



## A solvent extraction process with mixture of CA12 and Cyanex272 for the preparation of high purity yttrium oxide from rare earth ores

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### ABSTRACT

Solvent extraction and separation of yttrium from other rare earths in chloride medium using the mixture of sec-octylphenoxy acetic acid (CA12, HA) and bis(2,4,4-trimethylpentyl) phosphinic acid (Cyanex272, HB) has been investigated. Tri-*n*-butyl phosphate (TBP) was used as the phase modifier to achieve fast phase separation and to improve the stability of the organic phase. The separation coefficients ( $\beta$ ) between yttrium and heavy rare earths (HRE) are more significant in the double solvent (HAB) extraction system than the CA12-TBP extraction system. In a laboratory scale test with a fractional extraction process including 15 stages of extraction section and 10 stages of scrubbing section, yttrium was separated from all the other rare earths with a yield of 95% and an yttrium oxide product with 99.94% purity was obtained.

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### 1. Introduction

Yttrium is widely used for cathode ray tube, plasma display panel, light emitting diode, fluorescent lamp and other phosphors [1]. In recent years, the market demands for highly purified yttrium (Y) compounds are significantly increased. The solvent extraction methods with extractants, such as high molecular weight amines and naphthenic acids, are widely used for separation and purification of Y from other rare earths [2–5]. The main advantages of naphthenic acids include low cost and easy preparation. However, some problems gradually emerge for separation process with naphthenic acid during the industrial practice. For example, as the operational pH values for high extraction efficiency are relatively high, unexpected emulsification appears and leads to difficulties in phase separation. The extraction performance is not stable because of the complicated composition of naphthenic acids, which is varied depending on the manufacturer and will change after being used for a long time. More over, the separation of Y from light-group rare earth (LRE) is difficult due to the low separation factors between them [6].

A carboxylic acid extractant, sec-octylphenoxy acetic acid (CA12), has shown some advantages over the naphthenic acid for rare earth separation. Because the pKa value of naphthenic acid is 7.57 while the pKa of CA12 is 5.35, the pH<sub>1/2</sub> value (the pH value point with 50% metal extraction) of CA12 system is much lower

than the naphthenic acid system. The extractability of CA12 for LRE is higher than naphthenic acid with a cation exchange mechanism [7,8]. For example, with CA12 as extractant and iso-octanol as phase modifier, the separation factors ( $\beta$ ) between yttrium and other light rare earths are 5.26, 8.29, 10.73, 6.14 and 7.07 for  $\beta_{La/Y}$ ,  $\beta_{Ce/Y}$ ,  $\beta_{Pr/Y}$ ,  $\beta_{Nd/Y}$  and  $\beta_{Sm/Y}$ , respectively. As a comparison, the corresponding  $\beta$  values are 0.91, 1.50, 1.90, 1.60 and 4.0 for the naphthenic acid-iso-octanol system [9]. The lower operational pH values of CA12 system decrease the risk of emulsion in the liquid–liquid extraction process. In addition, the composition of CA12 is consistent and stable.

The CA12 system with phase modifiers such as long carbon chain alcohol and TBP has been used for separation of yttrium from the leaching solution of the yttrium-enrichment rare earth deposit in pilot plant scale [9]. Y<sub>2</sub>O<sub>3</sub> product was obtained with a purity of 99.5% and a yield of 95%. However, the separation efficiency between Y and the heavy-group rare earth elements (HRE) was low. For example, the  $\beta_{Yb/Y}$  and  $\beta_{Lu/Y}$  values are 2.19 and 1.66, respectively, suggesting it is difficult to achieve complete Y and HRE separation in industrial practice. Sun et al [10] found the mixture of CA12 and bis(2,4,4-trimethylpentyl) phosphinic acid (Cyanex272) has synergistic effects on Y and HRE (Ho, Er, Tm, Yb and Lu) extraction. The largest synergistic coefficient,  $R_{mix}$ , was obtained at the mole fraction  $X_{CA12} = 0.6$ .

In order to enhance the separation coefficients between Y and HRE, we developed a novel extraction system called double solvent extraction (or HAB extraction) from an industry point of view. CA12 was taken as the main extractant (HA) for improving the

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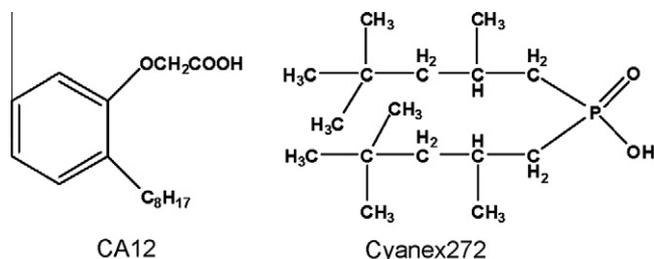


Fig. 1. Molecular structure of CA12 and Cyanex272.

extraction efficiencies of light rare earths and yttrium. The extraction efficiencies of lanthanides with CA12 decrease with the increase of atomic number. With the use of acidic organophosphorus extractants or their mono-sulfur substituted derivatives, such as bis(2-ethylhexyl) ester (P204) [11], 2-ethylhexyl phosphonic acid mono-2-ethylhexyl ester (P507) [12], bis(2,4,4-trimethylpentyl) phosphinic acid (Cyanex272) [13] and bis(2,4,4-trimethylpentyl) dithiophosphinic acid (Cyanex301) [14] as co-extractants (HB), the extraction efficiencies increase with the increase of atomic number of lanthanides. The acidic organophosphorus extractants are added in the system for improving extraction of HRE. Therefore, with the HAB system, the separation coefficients between Y and HRE,  $\beta_{\text{HRE/Y}}$ , are enhanced. The phase modifiers are added to extraction system to accelerate phase separating and avoid emulsifying.

In this paper, the effects of different co-extractants and phase modifiers were compared systematically. Distribution ratio of RE was investigated at concentrated HAB solutions. Simulation of fractional extraction was also carried out to separate and purify yttrium from Ion-absorbed-type rare earth (IATRE) minerals.

## 2. Experimental

### 2.1. Reagents and apparatus

CA12, P204, P507, TBP, sulfonated kerosene and iso-octanol were kindly provided by Shanghai Rare-earth Chemical Co. Ltd. of China. Cyanex272 was supplied by CYTEC Canada Inc. Molecular structure of CA12 and Cyanex272 are shown in Fig. 1. All extractants were used without further purification under the experiment of fractional extraction. The concentrations of acidic extractants were titrated by standard solution of sodium hydroxide [15].

Mixed rare earth concentrate benefited from Ion-absorbed-type rare earth (IATRE) minerals was provided by Jiangxi Institute of Rare Earth of China. Feed solution was prepared by leaching the rare earth concentrate with HCl and its ingredients were given in Table 1. The total concentration of mixture rare earth was determined by volumetric titration with standard solution of EDTA at pH 5.5 using xylenol orange as an indicator [16]. Mixture of rare earth elements were accurately determined by inductively coupled plasma optical emission spectrometer (ICP-OES, Thermo icap 6000 series). Digital pH meter (pHs-3C) made by Shanghai Rex Instruments Factory was used for pH measurements.

### 2.2. Solvent extraction process

Extraction equilibrium experiments were carried out by shaking equal volumes (5 mL) of feed solution and organic phase for

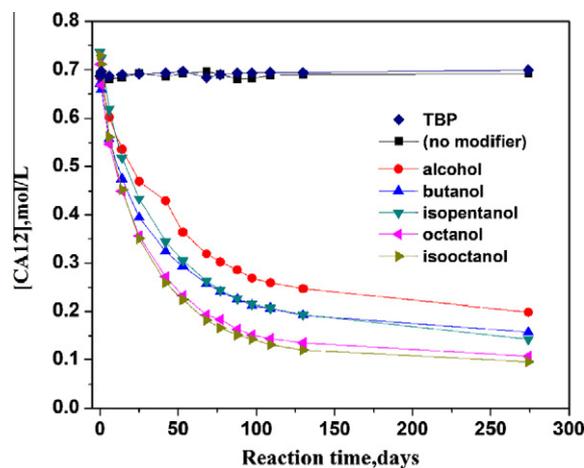


Fig. 2. The effect of the phase modifiers on CA12 concentration.  $[\text{CA12}]_{\text{ini}} = 0.7$  mol/L, modifiers = 30% (v/v), in kerosene.

30 min in 30 mL separatory funnels at room temperature. Trial of phase equilibrium showed that 10 min were enough for extraction equilibrium. When phase separated, the equilibrium concentration of RE in aqueous phase,  $[\text{RE}]_{\text{aq}}$  was determined by titration method or ICP-OES. The amount of RE in organic phase,  $[\text{RE}]_{\text{org}}$ , was determined by mass balance. The distribution ratio,  $D$ , can be obtained as:  $D = [\text{RE}]_{\text{org}}/[\text{RE}]_{\text{aq}}$ .

Fractional extraction was carried out by “funnel method” to simulate multistage counter-current extraction in the laboratory.

## 3. Results and discussion

### 3.1. The effect of phase modifiers

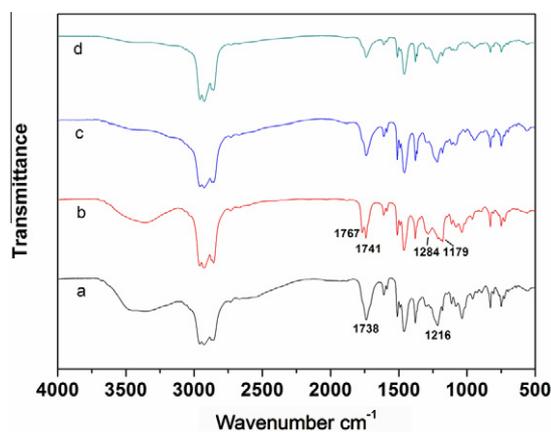
As a modifier, iso-octanol is commonly added to extraction system of carboxylic acids [17]. However, it is unsuitable to use aliphatic alcohols as modifiers in CA12 system during long term industrial test [18].

In order to determine the effect of phase modifiers on CA12 extraction, a series of CA12 solutions with 0.7 mol/L CA12 and 30% (v/v) alcohols or TBP in kerosene were prepared, placed at room temperature, and then analyzed periodically. As shown in Fig. 2, concentration of CA12 decreases by 87% in 30% iso-octanol during 9 months. Not only iso-octanol but also other alcohols cause continuous decrease of CA12 concentration over time.

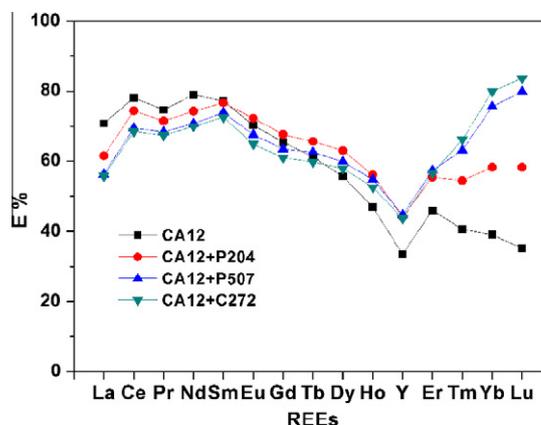
IR spectra were resorted to compare variation of CA12-octanol or CA12-C272 compositions in a whole year. The IR spectra of mixture of CA12 and C272 (Fig. 3c and d) did not change significantly after 365 days. The peak at  $1216 \text{ cm}^{-1}$  (Fig. 3a) is assigned as the hydroxyl deformation vibration of COOH group of CA12. With the addition of iso-octanol as phase modifier, the peak disappeared (Fig. 3b), suggesting the degradation of CA12. Three new peaks emerged at  $1767 \text{ cm}^{-1}$ ,  $1284 \text{ cm}^{-1}$  and  $1179 \text{ cm}^{-1}$  (C–O stretching vibration in esters). The  $1767 \text{ cm}^{-1}$  and  $1179 \text{ cm}^{-1}$  peaks are attributed by C=O stretching vibration in carboxylate esters and C–O stretching vibration in esters, respectively. Based on the above IR spectra, it is deduced that esterification occurred between CA12 and the alcohols.

Table 1  
Composition of feed solution by HCl leaching.

Ingredients	Y <sub>2</sub> O <sub>3</sub>	La <sub>2</sub> O <sub>3</sub>	CeO <sub>2</sub>	Pr <sub>6</sub> O <sub>11</sub>	Nd <sub>2</sub> O <sub>3</sub>	Sm <sub>2</sub> O <sub>3</sub>	Eu <sub>2</sub> O <sub>3</sub>	Gd <sub>2</sub> O <sub>3</sub>	Tb <sub>4</sub> O <sub>7</sub>	Dy <sub>2</sub> O <sub>3</sub>	Ho <sub>2</sub> O <sub>3</sub>	Er <sub>2</sub> O <sub>3</sub>	Tm <sub>2</sub> O <sub>3</sub>	Yb <sub>2</sub> O <sub>3</sub>	Lu <sub>2</sub> O <sub>3</sub>
Mol fraction	0.674	0.0230	0.0040	0.0105	0.0543	0.0274	0.0001	0.0501	0.0110	0.0544	0.0174	0.0383	0.0055	0.0269	0.0029



**Fig. 3.** IR spectra of CA12 – iso-octanol new prepared (a), CA12-iso-octanol placed for a year (b), CA12-C272 new prepared (c) and CA12-C272 placed for a year (d), CA12 = 70%.



**Fig. 4.** The effect of co-extractants on RE extraction.

**Table 2**

The distribution ratio ( $D$ ) and separation coefficients ( $\beta$ ) of HRE in CA12-TBP and HAB system.  $[HA] = 0.7$  mol/L;  $[HB] = 0.1$  mol/L, TBP = 15% (v/v), in kerosene, saponification rate = 90%. Feed:  $\sum RE = 0.30$  mol/L, initial pH = 4, leached from Longnan rare earth minerals.

System	$D$					$\beta$					
	Ho	Y	Er	Tm	Yb	Lu	Ho/Y	Er/Y	Tm/Y	Yb/Y	Lu/Y
CA12-TBP	0.883	0.507	0.851	0.685	0.642	0.546	1.74	1.68	1.35	1.27	1.08
CA12-P204-TBP	1.28	0.790	1.25	1.20	1.40	1.40	1.62	1.58	1.52	1.77	1.77
CA12-P507-TBP	1.21	0.808	1.35	1.72	3.10	3.98	1.50	1.66	2.12	3.84	5.17
CA12-C272-TBP	1.11	0.775	1.31	1.96	4.01	5.13	1.43	1.69	2.53	5.17	6.62

**Table 3**

Parameters of process in fractional extraction simulation.

System	Organic phase	Feed	Scrubbing acid
CA12-TBP [9]	0.70 M CA12 and 15% TBP in kerosene, saponification rate = 85–90%	1.0 M $RECl_3$	3.0 M HCl
HAB-I	0.75 M CA12, 0.05 M C272 and 15% TBP in kerosene, saponification rate = 90%	1.03 M $RECl_3$	2.81 M HCl
HAB-II	0.68 M CA12, 0.12 M C272 and 15% TBP in kerosene, saponification rate = 90%	1.05 M $RECl_3$	2.98 M HCl

The concentration of CA12 did not change obviously with TBP as modifier. Therefore, TBP was selected as the modifier in the HAB system.

### 3.2. The effect of the co-extractants

P204, P507, and Cyanex272 were selected to investigate the effects of co-extractants. The mono-stage extraction behavior of CA12-TBP, CA12-P204-TBP, CA12-P507-TBP, CA12-C272-TBP in mixed RE solution were compared (Fig. 4). The distribution ratio ( $D$ ) and separation coefficients ( $\beta$ ) of HRE were determined (Table 2). The results show that, separation coefficients between HRE and Y in HAB system are higher than that of CA12 system. For instance, Separation coefficients between Y and Lu increase in this order: CA12-TBP < CA12-P204-TBP < CA12-P507-TBP < CA12-C272-TBP. This means that co-extractants promote the extraction of HRE significantly in HAB system.

Cyanex272 is selected to constitute the HAB system in the current work, considering the stripping acidity of rare earths in Cyanex272 system is lower than in P204 and P507 systems [19], and low acid consumptions in the stripping stages are expected.

### 3.3. Fractional extraction

Ion-absorbed-type rare earth (IATRE) minerals, also called weathering crust rare earth minerals, are characteristic of higher

content of medial and heavy RE elements, which have high economic value [20]. IATRE minerals are widely distributed in southern China such as Guangdong, Fujian, Hunan, especially Jiangxi province. Yttrium accounts for a mole proportion of 67.4% in the total REE calculating as oxides. Because yttrium is relatively high than the other medial and heavy RE elements, the suitable method is to separate Y at first step. However, the chemical characters of rare earths are very similar to yttrium, it is difficult to separate RE from Y by adjusting proportion of main extractant and co-extractant. The fractional extraction method with multiple stages of extraction sections and stripping sections was used to obtain yttrium product with high purity. Method of static calculation [20] is used to obtain the process parameters of fractional extraction. When the purity and yield of  $Y_2O_3$  product is required as 99.9% and 95%, the number of the extraction section and scrubbing section are calculated to be 15 and 10, respectively. The flow rate ratio of organic phase, feed and scrubbing acid are deduced to 23:2:4.5. Other parameters and scheme of the process are given in Table 3 and Fig. 5.

In a process with fractional extraction for one year of operation, the concentration and extractability was stable after the organic phases was recycled and used for three times.  $Y_2O_3$  products were obtained in HAB-I and HAB-II processes with purity of 99.80% and 99.94%. Comparison of  $Y_2O_3$  products in CA12 system and HAB system are shown in Table 4. Yttrium containing in the stripped RE solution is about 2%. Concentration of RE in each stage of HAB-I were also determined, some of them are presented in Fig. 6.

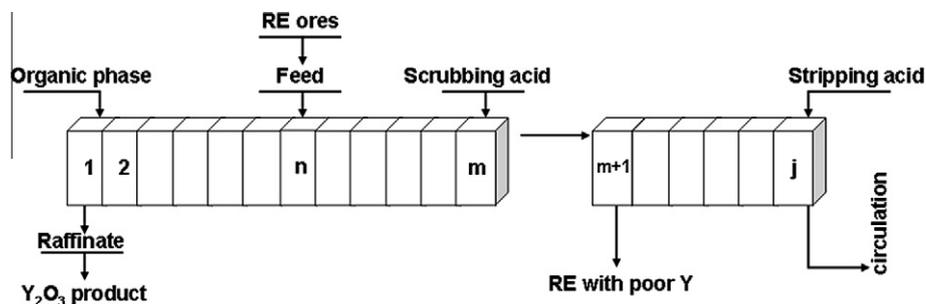


Fig. 5. Process scheme for separating Y by double solvent extraction.

Table 4  
Composition of  $Y_2O_3$  products (proportion by weight).

Ingredients	$Y_2O_3$ , % [9]	$Y_2O_3$ -I, %	$Y_2O_3$ -II, %
$Y_2O_3$	99.47	99.80	99.94
$La_2O_3$	0.026	0.001	<0.001
$CeO_2$	0.022	0.003	0.002
$Pr_6O_{11}$	<0.002	<0.001	0.002
$Nd_2O_3$	0.003	<0.001	0.008
$Sm_2O_3$	0.010	<0.001	<0.001
$Eu_2O_3$	<0.002	<0.001	<0.001
$Gd_2O_3$	<0.002	<0.001	<0.001
$Tb_4O_7$	<0.002	<0.001	<0.001
$Dy_2O_3$	0.051	0.003	<0.001
$Ho_2O_3$	0.068	0.005	0.009
$Er_2O_3$	0.130	0.113	0.032
$Tm_2O_3$	0.024	0.024	<0.001
$Yb_2O_3$	0.170	0.036	<0.001
$Lu_2O_3$	0.016	0.017	<0.001

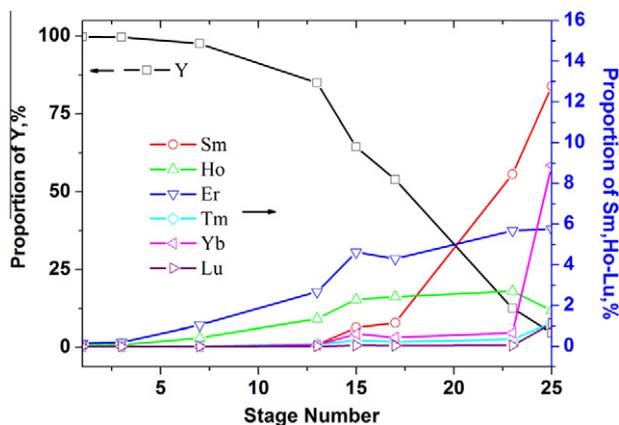


Fig. 6. Composition variation of Y, Sm and Ho-Lu in each stage.

According to the data presented above, it is confirmed that separation selectivity between Y and other rare earths is superior in HAB than in single solvent extraction system. With the addition of co-extractant the extraction of HRE enhanced effectively. purity of  $Y_2O_3$  products increases in HAB-I and HAB-II with the increasing Cyanex272 proportions. In the new extraction system, most rare earth elements, e.g. Sm, Eu, Gd, Tm, Yb and Lu can be separated with Y from mix rare earths almost completely.

#### 4. Conclusions

Double solvent (HAB) system using CA12 (HA) as main extractant and Cyanex272 (HB) as co-extractant, TBP as the phase

modifier is quite efficient in separating Y from mixed rare earths. Not only the HAB extraction system keeps advantages of high separation efficiency between Y and LRE, but also it overcomes drawbacks of low separation factor between Y and HRE.  $Y_2O_3$  product with a purity of 99.94% was obtained by HAB extraction from IATRE minerals which was higher than by CA12 extraction. The total recovery of Y was about 95%.

Considering that CA12 and Cyanex272 are very valuable to industrial practice for their high performance, it has great potential to prepare Y product with high purity from IATRE minerals by double solvent extraction system.

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#### References

- [1] C.H. Yan, J.T. Jia, C.S. Liao, S. Wu, G.X. Xu, Rare earth separation in China, *Tsinghua Sci. Technol.* 11 (2006) 241–247.
- [2] G.X. Xu, Rare Earths (in Chinese), vol. 1, third ed., Metallurgy Industry Press, Beijing, 1995, pp. 578.
- [3] A. Peng, Z.R. Dai, C.X. Wang, Extraction and Serration of yttrium from rare earths using naphthenic acid, in: Symposium of rare earth chemistry, Science press, Beijing, 1982, pp. 39–49.
- [4] Z. R. Dai, C. X. Wang, Z. Y. Wang, Preparation of high purity  $Y_2O_3$  using naphthenic acid, CN Patent 85102220, 1985.
- [5] J.Z. Zhu, W.H. Duan, X.H. Zhou, C.Q. Zhang, Application of annular centrifugal contactors in the extraction flowsheet for producing high-purity yttrium, *Hydrometallurgy* 85 (2007) 154–162.
- [6] D.Q. Li, Some chemical problems in the hydrometallurgical industries of rare earth progress, *Progress in Chemistry* 7 (1995) 209–213.
- [7] W. Z. Ye, Q. R. Xu, Y. F. Qian, Extractants for the rare earth separation, CN Patent 93112500.6 (1993).
- [8] W.Z. Ye, Synthesis and extraction behavior of new extractants for rare earth separation, in: *Advances in Rare Earth New Materials and New Processes*, Science Press, Beijing, 1998, pp. 3–10.
- [9] W. Li, X.L. Wang, S.L. Meng, D.Q. Li, Y. Xiong, Extraction and separation of yttrium from the rare earths with sec-octylphenoxy acetic acid in chloride media, *Sep. Purif. Technol.* 54 (2007) 164–169.
- [10] X.B. Sun, J.M. Zhao, S.L. Meng, D.Q. Li, Synergistic extraction and separation of yttrium from heavy rare earths using mixture of CA12 and Cyanex272, *Anal. Chim. Acta* 533 (2005) 83–88.
- [11] Q. Jia, Z.Y. Li, W.H. Zhou, H.F. Li, Studies on the solvent extraction of rare earths from nitrate media with a combination of di-(2-ethylhexyl)phosphoric acid and sec-octylphenoxyacetic acid, *J. Chem. Tech. Biotechnol.* 84 (2009) 565–569.
- [12] D.Q. Li, Z.C. Wu, Extraction and separation of light RE elements from  $HNO_3$  solution by P507, *Chinese Rare Earths* 9 (1981) 23–27.
- [13] X.F. Zhang, D.Q. Li, Extraction of RE(III) with bis(2,4,4-trimethylpentyl) phosphinic acid, *Chin. J. Appl. Chem.* 10 (1993) 72–74.
- [14] Q. Jia, S.S. Tong, Z.Y. Li, Solvent extraction of rare earth elements with mixtures of sec-octylphenoxy acetic acid and bis(2,4,4-trimethylpentyl) dithiophosphinic acid, *Sep. Purif. Technol.* 64 (2009) 345–350.

- [15] G.X. Xu, C.Y. Yuan, Solvent extraction of rare earth, Science Press, Beijing, 1987. pp. 303.
- [16] Institute of metallurgy of Baotou iron and steel Co., Combined determination of  $RE_2O_3$  and  $ThO_2$ , in: Analysis methods for rare earth ores and metallurgy chemistry, Baotou Publishers, Baotou, 1972, pp. 9–11.
- [17] D. Q. Li, S. L. Meng, a process of liquid-liquid extraction and separation of high-purity yttrium, CN Patent 99118261.8 (1999).
- [18] D. Q. Li, Progress in Separation Processes of Rare Earths, The 4th International Conference on Rare Earth Development and Application, Beijing, 2001, pp. 11–20.
- [19] J.D. Wang, J.Y. Chen, Handbook of Solvent Extraction, Chemical Industry Press, Beijing, 2001. pp. 538–553.
- [20] D.Q. Li, Separation of rare earth elements, in: Z.S. Yu, M.B. Chen (Eds.), Rare earth elements and their applications, Metallurgical Industry Press, Beijing, 1995, pp. 81–88.