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Extraction of scandium from ion-adsorptive rare earth deposit by naphthenic acid

Chunsheng Liao, Jiangtao Jia, Yi Zhang, Gang Xu, Chunhua Yan*, Biaoguo Li, Guangxian Xu

State Key Laboratory of Rare Earth Materials Chemistry and Applications, PKU-HKU Joint Lab in Rare Earth Materials and Bioinorganic Chemistry, Peking University, Beijing 100871, China

Abstract

An extraction method for producing high purity Sc(III) from ion-adsorptive rare earth deposit (IARED) is presented. Naphthenic acid diluted with *iso*-octanol and sulfated kerosene is selected as the extractant, chloride acid as the scrubbing and stripping solution. By two extraction processes in naphthenic acid system, scandium is concentrated from 0.02–0.04% to 15–20% (wt.), and further purified to 99.99–99.999% grade. The stoichiometry of the extraction of Sc(III) with naphthenic acid was also determined. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Scandium; Naphthenic acid; Cross-current extraction; IARED

1. Introduction

Scandium, an important element applied extensively in electronics, optics and other fields, is greatly dispersive on earth. Lacking minerals with considerable scandium content, it is mainly obtained as a by-product in Sn, Ti or W refinery, which makes it difficult to be prepared [1–3]. Due to the importance of scandium, its purification has been widely studied. Chromatography, ion-exchange, solvent extraction separating Sc from rare earth (RE) have been studied by scientists in Japan, Russia, Europe and India [4–13].

Solvent extraction and emulsified liquid membrane are focused on scandium separation in China. Extraction of Sc with crown ether, β-diketone, phosphorates and carboxylic acid has been reviewed [14–23]. Ion-adsorptive rare earth deposit (IARED) is a valuable RE resource in China with Sc content of 0.02%. Extraction of Scandium from IARED by naphthenic acid has not been reported.

As the RE element with smallest radius, scandium can be easily separated from other RE elements. Based on the study of the distribution of scandium in every separation steps from the treatment of the IARED to the preparation of $RECl_3$ solution, an extraction method for producing high purity Sc(III) from the IARED is presented in this paper.

2. Experimental

2.1. Reagents

Sc_2O_3 (>99%): Institute of Metallurgical Chemistry in Hunan Province
REO (REO%>99.5): Yangjiang Rare Earth Plant
Naphthenic acid (HA): Shanghai Organic Factory
Iso-octanol (ROH): Shanxi Changzhi Organic Factory
Sulfated kerosene (RH): home-made
Extract I, II, III: composed of HA:ROH:RH(20:10:70,10:5:85,22:20:58) respectively.
HCl and other reagents are Analytical Reagents.

2.2. Extraction equilibrium experiments

A 10.00 ml volume of extractant was added into 25 ml cuvette, saponified by $NH_3 \cdot H_2O$, then added 1.00 ml $ScCl_3$ (0.1003 mol l^{-1}), adjusting O/A=1, then shaking for 20 min and settling in 25±1°C for 30 min.

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*Corresponding author. Tel.: +86-10-627-541-79; fax: +86-10-627-541-79.

E-mail address: chyan@chem.pku.edu.cn (C. Yan).

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2.3. Analytical method and instruments

2.3.1. Concentration of HA in extract

Diluted with alcohol, titrated with NaOH, phenolphthalein as indicator.

2.3.2. Calibration of $ScCl_3$

Diluted with HCOOH–HCOONa buffer (pH = 3.7), Xylenol orange as indicator, titrated with standard EDTA.

2.3.3. Calibration of $RECl_3$ (without Sc)

Hexamethylenetetramine buffer (pH = 5~6), Xylenol orange as indicator, titrated with standard EDTA.

2.3.4. Total RE concentration measurement

Added HCOOH–HCOONa buffers, xylenol orange as indicator, titrated with standard EDTA, then added hexamethylenetetramine buffers, titrated with standard EDTA to obtain the total concentration of RE and Sc.

2.3.5. Measurement of Sc and RE in mixture

Analyzed by ICP, various Sc content RE are used as stock.

2.3.6. Acidity

Measured by PHS-3 acidity meter.

2.3.7. Measurement of RE in organic

Stripped with 1 mol l^{-1} HCl and analyzed.

3. Results and discussion

3.1. Principal

The reaction of Sc^{3+} and naphthenic acid (HA) can be expressed by (1).

$$\mathrm{Sc}^{3+} + (n+m)\mathrm{HA} = \mathrm{ScA}_n(\mathrm{HA})_m + n\mathrm{H}^+ \tag{1}$$

The extraction equilibrium constant can be formulated by (2).

$$K_{\mathrm{ex}} = \frac{[\mathrm{ScA}_n(\mathrm{HA})_m][\mathrm{H}^+]^n}{[\mathrm{Sc}^{3+}][\mathrm{HA}]^{n+m}} = D[\mathrm{H}^+]^n/[\mathrm{HA}]^{n+m} \tag{2}$$

Where [R] stands for the concentration of component R. The distribution ratio of Sc in HA and aqueous solution (D) is $D = [\mathrm{ScA}_n(\mathrm{HA})_m]/[\mathrm{Sc}^{3+}]$. The extract can be determined by measuring n and m through experiment according to (3).

$$\log D = \log K_{\mathrm{ex}} + n\mathrm{pH} + (n+m)\log[\mathrm{HA}] \tag{3}$$

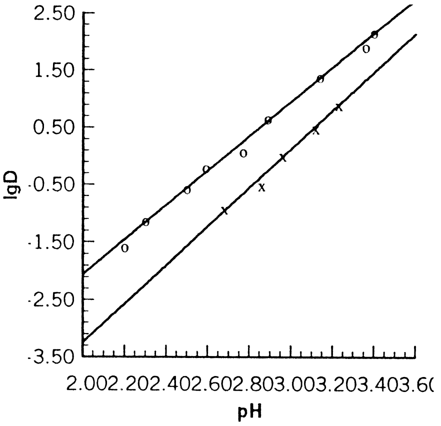

Fig. 1. log$D$~pH. ‘o’ $[\mathrm{Sc}^{3+}] = 0.01003$ mol l^{-1}; $[\mathrm{HA}] = 0.525$ mol l^{-1}. ‘x’ $[\mathrm{Sc}^{3+}] = 1.075 \times 10^{-3}$ mol l^{-1}; $[\mathrm{HA}] = 0.262$ mol l^{-1}.

3.2. Relationships between pH, [HA] and D

Keeping [HA] constant (when $[\mathrm{HA}] >> [\mathrm{Sc}^{3+}]$, [HA] can be regarded as a constant), and measuring D in various pH, we can plot log D vs. pH in Fig. 1. This shows log D–pH is linear and D decreases as the decreasing of pH in aqueous solution. The slope n of log$D$–pH can be got by least square method. When phase ratio O/A = 1, extraction percentage is the function of D as (4).

$$E = D/(1+D) \tag{4}$$

So as $D = 1$ (log$D = 0$), then $E = 50\%$, the pH is defined as half pH ($\mathrm{pH}_{1/2}$). Changing [HA] obtained another log$D$–pH line, which was also plotted in Fig. 1. The data are listed in Table 1.

Eq. (5) can be derived from Eq. (3).

$$(n+m)\log\{[HA]_2/[HA]_1\} = n\{(pH_{1/2})_1 - (pH_{1/2})_2\} \tag{5}$$

Substituting the data in Table 1 into Eq. (5), we found that the value of m was −0.1, which can be regarded as 0. Therefore, the extract can be expressed as ScA_3, K_{ex} can also be calculated by Eq. (3). That is $\mathrm{p}K_{\mathrm{ex}} = 7.20$.

3.3. Separation factors between Sc and RE

In order to measure the separation factors between Sc and RE, a mixture of Sc and RE with known composition is prepared (Table 2).

The RE composition of two phases and pH of aqueous solution are measured after extraction equilibrium, and D is calculated. log D vs. pH + log[HA] are plotted in Fig. 2

Table 1
Slope n and $\mathrm{pH}_{1/2}$ in different [HA]

[HA] (mol l^{-1})	$[\mathrm{Sc}^{3+}]$ (mol l^{-1})	n	$\mathrm{pH}_{1/2}$
0.525	1.003×10^{-2}	3.01	2.68
0.262	1.075×10^{-3}	3.37	2.97

Table 2
Composition of Sc and RE

Element	La	Nd	Sm	Eu	Gd	Yb	Y	Sc
Concentration (mol l^{-1})	0.283	0.158	0.0503	0.00528	0.00713	0.00261	0.0478	0.00401
mol %	50.68	28.35	9.001	0.945	1.277	0.467	8.560	0.718

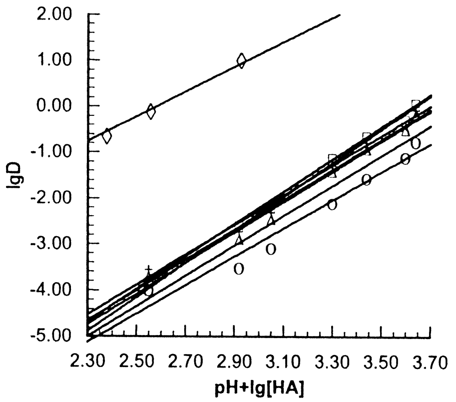

Fig. 2. log D~(pH+log[HA]). [HA]=0.525 mol l^{-1}; 'o' $[La^{3+}]=0.142$ mol l^{-1}. 'Δ' $[Nd^{3+}]=0.07920$ mol l^{-1}; '□' $[Sm^{3+}]=0.0251$ mol l^{-1}. '♦' $[Eu^{3+}]=2.64\times10^{-3}$mol l^{-1}; '+' $[Gd^{3+}]=3.57\times10^{-3}$mol l^{-1}. '×' $[Yb^{3+}]=1.31\times10^{-3}$mol l^{-1}; '∇' $[Y^{3+}]=0.0239$ mol l^{-1}. '◊' $[Sc^{3+}]=2.006\times10^{-3}$mol l^{-1}.

from which the extraction equilibrium constant can be obtained by least squares method, then the separation factors between Sc and RE ($\beta_{Sc/RE}$) are calculated by Eq. (6).

$$\beta_{Sc/RE} = K_{Sc}/K_{RE} \tag{6}$$

pK_{ex} and $\beta_{Sc/RE}$ are summarized in Table 3.

Refering to the data of $\beta_{Sc/RE}$, the sequence of extraction is Sm>Eu>Y>Nd>La>Yb>Gd. All $\beta_{Sc/RE}$ are more than 10^4, which are beneficial to concentrate and separate Sc from other RE.

3.4. Concentrating Sc from the IARED with HA

3.4.1. Distributions of Sc

The flow sheet of preparation of concentrated feed from IARED is shown in Fig. 3.

According to Fig. 3, each step is sampled to determine the content of Sc. Several random samples are analyzed. The results are summarized in Table 4.

Table 4 shows that the content of Sc in IARED is 8.7~11 ppm with the ratio of Sc to RE 0.39%~1.1%. Having been leached by $(NH_4)_2SO_4$, Sc/RE in dregs is 0.67%~0.85% ([Sc]=4.8~7.2 ppm), while that remaining in leach liquor, in filtrated stock and in concentrate are 0.022%~0.032%. After being dissolved in HCl, more than 90% Sc can be collected in the $RECl_3$ solution (Sc/RE= 0.022%), which is used to recover Sc by cross-current extraction in the next step.

3.4.2. Sc enrichment from $RECl_3$ by cross-current extraction

Extract I contacts with fresh $RECl_3$ (composition shown in Table 5) solution, by which Sc exchanges with other RE

Table 3
K_{ex} and $\beta_{Sc/RE}$

	Sc	La	Nd	Sm	Eu	Gd	Yb	Y
pK_{ex}	7.67	12.33	12.37	13.30	12.80	12.01	12.20	12.54
$\beta_{Sc/RE}$	1.00	4.57×10^4	5.01×10^4	42.7×10^4	13.5×10^4	2.19×10^4	3.39×10^4	7.41×10^4

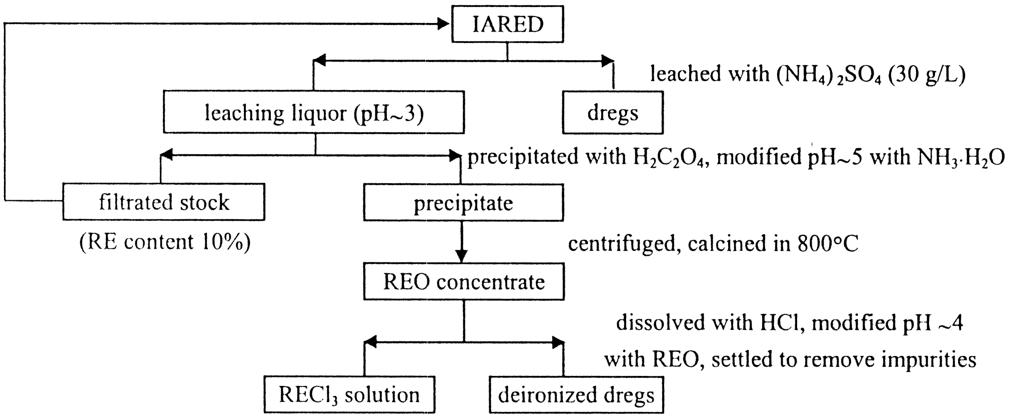

Fig. 3. Flow sheet of preparation of $RECl_3$ solution from IARED.

Table 4
RE and Sc contents in samples

Samples	Sc (ppm)	Sc/RE (%)[a]	Samples	Sc (ppm)	Sc/RE (%)[a]
IARED(1)	9.8	1.1	leaching liquor(2)	0.8	0.026
IARED(2)	8.7	0.56	precipitate	71	0.032
IARED(3)	11	0.39	REO concentrate(1)	260	0.023
dregs(1)	7.2	0.73	REO concentrate(2)	270	0.023
dregs(2)	6.3	0.85	REO concentrate(3)	260	0.022
dregs(3)	4.8	0.67	deironized dregs	17	0.018
leaching liquor(1)	1.6	0.024	$RECl_3$ solution	50	0.022

[a] The data are calculated by atomic number.

Table 5
Composition of the Sc contained $RECl_3$ (0.652 mol l^{-1}, pH=4)

RE	La	Ce	Pr	Nd	Sm	Eu	Gd	Tb
wt.%	2.92	4.23	5.16	16.81	6.81	0.12	12.09	2.17
RE	Dy	Ho	Er	Tm	Yb	Lu	Y	Sc
wt.%	21.17	2.66	9.73	1.18	8.17	1.26	5.52	0.04

effectively. After ten cross-current extractions (phase ratio O/A=1:5), Sc is enriched 400 times in organic phase with an extraction recovery of 89%. The obtained product (composition shown in Table 6) is suitable for further countercurrent extraction.

Table 6
Composition of Sc concentrate

	Sc		RE
concentration (g l^{-1})	1.850		10.90
concentration(mol l^{-1})	0.04113		0.1048
Sc/RE (wt.%)		16.97	
Sc/RE (mol%)		39.25	

3.5. Sc separation from RE by countercurrent extraction

Parameters in the countercurrent extraction are as follows:

Organic phase: extract III with saponification degree of 40%, the loaded RE 0.112 mol l^{-1};
Feed: $RECl_3$ containing La, Nd, Sm, Eu, Gd, Yb, Y and Sc, the total concentration 0.250 mol l^{-1}, the molar fractions $f_{Sc}=0.40$, $f_{RE}=0.60$;
Scrubbing acid: HCl (0.347 mol l^{-1});
Fractions of the outlets: $f'_{Sc}=0.368$, $f'_{RE}=0.632$.

According to the method in Ref. [1], the normalized extract flow-rate (S) and the normalized scrubbing flow-rate (W) are 0.600 and 0.232 respectively. Both extracting and scrubbing section are three stages. The flow-rate of the extract is 26.8 ml, that of the feed 20.0 ml and the scrubbing solution 10.0 ml. The composition variation of the extract outlet during 60 transfers is shown in Table 7. It shows that Sc in extract outlet was purified to 99%, 99.9%, 99.99% after 12, 30, 42 transfers respectively.

4. Conclusion

Based on the study of the distribution of scandium in every separation steps from treatment of the IARED to preparation of $RECl_3$ solution, an extraction method of producing high purity Sc(III) from the IARED was studied. Naphthenic acid diluted with *iso*-octanol and sulfated kerosene was selected as the extractant, chloride acid as the scrubbing and stripping solution. By two extraction processes in naphthenic acid system, scandium

Table 7
Composition of the extract outlet

Transfer	Content (ppm)								Sc/RE (%)
	La	Nd	Sm	Eu	Gd	Yb	Y	Sc	
6	1.29	3.43	2.48	0.24	1.14	0.58	0.51	80.7	89.30
12	0.04	0.20	0.06	0.01	0.06	0.03	0.03	75.6	99.43
18	0.04	0.20	0.06	0.01	0.05	[a]/	0.03	84.3	99.53
24	0.02	0.17	0.04	0.01	0.03	/	0.02	73.1	99.59
30	/	0.04	/	/	/	/	/	79.9	99.95
36	/	0.04	/	/	/	/	/	75.1	99.95
42	/	0.01	/	/	/	/	/	81.2	99.99
48	/	/	/	/	/	/	/	79.3	>99.99
54	/	/	/	/	/	/	/	83.7	>99.99
60	/	/	/	/	/	/	/	76.4	>99.99

[a] '/': less than limit of sensitivity.

is concentrated from 0.02–0.04% to 15–20% (wt%), and further purified to 99.99–99.999% grade. This Sc purification can be matched with RE separation processes conveniently. The extraction mechanism was also studied, the formula of Sc(III) in organic phase is ScA_3, which is very similar to other RE elements.

The production scale of $RECl_3$ from IARED in China is up to 20 000 tons per year recently. Suppose that Sc/RE in $RECl_3$ is 0.02% and the recovery is 80%, more than 3 tons Sc_2O_3 will be produced annually by the presented method. This will be a remarkable Sc resource.

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