

# RECOVERING RE FROM LEACHING LIQUOR OF RARE EARTH ORE BY EXTRACTION<sup>①</sup>

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**ABSTRACT** The extractive process for the production of rare earth chlorides from leaching liquor of some rare earth ores has been studied with organic phosphoric acid as extractive reagent. The feasibility of extractive technology has been confirmed in unitized experiment with a  $\phi$  20 cm centrifugal extractor. When leaching liquor was adjusted to pH=5 with ammonia-sodium sulfide, the heavy metal ions and 90% aluminum ion were removed, and purified liquor was obtained. Rare earth recovery rate was more 90% through two stages countercurrent extraction of purified liquor and three stages countercurrent stripping of organic phase loading rare earth with 6 mol/L HCl. Rare earth concentration of stripped liquor was above REO 150 g/L, and solid  $\text{RECl}_3$  that equivalently contained 45% to 46% REO was obtained through vaporization.

**Key words** rare earth ore leaching solvent extraction

## 1 INTRODUCTION

The rare earth concentration of leaching liquor of some rare earth ores is in the ranges of 1~5 g/L REO, the main recovery technology of rare earth from leaching liquor is producing rare earth oxalate by oxalic acid precipitation and then calcinating to form rare earth oxide product for sale<sup>[1]</sup>.

The mixed rare earth oxide bought by the factory of separating rare earth must be dissolved with hydrochloric acid to become rare earth chloride before it is separated in production line. If we can use a new technology to obtain directly chloride product from the diluting leaching solution of rare earth sulfate, it could not only not use oxalic acid, but also changes the structure of ore product and omits the steps of calcination and the solution of rare earth oxide in the factory of separating rare earth.

The technology of concentration and recovery of rare earth, which used kerosene solution of some organic phosphoric-acid as extrac-

tive reagent and hydrochloric acid as stripping reagent, has been studied in this paper. The whole technology can be divided into the following steps: removing impurities from leaching liquor and extracting rare earth, stripping rare earth with hydrochloric acid, vaporizing the of stripped liquor and crystallizing the rare earth chloride, thus a rare earth chloride containing crystal water was obtained, its total recovery rate of rare earth was 90.68%.

## 2 REMOVING IMPURITIES

The leaching liquor of weathering rare earth ore contains besides rare earth a lot of aluminum ions and other metal ions, for instance  $\text{Ca}^{2+}$  and  $\text{Pb}^{2+}$ . If these impurity ions are not removed, it results in emulsification of extraction system and influences product purity.

The pH of precipitation of  $\text{RE}(\text{OH})_3$  and  $\text{Al}(\text{OH})_3$  is different. When rare earth concentration of leaching liquor is 5 g/L REO, adjusting the pH of leaching liquor to 5,  $\text{Al}^{3+}$

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will be easily to form  $\text{Al}(\text{OH})_3$  and then precipitated, but rare earth does not precipitated, therefore  $\text{Al}^{3+}$  will be removed by adjusting pH of solution. Ammonia liquor and ammonium bicarbonate can be chosen as reagent of adjusting pH value, but ammonium bicarbonate contains carbonate ion that can react with rare earth to form carbonate precipitation and lose rare earth, so ammonia liquor is more suitable. The heavy metal ions of leaching liquor can be removed by using sodium sulfide to form precipitation of sulfide.

When 1 + 1 ammonia liquor and solid sodium sulfide are applied and the quantity of application is 9 ml/L and 0.5 g/L respectively, 90% aluminum ion and almost whole heavy metal ions can be removed. The rare earth loss was less than 5% and the rare earth solution for extraction was obtained.

### 3 THE TECHNOLOGY OF EXTRACTION

#### 3.1 Selection of Extractive Reagent

The extractive reagent for rare earth separation is usually organic acid and organic phosphoric acid, such as  $\text{P}_{204}$  and  $\text{P}_{507}$ . An organic phosphoric acid (HP) as extractive reagent were selected in this study. The extractive reaction is one kind of cation exchange and the extractive property is very good. Not

only the capacity of extraction and speed of extraction are big and fast respectively, but also the solubility in acidic medium is very small. So this extractive reagent in this system is fairly suitable.

#### 3.2 The Relation Between Extraction Distribution Ratio and the Acidity of Aqueous Phase

Rare earth solution which contains 1.75 g/L REO was extracted with kerosene solution of extractive reagent (HP) having different saponification value, experimental results are shown in Table 1. With saponification value increasing, the pH of equilibrium of aqueous phase is increased and the distribution ratio of extraction is fast raised.

#### 3.3 Extractive Phase Ratio

The rare earth concentration of leaching liquor of weathering type rare earth ore was 1 ~ 5 g/L REO. In order to decrease the vaporization quantity of enrichment, rare earth concentration of back extraction liquor is required above 150 g/L REO. Thus it must be concentrated by 50 ~ 10 times through extraction and stripping. Rare earth concentration of load organic phase should be above 12 g/L REO, extractive ratio (O/A) should be selected in the range from 1/4 to 1/12.

**Table 1 Distribution ratio of extraction in kerosene-HP solution having different saponification value \***

Saponification value/%	Aqueous phase pH		REO Equilibrium concentration/g·L <sup>-1</sup>		distribution ratio
	before equi.	after equi.	organic phase	aqueous phase	
0	5.02	1.77	8.10	0.49	16.32
5	5.02	1.80	8.35	0.48	17.89
10	5.02	1.93	8.62	0.45	31.22
15	5.02	1.97	9.90	0.37	36.44
20	5.02	2.01	10.81	0.32	42.96
25	5.02	2.07	10.48	0.24	53.68
30	5.02	2.16	10.92	0.21	75.33
35	5.02	2.33	11.43	0.20	140.73
40	5.02	2.47	11.66	0.18	221.89

\* extractive time 3 min, phase ratio O/A = 1/8, concentration 40% HP, one stage extraction

The experimental results of extractive phase ratio are listed in Table 2. Larger phase ratio is advantageous to raise extraction rate of rare earth, but are disadvantageous to obtain high concentration of rare earth in load organic phase.

**Table 2 Test results of extractive phase ratio(O/A) \***

Phase ratio (O/A)	Con. of organic phase C (REO) /g·L <sup>-1</sup>	Con. Extractive rate /%	Con. of raffinate C (REO) /g·L <sup>-1</sup>	t /min
1/6	9.74	92.8	0.12	5.57
1/8	12.34	88.1	0.23	7.05
1/10	14.30	81.8	0.31	8.20
1/12	15.61	74.3	0.44	8.92

\* extraction of one stage, saponification value 30%, 40% HP solution of kerosene, rare earth concentration 1.75 g/L REO

### 3.4 Extraction Stages

According to the data of extraction equilibrium, countercurrent extraction was applied. The recoveries of rare earth with one, two and three stages were 86.5%, 97.2% and 98.3% respectively. The experimental results of extraction with two-stages is close to that with three stages, so countercurrent extraction with two stages was chosen.

### 3.5 Platform-Frame Experiment

The centrifugal extractor employed in the experiment was a new extractive equipment exploited by the Institute of Nuclear Energy Technology, Tsinghua University, and particularly suited for extraction and concentration of low concentration leaching liquor of rare earth. The platform-frame experiments were conducted in a  $\phi$  20 mm centrifugal extractor through two stages of countercurrent extraction with 40% HP kerosene solution. The experimental results of two kinds of rare earth leaching liquor are listed in Table 3.

Table 3 shows higher recovery rate of rare earth was obtained from platform-frame experiment. For high leaching concentration

**Table 3 The results of platform-frame experiment**

Leaching liquor C (REO) /g·L <sup>-1</sup>	Phase ratio (O/A)	Raffinate C (REO) /g·L <sup>-1</sup>	pH of raffinate	Organic phase C (REO) /g·L <sup>-1</sup>	Recovery rate /%
1.75	1/8	0.11	2.23	13.14	94.29
3.51	1/5	0.25	2.38	16.22	92.45

of rare earth, more than 95% recovery rate should be considered in extraction. It will be realized by selecting the phase ratio of extraction under the condition of the rare earth concentration no more than 20 g/L REO in organic phase.

### 3.6 Reuse of Raffinate

The raffinate with pH about 2 and contains 0.1 ~ 0.3 g/L REO by adding some reagent can be reused for ore leaching, having a higher recovery rate of rare earth than that of using fresh leaching liquor.

## 4 THE STRIPPING TECHNOLOGY OF LOAD ORGANIC PHASE

### 4.1 Acidity of Stripping Solution and Stripping Stages

Not only high stripping rate but also further concentration is expected in stripping operation, at the same time, the residual acid should be considered for the convenience of successive vaporization. The stripping results at different acidity indicated that stripping rate of single stage stripping was too low and the residual acid concentration was too high. So to raise the stripping rate of rare earth and the utilization rate of stripping acid, the multiple stages of countercurrent must be used.

The relation between stripping stages and stripping rate is shown in Table 4. It can be seen from Table 4 that three stages can completely strip the rare earth in organic phase by using 6 mol/L HCl stripping solution. Although residual acid was a little high, it can be recovered in vaporization step. So stripping with three stages was chosen.

**Table 4 Stripping stages experiments \***

Stages	Stripping rate /%	Stripping liquor C (REO) /g·L <sup>-1</sup>	Residual acid /mol·L <sup>-1</sup>	Concentration mutiple
1	83.11	134.80	3.64	8.31
2	94.93	153.97	3.23	9.49
3	100.00	163.81	3.08	10.00

\* O/A=10/1, Stripping liquor HCl 6 mol/L, originally organic phase REO 16.22 g/L

#### 4.2 Platform-frame experiment

Platform-frame experiment was carried out at a  $d$  20cm centrifugal extractor. The organic phase load rare earth was stripped by three stages, the results are listed in Table 5.

**Table 5 Platform-frame experiment \***

Phase ratio (O/A)	Import organic phase **	Export organic phase **	Stripping liquor * *	Stripping rate /%	Residual acid /mol·L <sup>-1</sup>
10	16.22	0.42	158.09	97.47	3.18
15	13.04	0.47	190.69	96.75	2.66

\* Stripping acid 6 mol/L HCl, \* \* rare earth concentration C (REO)/g·L<sup>-1</sup>

The stripping rates of rare earth in platform-frame experiment were more than 95%, and the rare earth concentration in stripping liquor was more than 150g/L REO. It accords with the requirement of design.

#### 4.3 Treatment of Stripping Liquor of Rare Earth

The mother liquor of rare earth from stripping contained above 150 g/L REO and about 2 to 3 mol/L acid.

Under normal pressure, both the sealed ground-mouth glass vaporator was used for the vaporization of stripping liquor and the collecting liquor flask was used for the collection of vaporated liquor. The results indicated that recovery rate of HCl in stripping liquor was about 97%, and the HCl concentration of collected liquor was about 2~3 mol/L which can be reused as stripping liquor by adding concentration HCl into that. The rare earth chloride was obtained by vaporization of residual liquor, and the rare earth content was e-

quivalently 45%~46% REO.

### 5 THE UNITIZED OPERATION EXPERIMENT OF ALL PROCESS

The pH value of leaching liquor of rare earth was first regulated to 4.6 with 1+1 ammonia liquor, subsequently to 5.1 with solid Na<sub>2</sub>S; and then the liquor was filtrated to remove the residual dregs. The dregs was washed with water and the washing liquor and the filtrating liquor were mixed to obtain the liquor used for extraction.

With 40% HP kerosene solution of 30% saponification value with ammonia and under phase ratio (O/A) 1/5 were used in two stages of countercurrent extraction. The rare earth stripping liquor was obtained by three stages of countercurrent stripping of load organic phase with 6 mol/L HCl as stripping solution and under phase ratio (O/A) 12/1. By vaporizing stripping liquor, rare earth chloride and diluted HCl solution were obtained. The results of unitized operation experiment are shown in Table 6.

The total recovery rate of rare earth in-unitized operation experiment was 90.68%. The rare earth in raffinate can be recovered in next leaching ore process. So the loss of rare earth was little. The unitized operation experiment indicated actually that the process is feasible.

### 6 CONCLUSION

When organic phosphoric acid is selected as extractive reagent, it was proved that the extractive technology for the leaching liquor of weathering type rare earth ore is feasible through mutiple stages extraction of hand-shaking, platform-frame and unitized operation experiment.

(1) Regulating pH value to about 5 with ammonia liquor, the heavy metal ions and about 90% aluminium ion were removed. The material liquor of rare earth suiting for extractive technology was obtained. The loss of rare

**Table 6 The results of unitized operation experiment**

Step		Liquor amomut/L	con. of rare earth $C(\text{REO})/\text{g}\cdot\text{L}^{-1}$	rare earth amount/g	Recovery/%
Removing impurity	leaching liquor	40.6	3.47	138.80	100.0
	impurity liquor	40.6	3.31	134.29	96.75
	dreg of impurity	89.4/g	3.51/%	3.14/g	2.26
Extraction	load organic phase	8.1	15.94	129.11	96.15
	raffinate	41.3	0.15	6.20	4.62
Stripping	stripping liquor	0.68	185.06	125.84	97.48
	organic phase after stripping	0.2	0.42	3.44	2.66
Vaporization	HCl of		$C(\text{HCl})/\text{mol}\cdot\text{L}^{-1}$		(HCl)
	vaporated liquor	0.61	2.77		97.28
	solid of rare earth chloride	273.62/g	46.17/%		100.0
Total recovery rate of rare earth/%			$0.9675 \times 0.9615 \times 0.9748 \times 100 = 90.68$		
Concentration times of rare earth			55.91		

earth in the operation was under 5%.

(2) The organophorous acid used in the investigation has good extraction properties. The extracting recovery rate of rare earth was above 95% under the condition of phase ratio (O/A) 1/5 to 1/10 and two stages of counter-current extraction.

(3) The stripping rate of rare earth of load organic phase was above 97% with 6mol/L HCl as stripping solution, phase ratio from 10/1 to 15/1 and through three stages of countercurrent stripping. The stripping liquor of rare earth with above 150g/L REO can be obtained.

(4) The solid rare earth chloride equivalently containing REO from 45% to 46% can be obtained by vaporizing and concentrating the stripping liquor and this accords with the

demand of the factory of separating rare earth.

(5) The raffinate pH was 2 to 3 and rare earth concentration was about 0.28g/L REO. It can be reused in leaching ore by adding some reagent.

(6) Extractive technology can change the structure of ore products. The rare earth chloride ( $\text{RECl}_3 \cdot 6\text{H}_2\text{O}$ ) is more favourable to separation factory than mixed rare earth oxide produced by the precipitation technology of oxalic acid.

#### REFERENC

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