

Mixed rare earth concentrate leaching with HCl–AlCl₃ solution

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Received: 31 August 2012/Revised: 25 September 2012/Accepted: 8 October 2012/Published online: 24 April 2013
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Abstract A method of Baotou mixed rare earth concentrate leaching was investigated. According to the principle of complex leaching, the quadratic orthogonal regression experiment was used to investigate effect of six factors. An optimal condition of low energy and environment friendly was determined as follows: HCl acidity is 4 mol·L⁻¹, AlCl₃ concentration is 2 mol·L⁻¹, reaction temperature is 85 °C, reaction time is 90 min, liquid to solid ratio is 35 ml·g⁻¹, and stirring speed is 100 r·min⁻¹. According to this condition, the leaching ratio of mixed rare earth concentrate is 76.5 %. The analyses of X-ray diffraction shows that bastnasite disappears, and the main peaks of filter residue is monazite and cheralite after leaching of HCl–AlCl₃ solution. The result indicates that REFCO₃ of the mixed rare earth concentrate can be dissolved, but REPO₄ remains in the leaching residue. This method provides a way to separate and extract rare earth.

Keywords HCl–AlCl₃ solution; Mixed rare earth concentrate; Leaching

1 Introduction

Bastnasite (REFCO₃) is a magma-derived fluorocarbonate mineral containing 65 wt%–75 wt% rare earth oxides (REO). The two major sources in the world for lanthanides are bastnasite deposits at Mountain Pass, California (USA), solely for REE production, and Bayunebo, Inner Mongolia (China), mined primarily for iron ore and REE as a by-product. Monazite (REPO₄) is an REE phosphate containing 55 wt%–65 wt% REO, associated with granites and beach sands in Australia, Brazil, and India [1]. The mixed rare earth ore is a paragenetic mineral that is composed of REFCO₃ (bastnasite) and REPO₄ (monazite and cheralite); it is an important rare earth resource, and it contains about 40 % important ore of rare earth industry minerals in the world [2]. This mineral is distributed in the Baiyunebo Baotou and is considered to be the mineral that is hardest to decompose due to its complex composition [3, 4]. The proportion of REFCO₃ and REPO₄ in minerals is 9:1–1:1 in 1990s [5], and according to the analysis of minerals, this number becomes 6.5:3.5 in recent years [6]. Nowadays, the sulfuric acid calcinations method is mainly used to decompose mixed rare earth; however, the problem of this method releases SO₂ and HF gases, which are difficult to be recycled economically. Environmental pollution is serious [7]. Some new green technologies of mixed rare earth concentrate have been investigated by many researchers, such as the method of Roasting with CaO and NaCl [8], the carbochlorination–oxidation method [9], or the method of roasting with CaO–NaCl–CaCl₂ [10], etc., but these methods have not been applied to industry production.

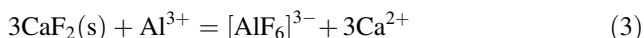
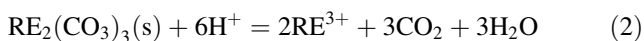
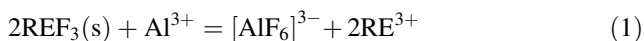
In this paper, Baotou mixed rare earth concentrate was leached out by the method of hydrometallurgy. REFCO₃ is a composite compounds, and the compositions are RE₂(CO₃)₃ and REF₃. Rare earth carbonate is easily dissolved in

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hydrochloric acid, but the rare earth fluoride is hard to be dissolved in hydrochloric acid. Previous investigations showed that Al³⁺ can form complex with F⁻ strongly [11]. The HCl–AlCl₃ solution was used to leach out rare earth oxide and CaF₂, the Baotou mixed rare earth concentrate was decomposed by CaO–NaCl–CaCl₂. The experiment results show that the leaching ratio of RE₂O₃ and CaF₂ is up to 70.8 % and 55.8 %, and the leaching ratio of RE₂O₃ and CaF₂ is to 99.62 % and 98.56 %, respectively, when quintic contraflow leaching at the same parameters [12]. However, in this experiment, the unroasted Baotou mixed rare earth concentrate was leached by the HCl–AlCl₃ solution. Due to its high electronegativity and small ionic size, the fluoride ion is classified as a hard base, which has a strong affinity toward metal ions including Al³⁺, Fe³⁺, and La³⁺. Al³⁺ has a good affinity with fluoride ions based on the soft and hard acid base concept, which is frequently used in defluoridation [13–16]. Al³⁺ and F⁻ easily generates a stable complex ion [AlF₆]³⁻ with stability constant of 6.9 × 10¹⁹. The metals in bastnaesite and fluorite can be leached out by forming complex ions with Al³⁺. The important chemical reactions are given as follows:



The advantage of this method is that there is no HF and SO₂, and the fluorine element can be transformed to a useful product in the follow-up process [17]. The leaching residue can be decomposed by NaOH. The whole process not only reduces energy consumption and environment pollution but also makes the resources more rationally utilized.

2 Experimental

2.1 Experimental materials

The mixed rare earth concentrate was supplied by Baogang Gaoke Rare Earth Co. Ltd. The particle size of the gray mineral by floating is below 40 μm. The chemical compositions are listed in Table 1. Other reagents in the experiment are AR grade.

Table 1 Chemical compositions of mixed rare earth concentrate (wt%)

REO	CaO	Al ₂ O ₃	FeO _n	P ₂ O ₅	F
59.51	7.94	1.66	2.13	9.03	7.61

2.2 Experimental process and analysis

The leaching experiments were performed in a 500 ml three neck glass flask connecting with a condenser pipe. A mechanical stirrer and a thermostat were facilitated to keep the reaction medium at constant temperature [18]. In the leaching process, HCl solution and AlCl₃ solution was put into the reactor and then distilled water was added to a certain volume according to the orthogonal regression experiment design. After the reaction temperature was reached, a specific amount of the mixed rare earth concentrate sample was added to the HCl–AlCl₃ solution and stirred. After a certain period of time, the solution was filtered. Leaching residue was dried in an oven with constant temperature at 120 °C for 30 min.

The mixed rare earth concentrate leaching ratio (%) = (mass of the mixed rare earth concentrate – mass of leaching residue)/mass of the mixed rare earth concentrate × 100 %. The calculation of theory indicated that the maximum leaching ratio of mixed rare earth is less than 77.98 %. The reproducibility of the measurements was averaged in triplicates. Relative standard deviations were within ±2.0 %. The phase compositions were determined in a D/max 2400 diffraction instrument with the Cu Kα.

2.3 Quadratic orthogonal regression experiment design

The initial HCl acidity of mixed solution, AlCl₃ concentration of mixed solution, reaction temperature, reaction time, liquid to solid ratio, and stirring speed were selected as the studying factors. Forty-eight experiments were designed in accordance with these six factors regression in the quadratic orthogonal regression experiment including four experiments of zero level. We used the half implementing method. Table 2 is the encode table of six factors in the quadratic orthogonal regression experiment, γ = 1.896 [19–21]. The results of the mixed rare earth concentrates leaching ratio by the regression orthogonal experiment are listed in Table 3. The regression equation is obtained from the results shown in Table 3.

$$y = 54.15 + 4.5x_1 + 2.64x_2 + 14.63x_3 + 2.76x_4 + 3.64x_5 + 0.73x_6 - 1.13x_1x_2 - 0.2x_1x_3 - 0.94x_1x_4 - 1.78x_1x_5 + 0.56x_1x_6 + 1.06x_2x_3 + 0.49x_2x_4 + 0.64x_2x_5 - 0.71x_2x_6 + 0.52x_3x_4 + 1.91x_3x_5 - 1.40x_3x_6 + 1.1x_4x_5 - 0.48x_4x_6 + 0.06x_5x_6 - 2.06x_1^2 - 0.82x_2^2 - 0.42x_3^2 + 0.92x_4^2 + 0.47x_5^2 - 0.31x_6^2$$

x_i (x_1, x_2, \dots, x_6) is the code of the orthogonal regressive table factors, which take linear transformation, x_i

$$(x_1, x_2, \dots, x_6) = [a_i(a_1, a_2, \dots, a_6) - a_{0i}] / \Delta_j$$

Table 2 Encode of factors

Factors	Initial HCl acidity/(mol·L ⁻¹)	AlCl ₃ concentration/(mol·L ⁻¹)	Temperature/°C	Reaction time/min	Liquid to solid ratio/(ml·g ⁻¹)	Stirring speed/(r·min ⁻¹)
Numbers	a_1	a_2	a_3	a_4	a_5	a_6
Up asterisk arm (+ γ)	6	3.0	100	145	35	500
Up level (+1)	4	2.0	85	120	30	400
Base level (0)	3	1.5	65	90	20	300
Down level (-1)	2	1.0	45	60	10	200
Down asterisk arm (+ γ)	0	0	25	15	5	100
Change range (Δ_j)	1	0.5	20	30	10	100

Where y is the leaching ratio of mixed rare earth concentrate, a_1 is the initial HCl concentrate (mol·L⁻¹), a_2 is AlCl₃ concentration (mol·L⁻¹), a_3 is temperature (°C), a_4 is reaction time (min), a_5 is liquid to solid ratio (ml·g⁻¹), and a_6 is the stirring speed (r·min⁻¹), Δ_j is change spacing of a_i .

The F test of the regression equation is listed as follows:

$$S_{\text{total}} = 12243.22,$$

$$S_{\text{regression}} = 10973.82,$$

$$S_{\text{remain}} = S_{\text{total}} - S_{\text{regression}} = 12243.22,$$

$$F = (S_{\text{regression}}/27)/(S_{\text{remain}}/20) = 6.4, \text{ and}$$

$F = 6.4 > F_{(0.01)} = 2.81$ [20, 21]. The equation is conspicuous at 0.01 level. It is shown that the effects of the experiment on the leaching method of mixed rare earth concentrate can be described by this equation.

3 Results and discussion

3.1 Effect of the initial concentration of HCl acid

When AlCl₃ concentration of mixed solution is 1.5 mol·L⁻¹, liquid to solid ratio is 20 g·ml⁻¹, reaction time is 90 min, stirring speed is 300 r·min⁻¹ with reaction temperatures at 45, 65, and 85 °C, respectively. The mixed rare earth concentrate leaching ratio versus the concentration of HCl acid at different temperatures were calculated based on the regression equation (Fig. 1).

The leaching ratio increases obviously with increasing the reaction temperature at the specific initial concentration of HCl acid (Fig. 1). When the concentration of HCl increases from 1 to 3 mol·L⁻¹, the leaching ratio rapidly increases for all reaction temperatures in 45, 65, and 85 °C. The leaching ratio reaches maximum in 4 mol·L⁻¹ HCl concentration in each curve. The leaching ratio increases 19.8 %, while the HCl concentration increases from 1 to 4 mol·L⁻¹ at 85 °C.

3.2 Effect of AlCl₃ concentration

The leaching ratio versus AlCl₃ concentration was calculated based on the regression equation (Fig. 2). The AlCl₃ concentration increased from 0.5 to 2.5 mol·L⁻¹, while the reaction temperature is 65 °C, liquid to solid ratio is 20 g·ml⁻¹, reaction time is 90 min, and the stirring speed is 300 r·min⁻¹. Under this condition, the mixed rare earth concentrate leaching curves in 1, 2, and 3 mol·L⁻¹ are obtained (Fig. 2).

The mixed rare earth concentrate leaching ratio increases with increasing the AlCl₃ concentration from 0.5 to 2 mol·L⁻¹ and reaches the maximum value at the AlCl₃ concentration of 2 mol·L⁻¹ for the three curves of specific HCl concentration. The leaching ratio almost do not change when the AlCl₃ concentration increases from 2 to 2.5 mol·L⁻¹ for the curves of 3 and 4 mol·L⁻¹. This indicates that the AlCl₃ concentration of 1.5 mol·L⁻¹ is optimal enough for the best leaching efficiency. The leaching ratio

Table 3 The results of the regression orthogonal experiment

Nos.	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16
$y/\%$	29.3	31.8	31.3	37.0	49.5	66.3	58.5	71.8	29.7	33.4	29.7	33.4	60.1	71.1	61.4	75.7
Nos.	17	18	19	20	21	22	23	24	25	26	27	28	29	30	31	32
$y/\%$	55.0	35.0	37.0	43.8	59.7	69.5	67.0	75.5	36.1	39.7	38.1	44.0	65.7	74.4	73.2	75.1
Nos.	33	34	35	36	37	38	39	40	41	42	43	44	45	46	47	48
$y/\%$	22.5	64.0	32.0	63.4	21.7	76.6	43.1	64.8	43.1	61.6	43.0	56.1	58.5	57.7	58.1	57.6

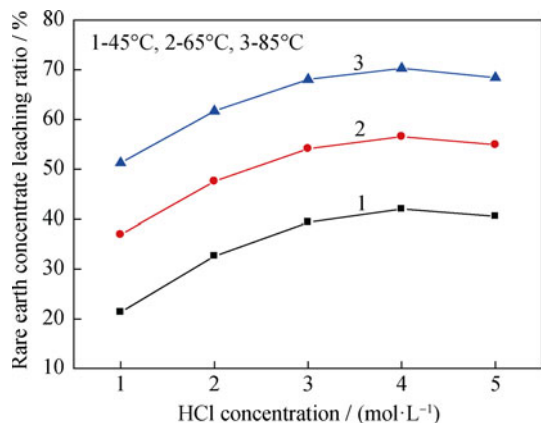


Fig. 1 Mixed rare earth concentrate leaching ratio versus HCl concentration

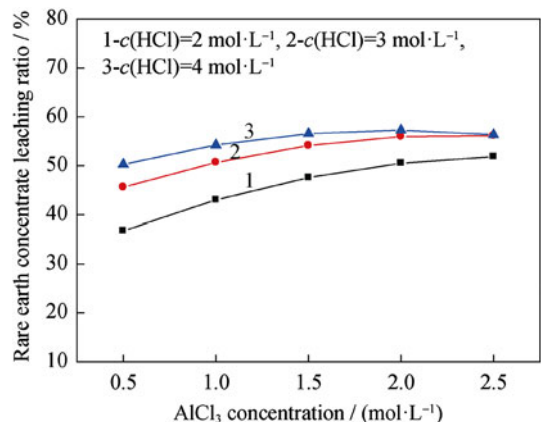


Fig. 2 Mixed rare earth concentrate leaching ratio versus AlCl₃ concentration

increases 7 % when HCl concentration is 4 mol·L⁻¹, and the AlCl₃ concentration increases from 0.5 to 2 mol·L⁻¹.

3.3 Effect of reaction temperature

The mixed rare earth concentrate leaching ratios versus the reaction temperature were obtained under the following conditions: HCl concentration is 4 mol·L⁻¹, AlCl₃ concentration is 2 mol·L⁻¹, reaction time is 90 min, and liquid to solid ratio is 20 ml·g⁻¹ with the stirring speed of 200, 300, and 400 r·min⁻¹ (Fig. 3).

The leaching ratio of rare earth concentrate rapidly increases with the temperature changing from 25 to 100 °C. However, leaching ratio effect of the stirring speed is not critical. When the stirring speed is 300 and 400 r·min⁻¹, the leaching ratio increases by 57.19 % and 49.69 %, with the reaction temperature increasing from 25 to 100 °C, respectively. Then, the reaction temperature of 85 °C is the optimal condition considering the volatility of the hydrochloric acid and energy saving.

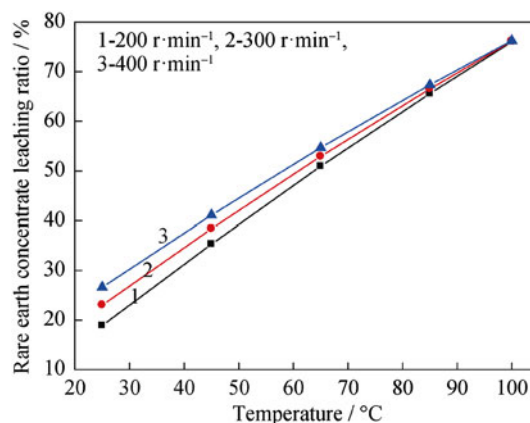


Fig. 3 Mixed rare earth concentrate leaching ratio versus reaction temperature

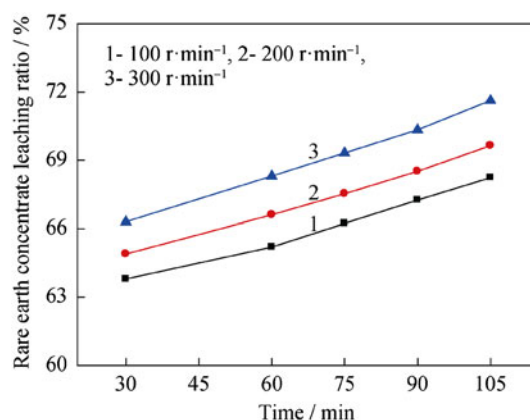


Fig. 4 Mixed rare earth concentrate leaching ratio versus reaction time

3.4 Effect of the reaction time

The effect of the reaction time on the mixed rare earth concentrate leaching ratio was obtained with stirring speed of 100, 200, and 300 r·min⁻¹, while concentration of HCl is 4 mol·L⁻¹, AlCl₃ concentration is 2 mol·L⁻¹, the reaction temperature is 85 °C, and the liquid to solid ratio is 20 ml·g⁻¹ (Fig. 4).

The leaching ratio increases with increasing the reaction time and the stirring speed. However, time and energy consumption need to be balanced. For time, 90 min is selected in this experiment with the leaching ratio 69.32 % at 300 r·min⁻¹.

3.5 Effect of the liquid to solid ratio

The liquid to solid ratio is an important factor in chemical reaction. The following conditions have been used, 4 mol·L⁻¹ HCl acidity, 2 mol·L⁻¹ AlCl₃, 85 °C as the reaction temperature, and 300 r·min⁻¹. The results for 15, 60, and 90 min have been compared (Fig. 5).

The mixed rare earth concentrate leaching ratio increases with liquid to solid ratio increase from 10 to 30 ml·g⁻¹. The maximum leaching ratio reaches to 76.73 % when reaction time is 120 min with the liquid to solid ratio is 30 ml·g⁻¹. Effect of the reaction time is not obvious when the liquid to solid ratio is low. However, at higher liquid to solid ratio, the effects are obvious, while the leaching ratio is 3.9 % higher at 120 min than at 60 min reaction time. From the analysis above, the liquid to solid ratio of 30 ml·g⁻¹ is the optimal ratio (Fig. 6).

3.6 Effect of stirring speed

The optimal conditions of five factors have been determined by the results analyzed above based on the orthogonal regression equation 4 mol·L⁻¹ HCl acid mixed with 2 mol·L⁻¹ AlCl₃ as the liquid to solid ratio is 30 ml·g⁻¹ and react at 85 °C for 90 min.

The leaching ratio slightly decreases with increasing the stirring speed under this condition. The stirring speed of 100 r·min⁻¹ is determined as the optimal condition with 77.41 % leaching ratio.

3.7 Experimental verification on the optimal conditions

The optimal conditions of six major factors were obtained via the analysis based on the orthogonal regression equation and the consideration of energy saving and HCl volatility as follows: 4 mol·L⁻¹ HCl acid mixed with 2 mol·L⁻¹ AlCl₃, the liquid to solid ratio being 30 ml·g⁻¹, and reacting at 85 °C with 100 r·min⁻¹ for 60 min. A triplet experiment set was performed to verify this optimal condition. The *F* mixed rare earth concentrate exhibits an average value of 76.5 %, only 0.91 % difference with the value from the analysis results of orthogonal regression experiment. Therefore, the results obtained from the orthogonal regression experiment is much more reliable.

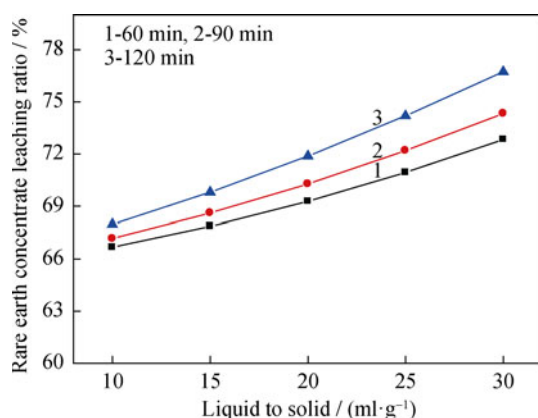


Fig. 5 Mixed rare earth concentrate leaching ratio versus liquid to solid ratio

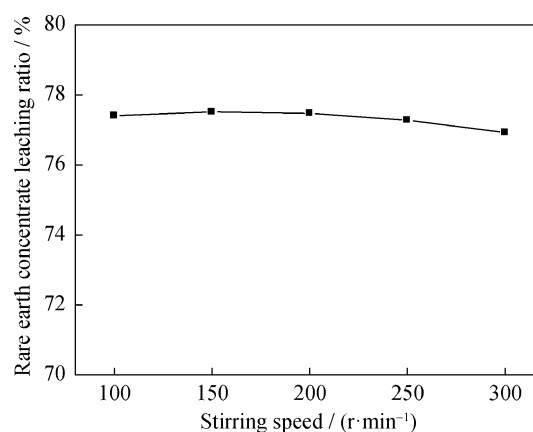


Fig. 6 Mixed rare earth concentrate leaching ratio versus stirring speed

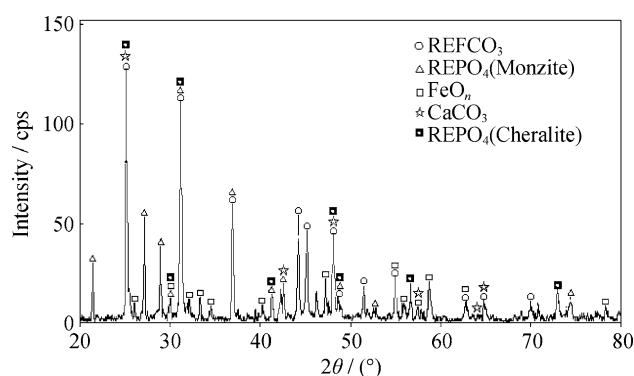


Fig. 7 XRD spectrum of mixed rare earth concentrate

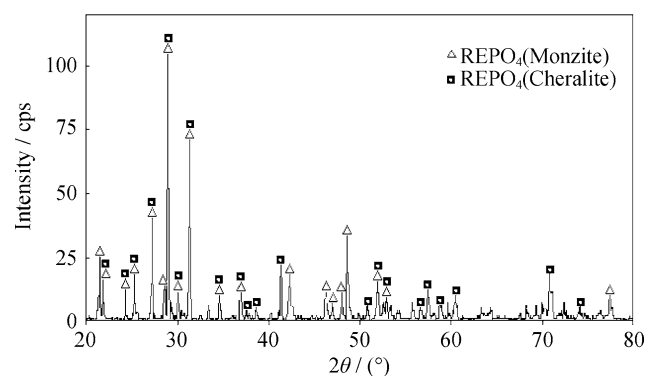


Fig. 8 XRD spectrum of leaching residue in optimal experiment condition

3.8 XRD analysis

The mixed rare earths concentrate and leaching residue from the leaching experiment at the optimal experiment condition were analyzed by X-ray diffractometer (Figs. 7, 8).

The XRD analysis shows that the mixed rare earths concentrate mainly consisted of REFCO₃, REPO₄, FeO_n,

and CaCO₃ (Fig. 7), and the leaching residue mainly consisted of REPO₄. Figure 8 shows that bastnasite disappears, and monazite still remains. It can be explained that REFCO₃, FeO_n, and CaCO₃ were almost dissolved in the leaching progress by HCl–AlCl₃ solution. Rare earth recovering from the leaching solution and complex anion of fluorine and aluminum retained in the solution that transformed into cryolite will be studied in other investigation.

4 Conclusion

The mixed rare earths concentrate was leached by HCl–AlCl₃ solution. Using the method of quadratic orthogonal regression experiment, the effect of six factors on the mixed rare earth concentrate leaching ratio was investigated, and the regression equation was obtained. The optimal condition is determined as follows: HCl concentration is 4 mol·L⁻¹, AlCl₃ concentration is 2 mol·L⁻¹, reaction temperature is 85 °C, reaction time is 90 min, and stirring speed is 100 r·min⁻¹. Using this condition for leaching experiment, the mixed rare earths concentrate leaching ratio reaches 76.5 %, which only has 0.91 % difference from the analysis results based on orthogonal regression equation. The result obtained with the orthogonal regression experiment is much more reliable.

The result of XRD analysis reveals that the major composition of the leaching residue is monazite, and cheralite, REFCO₃, FeO_n, and CaCO₃ in the mixed rare earth concentrate are dissolved in the leaching solution. The result indicates that the REPO₄ (monazite and cheralite) are not dissolved by HCl–AlCl₃ solution in this experiment condition.

Acknowledgments This work was financially supported by the National Nature Science Foundation of China (No. 51174115), National Outstanding Youth Science Foundation of China (No. 51025416), and Program for Changjiang Scholars and Innovative Research Team in University (No. IRT1065).

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