



Study on column leaching process of rare earths from ion adsorption clays by ammonium sulfate

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Abstract: This report presents the results of study on the column leaching process of rare earths from ion adsorption clay by ammonium sulfate at laboratory scale. Total rare earths content in ion adsorption clay about 350 - 550 ppm. The influence of factors such as solution concentration $(\text{NH}_4)_2\text{SO}_4$, time leaching, solid/liquid ratio, number of stage washing ... on the rare earth recovery efficiency was evaluated. The obtained results showed that the rare earth recovery efficiency was up to about 90% under optimal conditions. The obtained technological parameters will re-evaluated at pilot scale (500 kg/batch) to assess the possibility of larger scale development.

Keywords: *Rare earth, column leaching, ion adsorption clays....*

I. INTRODUCTION

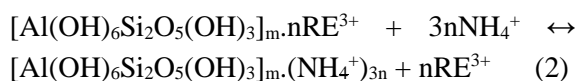
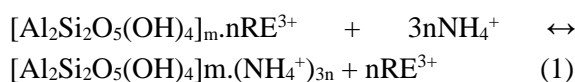
Weathered crust elution-deposited rare earth (RE) ore, also named ion-adsorbed RE ore, is a unique mineral resource due to the rich middle and heavy RE [1,2]. For the tremendous commercial value, great attention is paid to the exploitation of this ore. The main mineral compositions of the weathered crust elution-deposited RE ore are quartz, potash feldspar, plagioclase, kaolinite and white mica. In a warm and humid climate, original rocks containing RE are weathered and clay minerals are formed by biological, chemical and physical effects. During this weathering process, REs in the minerals are dissociated to be hydrated or hydroxyl-hydrated RE ions and further adsorbed on clay minerals with the migration of natural water [3, 4].

The leaching process of RE from ion-adsorbed RE ore is a mass transfer process. The cations in the leaching agent diffuse from

solution to the ore particles, and then the RE ions adsorbed on the ore particles are replaced and transferred into the solution [5, 6].

Due to the strong exchangeability with RE, minor environmental pollution and low cost, ammonium salts are generally recognized as the optimal leaching agents at present. Ammonium sulfate $(\text{NH}_4)_2\text{SO}_4$ is widely used in the actual RE recovery [7, 8].

In the ion-adsorbed RE ore, RE in ion-exchangeable state, mainly adsorbed on clay mineral, could be exchanged by electrolyte solution through ion-exchange method [9, 10]. The main clay minerals are aluminosilicate. The leaching chemical reaction with ammonium salt can be expressed as below:



Various investigations of the desorption of REE from clays via ion-exchange leaching [11-13] indicated that, regardless of the initial content, not all REE reached similar extraction levels (i.e. the percentages of desorbed/recovered REE varied widely). Coppin et al. reported that the amount of trivalent lanthanide ions adsorbed on smectite and kaolinite was inversely proportional to the ionic radii and pointed to a fractionation during selective sorption of lanthanides, with heavy elements (i.e. higher atomic number: Tb to Lu) being adsorbed stronger than the light ones (i.e. La to Gd) [14]. They related this behavior to the lanthanide contraction in the ionic radii going from light to heavy REE. Based on these observations, it was inferred that desorption must exhibit a similar trend, with HREE being more easy to extract, probably according the trend $La < Ce < Pr < Nd < Sm < Eu < Gd < Tb < Dy < Ho < Y < Er < Tm < Yb < Lu$.

In this study, the leaching process of RE by the ammonium sulfate was investigated in the fixed bed column. The influence of factors such as solution concentration $(NH_4)_2SO_4$, time leaching, solid/liquid ratio, number of stage washing... on the rare earth recovery efficiency were evaluated.

II. CONTENT

A. Material and method

The experimental RE ore sample is original RE ores collected from Huaphan Province of Lao People's Democratic Republic. The RE ore sample was classified by vibrating screen with particle sizes ranging from 0-0.5; 0.5-1.0; 1.0-2.0; 2.0-

5.0 and +5.0 mm and dried in an oven at 50°C for 8 h.

The main mineral composition of the RE ore was analyzed by X-ray diffraction (D8-Bruker Advance) and the results were listed in Table I.

The composition and partitioning of the RE in the ore and residue after leaching was analyzed by inductively coupled plasma mass spectrometry (ICP-MS 8900QQQ, Agilent Technologies Inc.).

The occurrence states of RE in RE ore was determined with the sequential fractionating extraction method [15].

All chemicals in this study were analytical grade.

The experiments were processed at ambient temperature in a PVC column with an inner diameter of 65 mm and a column length of 500, 1000 and 1500 mm, respectively. 2500 g of dried RE ore sample was packed uniformly in the PVC column and the packed ore height was measured. A sand core filter plate was fixed at the bottom of the leaching column to retain soil particles and two layers of filter paper were put on the upper of the RE ore sample to resist preferential flow. The leaching agent was added from the top of the leaching column at a constant flow rate by a peristaltic pump. Leachate was collected from the bottom of the leaching column and the concentrations of RE was analyzed by inductively coupled plasma mass spectrometry. Leachate was collected from the bottom of the glass column at the same time interval, and the volume of leachate was measured.

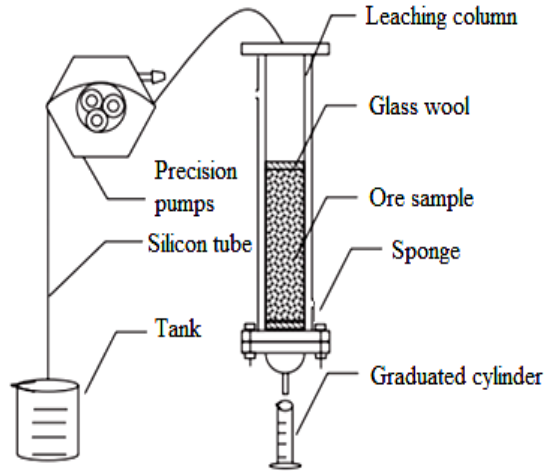


Fig. 1. The schematic plot of the column leaching test

The rare earth leaching efficiency (H) was calculated according to equation:

$$H = \frac{\sum REEs_{Lechate}}{\sum REEs_{Lechate} + \sum REEs_{Residue}}$$

Where:

$\sum REEs_{Lechate}$: the total amount of REEs in leached (without Ce).

$\sum REEs_{Residue}$: the total amount of REEs in residues (without Ce).

B. Result

Table I. Mineral composition and content

Particle size (mm)	Ratio (%)	Mineral composition and content (~%)						REEs content (ppm)
		Mica	Kaolinite	Clorite	Quartz	Feldspar	Others	
-0.5	12.94	23 - 25	15 - 17	2 - 4	32 - 34	20 - 22	Hematite	535.89
+0.5-1.0	21.40	17 - 19	13 - 15	2 - 4	44 - 46	16 - 18	Gotit	434.06
+1.0-2.0	16.25	18 - 20	13 - 15	2 - 4	37 - 39	22 - 24	Gotit	394.29
+2.0-5.0	15.56	11 - 13	13 - 15	2 - 4	46 - 48	20 - 22	-	339.60
+5.0	33.85	10 - 12	19 - 21	2 - 4	34 - 36	26 - 28	Gotit	430.67

Table II. Partitioning of RE (mass fraction, %)

Elements	Content of RE (ppm)					Partitioning of RE (%)				
	Particle size (mm)									
	-0.5	+0.5-1.0	+1.0-2.0	+2.0-5.0	+5.0	-0.5	+0.5-1.0	+1.0-2.0	+2.0-5.0	+5.0

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Sc	8.45	6.21	5.00	4.36	6.44	1.58	1.43	1.27	1.28	1.50
Y	143.35	100.36	88.28	72.61	103.13	26.75	23.12	22.39	21.38	23.95
La	77.86	76.60	60.29	47.79	61.01	14.53	17.65	15.29	14.07	14.17
Ce	87.20	61.77	81.33	86.27	92.82	16.27	14.23	20.63	25.40	21.55
Pr	21.19	20.63	16.90	13.06	16.66	3.95	4.75	4.29	3.85	3.87
Nd	75.84	73.48	61.45	47.30	60.57	14.15	16.93	15.58	13.93	14.06
Sm	18.37	16.87	13.85	11.45	14.88	3.43	3.89	3.51	3.37	3.46
Eu	2.21	2.41	2.53	1.46	1.62	0.41	0.56	0.64	0.43	0.38
Gd	23.03	19.80	17.29	15.39	18.84	4.30	4.56	4.39	4.53	4.37
Tb	4.06	3.39	2.73	2.34	3.03	0.76	0.78	0.69	0.69	0.70
Dy	25.71	19.68	16.56	13.82	18.78	4.80	4.53	4.20	4.07	4.36
Ho	5.45	4.12	3.39	2.86	3.89	1.02	0.95	0.86	0.84	0.90
Er	18.61	12.31	10.59	8.88	12.26	3.47	2.84	2.69	2.61	2.85
Tm	2.78	1.97	1.64	1.43	1.90	0.52	0.45	0.42	0.42	0.44
Yb	19.01	12.55	10.90	9.24	12.98	3.55	2.89	2.76	2.72	3.01
Lu	2.77	1.91	1.56	1.34	1.86	0.52	0.44	0.40	0.39	0.43
REEs	535.89	434.06	394.29	339.60	430.67	100.00	100.00	100.00	100.00	100.00

Table III. Occurrence states of RE in rare earth ore

Phase state	Phase distribution rate (%)
Ion-exchangeable	85.00
Colloid sediment	4.50
Mineral	10.50
Full phase	100.00

Table IV. Partitioning of RE in ion-exchangeable state (mass fraction, %)

Y	La	Ce	Pr	Nd
29.04	18.70	2.48	5.11	18.44
Sm	Eu	Gd	Tb	Dy
4.36	0.60	5.47	0.89	5.42
Ho	Er	Tm	Yb	Lu
1.13	3.57	0.56	3.69	0.54

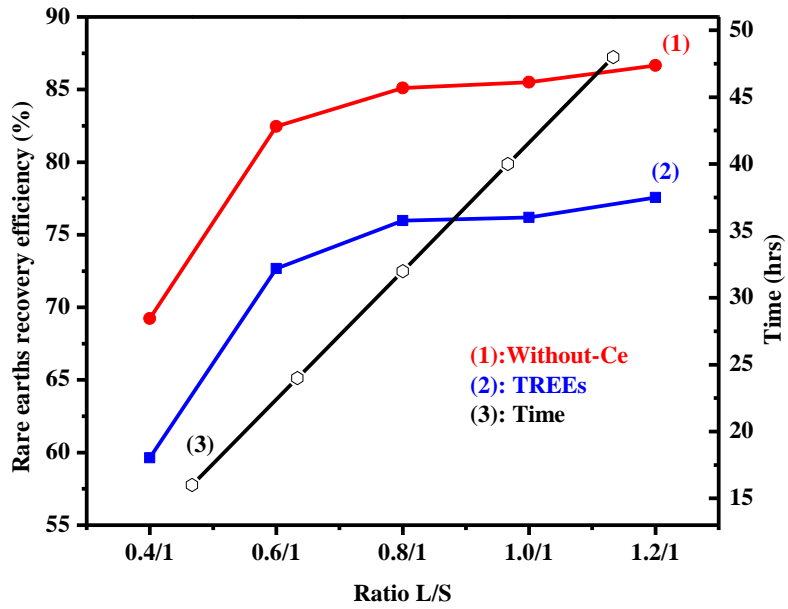


Fig. 2. Column leaching results as a function of L/S ratio and time
 ((NH₄)₂SO₄ 0.5 M, height column 500 mm)

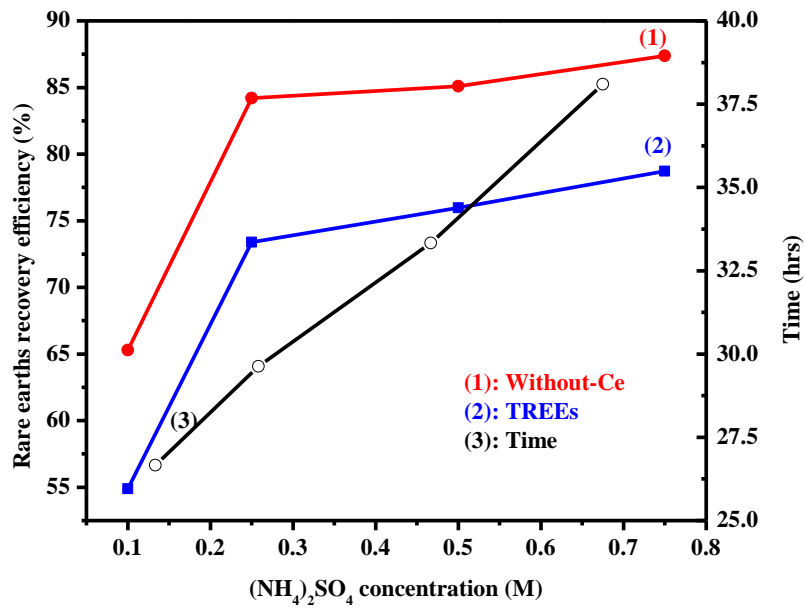


Fig. 3. Column leaching results as a function of concentration and time
 (L/S ratio: 0.8/1, height column 500 mm)

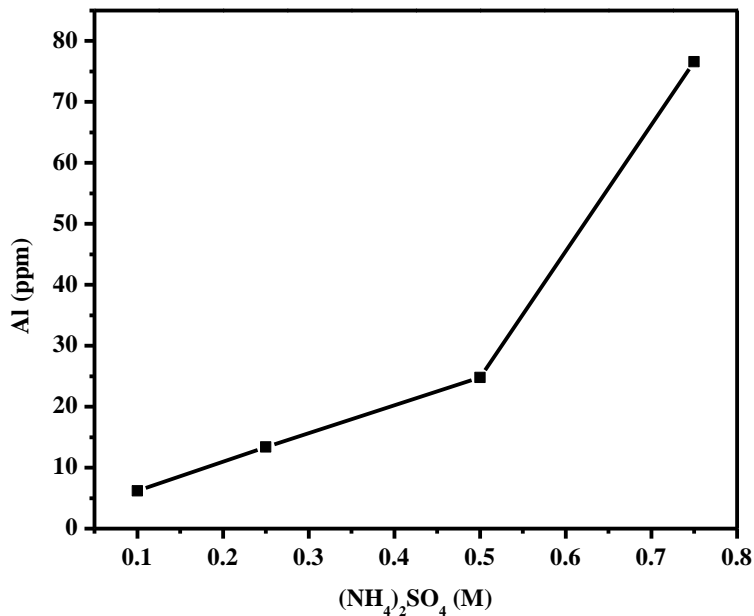


Fig. 4. Al content in the leachate (L/S ratio: 0.8/1, height column 500 mm)

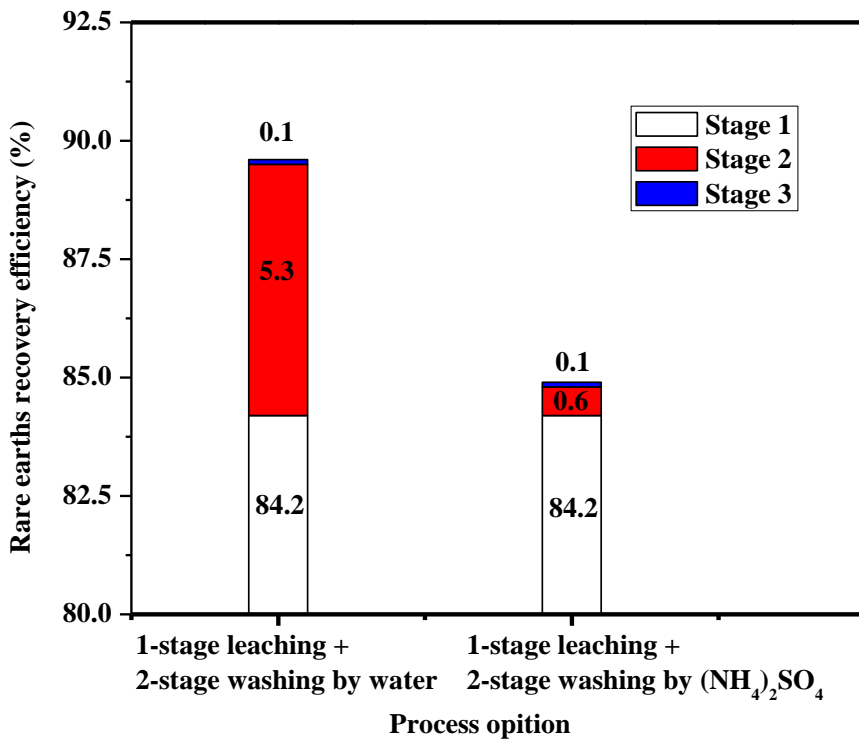


Fig. 5. Impact of multi-stage washing on overall TREE extraction (height column 500 mm, L/S = 0.8/1, (NH₄)₂SO₄ 0.25M)

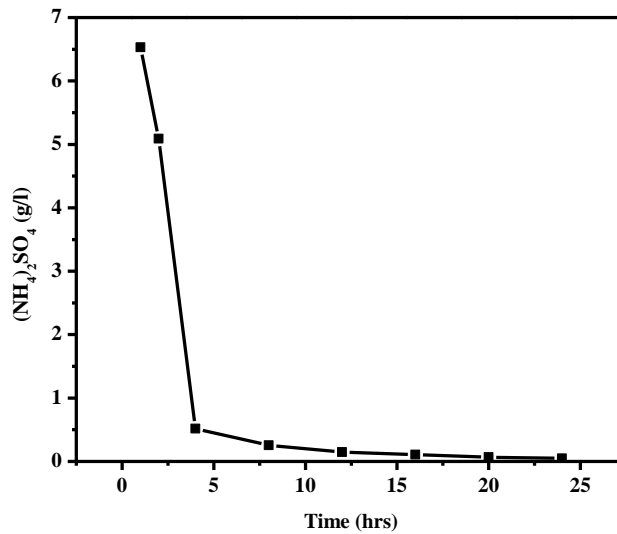


Fig. 6. Ammonium concentration in column wash water according to time (water/residues ratio: 0.8/1, height column 500 mm)

C. Discussion

The main mineral compositions of the ion-adsorbed RE ore were quartz, feldspar, kaolinite and mica (Table I), mainly clay-kaolin group minerals with about 70 to 75% (major rare earth adsorbents). In addition, there were a litter chlorite, hematite and goethite, from 2 to 5%.

The rare earth content in the particle size was corresponds to the mineral composition of the clay-kaolin group minerals. Partitioning of RE indicates that the middle and heavy REs with tremendous commercial value accounted for a large proportion of rare earth components (Table II). Total rare earth content ranges from 340 to 550 ppm and was a Dy-rich rare earth.

The results obtained in Table III showed that RE exists as ion-exchangeable state, colloid sediment state and mineral state. About 85% of RE in this ore exists as ion-exchangeable state. Cerium content in ion-exchangeable state has very low composition, about ~3% in total RE ion-exchangeable state

(Table IV). Thus, most of cerium exists in the form of CeO₂ mineral.

The results in Fig.2 showed that the rare earth recovery efficiency increased as the L/S ratio increased. The rare earth recovery efficiency was about 85% (without-Ce) and 75% (with TREEs) with liquid/solid ratio of 0.8/1. When the liquid/solid ratio increased more, the rare earth recovery efficiency increased insignificantly and the leaching time increased considerably. Therefore, the liquid/solid ratio of 0.8/1 was a suitable ratio for the separation process to recover rare earths from ion-adsorption RE ore.

Similarly, the results in Fig.3 showed that the rare earth recovery efficiency increased as the (NH₄)₂SO₄ concentration increased. The rare earth recovery efficiency was about 85% (without-Ce) and 75% (with TREEs) with (NH₄)₂SO₄ concentration of 0.25M. The rare earth recovery efficiency increased insignificantly and the leaching time and the amount of chemicals consumed increased greatly as (NH₄)₂SO₄ concentration

increased. Moreover, as the solution concentration increased, the content of impurities, especially Al, also increased (Fig.4). In the leaching process of RE, impurity ions, especially Al, accounting for 35%–75% of total amount of impurities in the leachate, were also exchanged into the leachate. The impurities in leachate would decrease the quality of RE product, increase the consumption of precipitator and even destroy the crystal forming of carbonate RE precipitation. In addition, in order to completely elute all REE in the column and to ensure that the solid residue is free of lixiviant prior to disposal, column flushing with fresh water becomes necessary. Then, the higher the solution concentration, the longer the washing time and more chemicals consumed. Therefore, to obtain rare earth products with high purity, a solution concentration of about 0.25M was suitable.

It can be seen that multi-stage washing of clays with fresh solution provided no benefit to additional extraction, increasing the overall TREE extraction by only ~0.7%; therefore, further use of fresh lixiviant is not recommended as it does not improve. Proper washing of leached material, however, plays an important role in maximizing the recovery of REE and the unspent lixiviant. Fig.5 also showed that the distribution of TREE recovery between the initial stage leachate, the first washing step and a second washing step for a single-stage leaching experiment. It can be observed that washing accounted for ~5.4% of the TREE recovered from leachate retained in the residue. Thus, the washing process helped recover rare earths more thoroughly and the overall efficiency of the leaching and washing process reaches about 90%.

In addition, in order to completely elute all REE in the column and to ensure that the

solid residue is free of lixiviant prior to disposal, column flushing with fresh water becomes necessary and the result was showed in Fig. 6. It can be observed that almost of NH_4^+ was removed after 20 hrs of operation in the first 0.6 ml/g wash water collected. This wash water would be reused for the next leaching process or treated as a wastewater at the end of the mining process.

III. CONCLUSIONS

Study on the column leaching process of rare earths from ion adsorption clay by ammonium sulphate at laboratory scale was done. Total rare earths content in ion adsorption clay about 350 - 550 ppm and was a Dy-rich rare earth. The total REE extraction was a function of L/S ratio, $(\text{NH}_4)_2\text{SO}_4$ concentration and time. The obtained results indicated that the 0.25M $(\text{NH}_4)_2\text{SO}_4$ solution concentration was suitable. It can be observed that ~90% of the total extracted REE was collected in the first ~0.8 ml/g of leachate after 24 hrs of leaching and in the first 0.6 ml/g wash water after 20 hrs washing. The HREE were extracted more easily to LREE. Almost of NH_4^+ was removed after washing and the wash water would be reused for the next leaching process or treated as a wastewater at the end of the mining process.

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