

# STUDY ON ALKALI LIQUOR ROASTING AND SULPHURIC ACID LEACHING OF BAYAN OBO RARE EARTH CONCENTRATE

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Take the roasted ore after the alkali liquor roasting and decomposition of Bayan Obo rare earth concentrate as the raw material, and use the sulphuric acid leaching to extract the elements including rare earth, thorium, tetravalent cerium, etc. The influence on the leaching of rare earth, thorium, tetravalent cerium made by the leaching conditions including mineral acid ratio, initial acidity, leaching temperature, and leaching time is researched. The result shows: when the mineral acid mass ratio is 1:1, the initial acid concentration is 6 mol/L, the reaction temperature is 90 °C, and the reaction time is 120 min, the gross leaching rate of rare earth is greater than 95 %, and the leaching rate of tetravalent cerium and thorium is greater than 97 %.

*Key words:* bastnaesite, monazite, mixed rare earth ore, alkali liquor, sulphuric acid

## INTRODUCTION

Bayan Obo rare earth concentrate is the mixed ore of monazite and bastnaesite. The concentrated sulfuric acid roasting decomposition is the main method for industrial production [1]. Now more than 90 % of Bayan Obo rare earth ore are handled by the method of concentrated sulfuric acid roasting decomposition. In this process, the concentrated sulfuric acid and the rare earth ore are mixed then directly charged into the rotary kiln for roasting, realizing the industrial mass production of continuous roasting. But the tail gas of this roasting process contains a large amount of sulfur and fluorine [2-4]. After the rare earth elements are leached out, the thorium element would concentrate in the leaching residue to become the waste radiant residue [5], and during the production, the tough problem of “three kind of wastes” such as the waste water containing sulfate radical would be brought about as well [6]. Therefore, many scholars are performing the research on the clean metallurgical technology of Bayan Obo rare earth concentrate. Wu Wenyuan et al. [7] use CaO-NaCl-CaCl<sub>2</sub> to roast and decompose the Bayan Obo ore, and use HCl complex to leach out the rare earth oxide while AlCl<sub>3</sub> assists for leaching. The overflow of fluorine can be avoided by this method, but it's difficult to realize the industrial production. Zhang Liqing et al. [8] use the re-

ducing agent of active carbon, the chlorinating agent of chlorine, the defluorinating agent of SiCl<sub>4</sub>, and the oxidizing agent of the gas mixture of O<sub>2</sub> and H<sub>2</sub>O, by the method of chlorination-oxidization, to extract the rare earth elements from the Bayan Obo rare earth ore, researching the mechanism of chlorination reaction. This method is still under the laboratory research.

The alkali liquor decomposition is another industrial production technology of Bayan Obo rare earth concentrate. In this method, use the sodium hydroxide solution to have a solid-liquid reaction with the rare earth concentrate in the reaction bin, then go through the soluble salt of fluorine and phosphorus generated by scrubbing, then use the hydrochloric acid to leach out the rare earth to get the chlorinated rare earth product. This process has no waste gas containing fluorine, and the amount of waste residue is little. No matter the research is on the optimization of the process that the alkali liquor decomposes the rare earth ore mixture [9, 10], or on the process that the alkali liquor directly decomposes the pure minerals of bastnaesite and monazite [11], they are all performed in the solid-liquid reaction system, and the process operation progress is not successive, which is bad for the mass production and application. On the basis of static experiment [12], we researched the process that the concentrated alkali liquor roasts and decomposes the Bayan Obo rare earth concentrate [13], and we directly blended the rare earth concentrate mixture and the concentrated alkali liquor to decompose them, solving the “ring agglomerate” problem of rotary kiln during roasting, realizing the continuous mass production that the alkali liquor decomposes the rare earth concentrate. The decomposing rate of rare earth minerals reaches above 97 %, and the oxidizing rate of cerium reaches above 92 %. In the research on the process that the hydrochloric acid dissolves the rare earth to make the chlorinated rare earth, the

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tetravalent cerium is reduced to the trivalent cerium, and chloridion is oxidized to become chlorine which pollutes the environment, and the addition of reducing agent can increase the production cost, meanwhile the tetravalent cerium is not fully utilized. For fully utilizing the high oxidizing rate of cerium and making the tetravalent cerium and the trivalent rare earth separate preferentially, we performed the research on the process of leaching out the rare earth, thorium and tetravalent cerium in the sulfuric acid system.

## EXPERIMENT AND MATERIALS

The roasted ore required by experiment is acquired by roasting after the mixing of the rare earth concentrate mixture and the alkali liquor. The roasting is performed in the "rotary tube resistance furnace". The inclination angle, rotating speed and roasting temperature of resistance furnace is adjustable. One side of furnace tube is for material charging, and one side for discharging. There are exhaust vents on the charging side. Every time the materials of a certain proportion are charged into the furnace hearth through the charging hole. The material liquid is roasted in the furnace with a temperature of 400 °C, and then discharged after a reaction of 90 min. After the product got by reaction is washed to be neutralized, it would be filtered to be the roasted ore (alkaline flat piece) for reserve. The decomposing rate of minerals is 97,3 %, and the oxidizing rate of cerium is 91,8 %. The chemical composition of roasted ore, see Table 1.

Table 1 The chemical composition of roasted ore /wt. %

Element	REO	P	F	CaO	ThO <sub>2</sub>	Fe <sub>2</sub> O <sub>3</sub>
Roasted ore	54,90	3,29	1,27	12,60	0,22	5,28

Take quantitative roasted ore, then make them have thermal-insulating mixing reaction at certain temperature by using sulfuric acid, then with hot filtration acid leaching solution is got; filtered flat piece is leached again by using water, filtered and washed, then water leaching solution and leach residue are got. Through analyzing rare earth, thorium and tetravalent cerium in the acid leaching solution, water leaching solution and leach residue, calculate the leaching rate of the rare earth, thorium, tetravalent cerium, etc. The gross leaching rate  $\mu$ ,  $\mu = (\text{mass in acid leaching solution} + \text{mass in water leaching solution}) / \text{mass in roasted ore} \times 100 \%$ , the percentage of gross leaching rate for element in acid leaching solution  $\varepsilon$ ,  $\varepsilon = \text{mass in acid leaching solution} / (\text{mass in acid leaching solution} + \text{mass in water leaching solution}) \times 100 \%$ .

Wash away soluble salt and excessive sodium hydroxide by water after mixing roasting of Bayan Obo rare earth concentrate with alkali liquor, then roasted ore used in the experiment is obtained, and measured mineral decomposition rate of rare earth is 97,3 % and oxidation rate of cerium is 91,8 %. Rare earth in roasted ore is mainly existed in forms of  $\text{Ce}_7\text{O}_{12}$ ,  $\text{Ce}_{0,75}\text{Nd}_{0,25}\text{O}_{1,875}$

composite oxides etc, and because tetravalent cerium and tetravalent thorium can exist stably in sulfuric acid system, at the same time have larger solubility. However, the solubility of trivalent rare earth sulfate is small and decreases with temperature increasing, and control dissolving conditions can make rare earth composite oxides dissolve into rare earth sulfate. Because trivalent rare earth sulfate has small solubility and reaches saturation then dissolved out in precipitation form, however tetravalent cerium and tetravalent thorium are reserved in solution with high acid, so design the two leaching processes of sulfuric acid leaching and water leaching to make tetravalent cerium and trivalent rare earth realize crude separation by using solubility difference. Tetravalent cerium content in roasted ore is 25,2 % ( $\text{Ce}^{4+}$  mass fraction) that can be calculated through chemical components of roasted ore.

## RESULTS AND DISCUSSION

### Effect of mineral acid ratio on leaching rate

Use sulphuric acid with 6 mol/L initial acidity for 90 °C thermal reaction in different mineral acid ratio and the reaction time is 120 min, after the end of the reaction and hot filtration, then acid leaching solution containing tetravalent cerium is got; filtered flat piece is leached again by using water to stir, and liquid-solid ratio is 8:1, and leaching time is 120 min, filtered and washed, then water leaching solution mainly containing trivalent rare earth is got. Results of the effect of mineral acid ratio on leaching rate for rare earth, thorium and tetravalent cerium are shown in Figure 1.

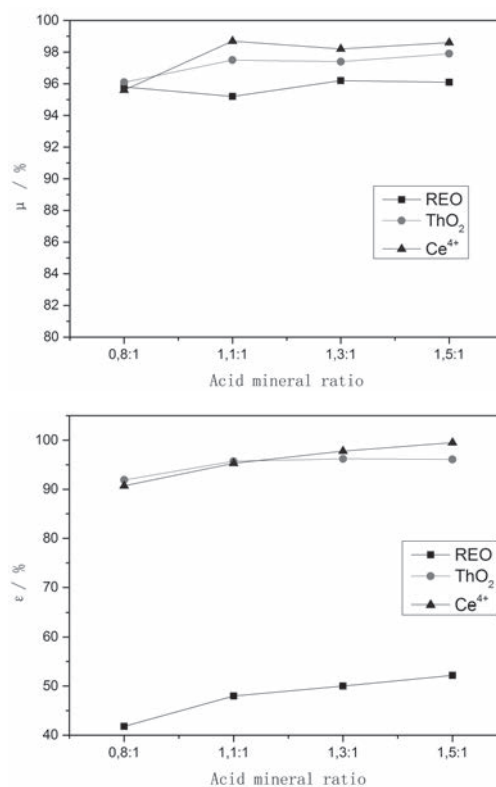


Figure 1 Effect of mineral acid ratio on leaching rate

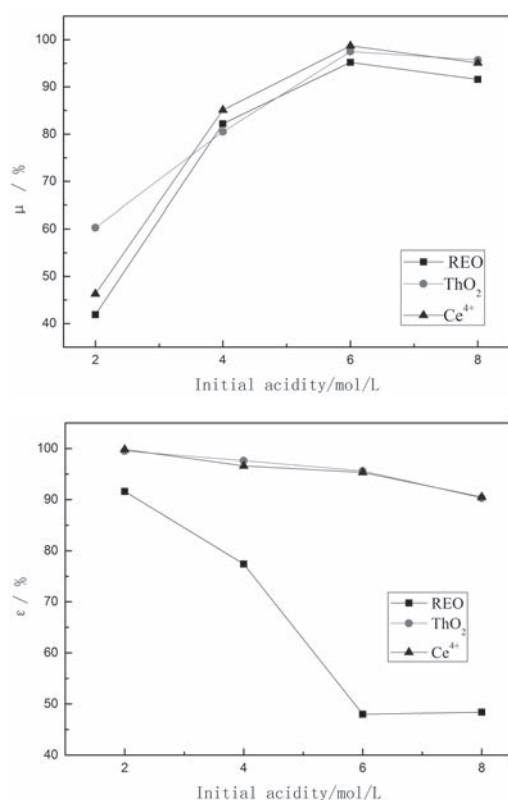


Figure 2 Effect of the initial acidity on leaching ratio

As can be seen from the results, under the experimental conditions, rare earth, thorium and tetravalent cerium have high leaching rate, but when the mass ratio of mineral acid is lower, tetravalent cerium and thorium take about 90 % proportions of acid leaching solution, the rest came into water leaching solution, which is disadvantageous to the separation of tetravalent cerium and trivalent rare earth, and when the mass ratio of mineral acid is lower, the reaction system is relatively viscous, which is disadvantageous to operate. With mass ratio of mineral acid increasing to 1:1,5, proportions for total leaching rate of thorium and tetravalent cerium increase, and 99,5 % of tetravalent cerium comes into acid leaching solution, but the proportion of total rare earths increases more, that is more trivalent rare earth comes into acid leaching solution and rare earth content decreases, which is disadvantageous to the separation of tetravalent cerium and trivalent rare earth. So as overall consideration, choose mineral acid ratio 1:1,1 as the follow-up study condition.

### Effect of initial acidity on leaching rate

Mass ratio of mineral acid is 1:1,1, using sulfuric acid with different initial acidity for thermal reaction under 90 °C and the reaction time is 120 min, after the end of the reaction and hot filtration, getting acid leaching solution; filtered flat piece is leached again by using water, and liquid-solid ratio is 8:1, and leaching time is 120 min, filtered and washed, then water leaching solution is got. Results of the effect of initial acidity on

leaching rate for rare earth, thorium and tetravalent cerium are shown in Figure 2.

The initial acidity has a great influence on the leaching rate of each element, and it also has a great influence on the distribution ratio of each element in the water leaching solution and acid leaching. When the initial pH value is 2 mol/L, the rate of leaching rare earth and tetravalent cerium are only 40 %, thorium leaching rate is about 60 %, and the elements were all entered into acid leaching solution, did not separate the tetravalent cerium, thorium and rare earth. Because of the fixed ore acid ratio, the lower the initial acidity, the greater volume of acid leaching, enough to dissolve all the leached elements into the acid leaching solution. The main part of the water leaching solution is the mass of the water contained in the alkaline flat piece after solid-liquid separation. When the initial pH was 6mol/L, the total leaching rate of rare earth, cerium and thorium were the highest, and the total rare earth in acid leaching accounted for less than 50 %, reached in the tetravalent cerium and thorium acid leaching solution of more than 95 %. Therefore, the initial acidity should be 6 mol/L.

### Effect of reaction temperature on leaching rate

Sulfuric acid of initial acidity of 6 mol/L, with mineral-acid mass ratio of 1:1,1, react under different temperatures with thermal preservation, and reaction time takes 120 min, heat filtration after the reaction finishes, then the acid leaching solution is got; The filtered flat piece is leached again by water, and the liquid-solid ratio is 8:1, the leaching time is 120 min, then filtered and washed, the water leaching solution is got. The effect that reaction temperature makes on the leaching rate of rare earth, thorium, and tetravalent cerium is shown on Figure 3. The result shows that the reaction temperature has a great effect on the leaching rate of rare earth, thorium and tetravalent cerium, and the leaching rate has a great extent of enhancement with the increase of temperature. The change of temperature has little effect on the percent in the acid leaching solution that each element accounts for.

### Effect of reaction time on the leaching rate

With the initial acidity of 6 mol/L sulfuric acid, the ratio of mineral acid to 1:1,1, the reaction temperature was kept at 90 °C for a certain period of time, and the acid leaching solution was obtained after the end of the reaction; The filtered flat piece was leached with water again, and the liquid solid ratio was 8:1, filtration and washing were used to obtain the water leaching solution. The effect of reaction time on the leaching rate of rare earth, thorium and cerium is shown in Figure 4. The result shows that the reaction time has a great influence on the leaching rate of rare earth, tetravalent cerium and thorium, and the leaching rate increases with

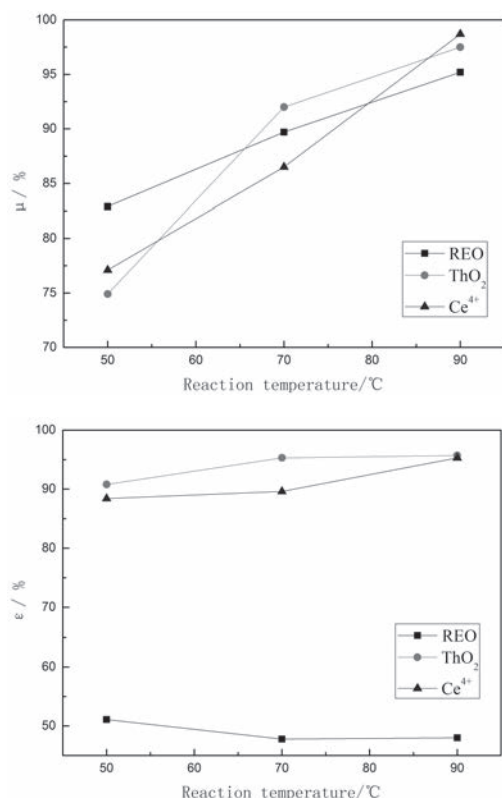


Figure 3 Effect of reaction temperature on leaching ratio

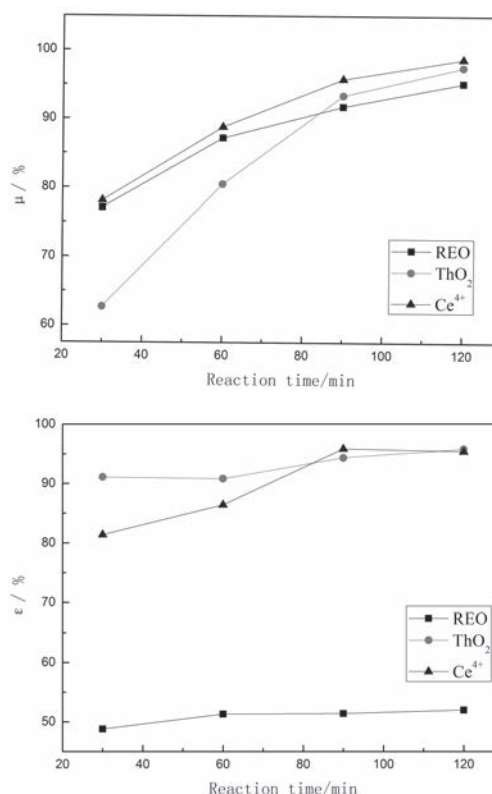


Figure 4 Effect of reaction time on leaching ratio

time. This is because in the process of sulfuric acid leaching reaction of rare earth, since there are a massive amount of calcium existing in minerals, and the calcium sulfate generated by the reaction between sulphuric acid and calcium deposit on the surface of mineral grains, and at the same time the trivalent rare earth sulfate taking mineral grains as crystallization nucleus crystallize, precipitate and deposit on the surface of mineral grains, which in turn hinders the further going of reaction. The extension of leaching time helps to the contact reaction between sulfuric acid and the mineral grain surface, which enhances the leaching rate as a result.

### Parallel test results of optimization conditions

Through the above experimental researches, the relatively proper conditions for sulfate leaching: the mineral-acid mass ratio---1:1,1; the initial pH value---6 mol/L; the reaction temperature---90 °C. The reaction time was---120 min. At the end of the reaction, the acid leaching solution was obtained by the thermal filtration; the filtered flat piece was leached again with water, the liquid-solid ratio was 8:1, and after being filtered and washed, the water leaching solutions were obtained. Five parallel experiments were carried out according to this condition. The results are shown in Table 2.

From the data in the table, the total leaching rare earth rate is between 95 % ~ 96 %, tetravalent cerium and thorium leaching rate is more than 97 %, and the tetravalent cerium and thorium in acid leaching accounted for 97 % and above, achieving the separation of

Table 2 Parallel test results

Experiment No.	leaching rate					
	REO		$\text{ThO}_2$		$\text{Ce}^{4+}$	
	$\mu$	$\epsilon$	$\mu$	$\epsilon$	$\mu$	$\epsilon$
0305-4	96,1	51,8	98,7	98,1	98,1	99,4
0315-4	95,9	50,3	97,5	97,8	98,8	98,6
0317-4	95,2	51,4	98,4	97,3	97,8	98,8
0325-4	95,0	50,1	97,6	97,2	99,7	98,3
0326-4	96,2	52,1	99,2	98,8	97,4	97,7

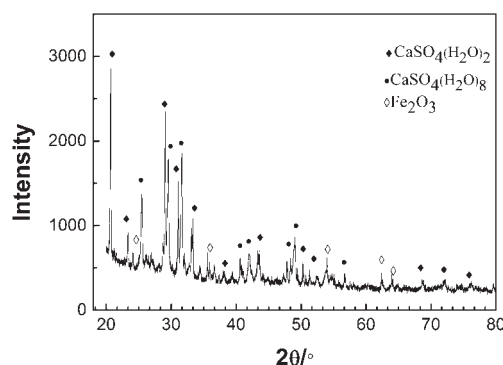


Figure 5 XRD spectrum of leaching residue

cerium, thorium and rare earth; results are stable and can meet the requirement of process.

The results of thorium content and radioactivity analysis of leached residue were shown in Table 3. The gross specific activity of water leached residue was less than  $1 \times 10^4$  Bq/kg, by (XRD) analysis (Figure5), water leaching residue mainly two hydrated calcium sulfate, eight hydrated calcium sulfate and hematite, including calcium sulphate accounting for more than 60 %, which can be further comprehensively recycled.

Table 3 Thorium content and radioactivity of leaching residue Bq/kg

No.	$\alpha$	$\beta$	Total	ThO <sub>2</sub> %
0305-4	5012	2537	7549	0,032
0315-4	4801	2473	7274	0,024
0317-4	4933	2518	7451	0,027
0325-4	3523	1864	5387	0,014
0326-4	3327	1716	5043	0,0087

## CONCLUSION

Liquid alkali roasting and decomposition of mixed rare earth ore, and water leaching after sulfuric acid leaching, when the leaching condition for ore-acid mass ratio is 1:1,1, initial pH value is 6 mol/L, extraction temperature is 90, extraction time is 120 min, the rare earth leaching rate can reach more than 95 %, the leaching rate of thorium and tetravalent cerium can reach more than 97 %. The two-step leaching can make more than 97 % of tetravalent cerium and thorium enter the acid leaching solution, which realizes the crude separation of tetravalent cerium, thorium and trivalent rare earth.

The specific activity of water leached residue radioactivity is less than  $1 \times 10^4$  Bq/kg, mainly calcium sulfate and hematite, which can be further utilized.

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Note: Responsible for English language is Lector from University Baotou, China.