kJ/mol, respectively, far less than that of the raw concentrate, between 12 and 41.8 kJ/mol, showing that the extraction process of the concentrate (the particle size distribution of 95% under 5 and 1.5 \( \mu \)m) within 60 min is controlled by a combination of chemical reaction and diffusion through the product layer. Although the process was controlled by a combination of chemical reaction and diffusion through the product layer, its chemical reaction step mostly plays a major role. With the decreasing particle size of the ore, it increases the specific surface area of the concentrate, causing the effects of diffusion through the layer to become less obvious.

### EXPERIMENTAL SECTION

**Materials.** The concentrates used in the experiment are obtained from Bayan Obo deposit, and the mixed rare-earth concentrate was selected by flotation. The compositions of REFCO\(_3\) and REPO\(_4\) are, respectively, 78.2 and 21.2\% in the ore. The chemical compositions of the sample are measured by inductively coupled plasma atomic emission spectroscopy (ICP-AES) with a Horiba ULTIMA ICP-AES, as shown in Tables 1 and 2. In addition, 8 mol/L of hydrochloric acid is required for the experiment (diluted by deionized water to analyze pure hydrochloric acid). All aqueous solutions are prepared with deionized water.

**Experimental Procedure.** The mixed rare-earth concentrate was finely ground by a ball mill to 95\% below 1.5, 5, and 10 \( \mu \)m, respectively, and the measurement of mineral particle size distribution was carried out by a laser particle analyzer (Beckman Coulter, Inc. LS230). All leaching experiments were operated in glass products. To keep the reaction at a stable temperature during acid leaching, a paddle agitator and water bath are used. For each experiment, 8 mol/L hydrochloric acid was first charged into the beaker slowly. When the temperature reached the preset value and became stable, the mixed rare-earth concentrates of different particle sizes of 20 g were also put into the beaker for the acid-leaching experiment, respectively, starting to set a timer. During the reaction, the system was fully mixed with the agitation speed of 300 rpm. After the reaction reaches the expected time, the solution was filtered to obtain the leaching solution and slag; the content of rare-earth elements in the solution and slag was measured separately to gain the extraction efficiency. To better explore the mechanism of the leaching process and confirm the existence of intermediate products, an additional experiment was needed. This experiment was conducted such that the raw concentrate was leached by hydrochloric acid for 2 h at 90 °C on the premise of not stirring. The compositions and phases of ore and leaching slag were analyzed by X-ray diffraction (XRD) conducted on an X-ray diffractometer (PANalytical company, the Netherlands). The microstructure of main components in the concentrate and residue was observed using a scanning electron microscope.

### Table 1. Composition and Distribution of the Mixed Rare-Earth Concentrate (% Mass Fraction)

| composition | REO | F | CaO | Fe\(_2\)O\(_3\) | P\(_2\)O\(_5\) | SO\(_4\)\(^{2-}\) | ThO\(_2\) |
|-------------|-----|---|-----|----------------|--------------|-------------|---------|
| content wt % | 68.42 | 8.63 | 3.41 | 1.23 | 1.73 | 0.26 | 0.26 |

**CONCLUSIONS**

The leaching rate can be greatly improved after a fine grinding process. The leaching efficiency of rare-earth elements was affected by different particle sizes more remarkably than temperature. Rare-earth extraction in the ore whose particle size is 95\% distributed in 1.5 \( \mu \)m can reach 39.24\%. XRD patterns of the residue (particle size of 95\% distributed below 1.5 \( \mu \)m) also showed that the bastnaesite in the ore was nearly decomposed. In the leaching process, bastnaesite of the unroasted ore was partly generated to REOF\(_{3-2x}\) and some of the rare-earth elements are released into the solution at the same time. REOF\(_{3-2x}\) continues to react with hydrochloric acid adding a large amount of F\(^-\) into the solution, resulting in the production of REF\(_x\). REOF\(_{3-2x}\) presents the phenomenon of original deposition, and REF\(_3\) precipitation presents the phenomenon of distant deposition. SEM patterns of the residue also prove the process. The kinetics of REEs follow the shrinking core model, whose kinetic equation follows as 1 - 3(1 - x)^{2/3} + 2(1 - x) = k_1t. The value of apparent activation energy is 62.1, 54.8, 35.1, and 34.9 kJ/mol, respectively.
Table 2. Composition and Distribution of Rare-Earth Elements (% Mass Fraction)

| Composition | REO | Y2O3 | La2O3 | CeO2 | Pr6O11 | Nd2O3 | Sm2O3 | Eu2O3 |
|-------------|-----|------|-------|------|--------|-------|-------|-------|
| content wt % | 68.42 | 0.21 | 28.38 | 52.00 | 4.65 | 13.33 | 0.94 | 0.20 |

Notes

The authors declare no competing financial interest.

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