

## A separation processing for industrial rare earth feed solution by phosphonium ionic liquid type saponification strategy

DONG Yamin (董亚敏)<sup>1,2</sup>, GUO Xiangguang (郭向广)<sup>1,2</sup>, WANG Yanliang (王艳良)<sup>1,2</sup>, ZHAO Zeyuan (赵泽原)<sup>1,2</sup>, HUANG Chao (黄超)<sup>1,3</sup>, SUN Xiaohui (孙晓琦)<sup>1,2,\*</sup>

(1. Xiamen Institute of Rare Earth Materials, Haixi Institute, Chinese Academy of Sciences, Xiamen 361021, China; 2. Fujian Institute of Research on the Structure of Matter, Chinese Academy of Sciences, Fuzhou 350002, China; 3. School of Metallurgy and Chemical Engineering, Jiangxi University of Science & Technology, Ganzhou 341000, China)

Received 20 June 2016; revised 20 September 2016

**Abstract:** A novel ionic liquid type saponification processing based on quaternary phosphonium type bifunctional IL was developed for yttrium separation from ion-adsorbed rare earth deposit. The extractabilities of ([trihexyl(tetradecyl)phosphonium][sec-octylphenoxy acetate] ( $[P_{6,6,6,14}][SOPAA]$ ) were pronouncedly higher than those of sec-octylphenoxy acetic acid (HSOPAA), a mixture of HSOPAA and  $[P_{6,6,6,14}][Cl]$  for rare earth elements (REEs). The ion association extraction mechanism contributed to avoiding the numerous saponification procedures using alkali and resulting in saponification wastewater. After 13 stages of extraction and 6 stages of scrubbing sections, the Y(III) was successfully separated from industrial heavy RREs feed, the purity of Y(III) in raffinate was approximately to be 98.9%. Stripping by distilled water was effectively achieved for REEs, which contributed to the decreased consumption of acid to a considerable extent.

**Keywords:** heavy rare earth; ionic liquid; saponification; fractional extraction

The unique properties of rare earth elements (REEs) render them important in permanent magnets, lighting phosphors, polishing compounds, and ceramics. Especially for applications that take advantage of the f-orbital electrons, substitutions outside the REE family are often difficult to impossible<sup>[1]</sup>. Extracting and separating individual elements from mined ore is not easy, requiring lengthy operations to separate them out, and this results in high costs and adverse effects on the environment. The low concentration of REE in the earth's crust makes economic exploitation difficult<sup>[2]</sup>, and the sustainability of the REE separation industry has aroused considerable attention<sup>[3]</sup>. To eliminate protons and break the dimers in organic phosphonic acids or carboxylic acids, the saponifications of acidic extractants by acid-base neutralization reactions are widely used in industrial REEs separation processings<sup>[4]</sup>. The saponification procedures contribute to the increased extractability and selectivity of acidic extractants to a considerable extent. The common industrial saponification mechanisms and technological processes are shown in Fig. 1 and include ammonium saponification (saponified by  $NH_3 \cdot H_2O$ ), sodium saponification (saponified by NaOH), calcium saponification (saponified by  $Ca(OH)_2$ ), and magnesium saponification

(saponified by MgO). These inevitably result in wastewater containing  $NH_4^+$ ,  $Na^+$ ,  $Ca^{2+}$  or  $Mg^{2+}$  because of the cation-exchange extraction mechanisms<sup>[5-7]</sup>.

The Chinese REE industry produces over 20 million tons of wastewater annually, with ammonia nitrogen level ranging from 300 to 5000 mg/L, exceeding the national emission standard by a dozen and even a hundred times<sup>[8]</sup>. In 2011, China produced 96,900 tons of rare earth products, accounting for more than 90% of the world's total output. Unfortunately, this created 10 million tons of saponification wastewater. The acid and alkali consumptions account for 20%–30% in the REE separation costs. On the one hand, the massive acid and alkali quantities are put into the REE separation processing,

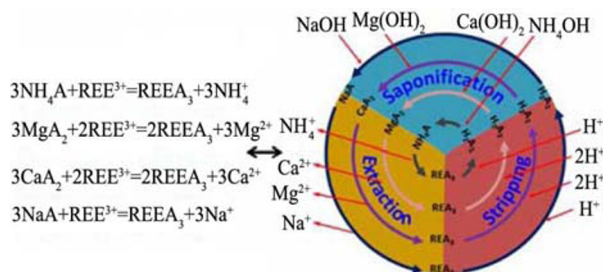


Fig. 1 Common saponification mechanisms and technological processes

**Foundation item:** Project supported by "Hundreds Talents Program" from Chinese Academy of Sciences, National Natural Science Foundation of China (21571179), Science and Technology Major Project of the Fujian Province, China (2015HZ0101), Xiamen Universities Research Institutions Jointing Enterprise Projects (3502Z20152009)

\* Corresponding author: SUN Xiaohui (E-mail: [xqsun@fjirsm.ac.cn](mailto:xqsun@fjirsm.ac.cn); Tel.: +86-592-6376370)

DOI: 10.1016/S1002-0721(17)60912-8

which results in higher costs. On the other hand, the industrial productions of acid, and base, together with resulting saponification waste waters lead to heavy pollution. In organic phase, the saponified acidic extractant is a water in oil microemulsion system in the organic phase and a high level of saponification will result in emulsification and third phase formation during extraction. New environmental legislations issued by the Chinese government require REEs producers to meet stricter emission standards on wastewater and the legislations are clearly challenges for most of the REE separation plants in China. Some technologies have been developed to omit the numerous saponification procedures decrease the requirements of acid and base, enhance the extractabilities and selectivities of acidic extractants and avoid saponification wastewater. These include magnesium bicarbonate saponification<sup>[9]</sup>, mixing extractant and rare earth solution with magnesium oxide<sup>[7]</sup>, controlling equilibrium acidity of aqueous phase<sup>[10]</sup>, and adding complexing agent in aqueous phase<sup>[11]</sup>.

Ionic liquid (IL) based extraction is one of the frontiers in separation chemistry and engineering<sup>[12–14]</sup>. In the field of IL based extraction for metal ions, considerable achievements have been reported by groups from Europe<sup>[15,16]</sup>, US<sup>[17,18]</sup>, China<sup>[19,20]</sup>, Japan<sup>[21,22]</sup>, and so on. Sun et al. developed some acid-base coupling bifunctional ionic liquids (ABC-BILs)<sup>[4]</sup>, and reported internal synergistic effects between their cations and anions<sup>[23]</sup>. When the precursor industrial extractants are prepared as ABC-BILs, their extractabilities can be increased by several orders of magnitude<sup>[24]</sup>. Another important advantage is that the millions of tons of saponification wastewater produced annually from traditional acidic extractants may be eliminated<sup>[5]</sup>. A commercially available phosphonium IL CyphosIL101 (trihexyl(tetradecyl) phosphonium chloride), is a promising candidate for industrial REE separation. Extraction systems based on CyphosIL101 have been recently studied for the recycling of REEs with satisfactory results, such as separation of neodymium and dysprosium from used NdFeB magnets<sup>[25]</sup>, separation of lanthanum and samarium from nickel and cobalt in magnets or batteries<sup>[26]</sup>. However, to the best of our knowledge, fractional extraction based on phosphonium IL has not been reported for a separating industrial feed solution from REE mineral deposit.

Heavy REEs have a series of specific properties making them essential in many applications including lighting, electronics, magnetism, catalysis, and energy. They have become critical to develop high-tech materials. Ion-adsorbed REE deposits were discovered in China. The deposits are rich in heavy REEs, accounting for more than 80% of world's total production. However, the separation of heavy REEs from ion-adsorbed deposits is difficult owing to their similar chemical properties. As

for the ion-adsorbed rare earth deposits, yttrium accounts for a mole proportion of 30%–70% REEs in the total REEs calculated as oxides. The sustainable and efficient separation of Y(III) from Ho(III), Er(III), Tm(III), Yb(III), Lu(III) is an industrial challenge. Naphthenic acids are widely used for separation of Y(III) in Chinese REE industry. However, emulsification and esterification always appear in naphthenic acids system. Many systems have been developed for separating yttrium, such as a mixture of bis(2,4,4-trimethylpentyl)phosphinic acid (Cyanex272) and 2-ethylhexyl phosphonic acid mono 2-ethylhexyl ester (HEHEHP)<sup>[27,28]</sup>, a mixture of sec-octylphenoxy acetic acid (CA-12, HSOPAA) and Cyanex272<sup>[29]</sup>, a mixture of CA-12 and Cyanex272 with tri-n-butyl phosphate (TBP) as phase modifier<sup>[30]</sup>. Very recently, two representative heavy REEs, i.e., Y(III) and Lu(III), were effectively separated using phosphonium type ILs<sup>[31]</sup>. In this article, we described the development of a novel laboratory scale test with a fractional extraction process based on ionic liquid type saponification strategy for separating Y(III) and other heavy REEs from industrial REE feed solution. The fractional extraction process using industrial feed solution is indispensable for evaluating potentials of phosphonium IL in REEs separation industry.

## 1 Experimental

### 1.1 Reagents and methods

Sec-octylphenoxy acetic acid (CA-12, HSOPAA) and sulfonated kerosene were purchased from Luoyang Aoda Chemical Co., Ltd. (China). Cyphos IL 101 ([P<sub>6,6,6,14</sub>Cl]) was supplied by Cytec Industries Inc. An anion-exchange resin (Dowex Monosphere 550A (OH)) was obtained from Dow Chemical Company. Sulfonated kerosene is the most commonly used diluent in Chinese REE separation industry<sup>[32,33]</sup>, which is characterized by slow evaporation rate, low aromatic content, low toxicity, high security, no smell, no residue after evaporation. To reduce the viscosity of extractant and develop a potential separation processing for REE separation industry, in this study, the extracting phases were prepared by dissolving the extractants in sulfonated kerosene for REE separation. The industrial REEs feed solution was supplied by Fujian Changting Golden Dragon Rare-Earth Co., Ltd. (China), including 88 mol.% YCl<sub>3</sub> and 12 mol.% other heavy rare earth (Ho(III), Er(III), Tm(III), Yb(III) and Lu(III)) (Table 1). To obtain about 0.2 mol/L REEs solution, the industrial feed solution was diluted with distilled water and hydrochloric acidity. Thermo scientific iCAP 6500 series inductively coupled plasma-atomic emission spectroscopy (ICP-OES) was used to determine the concentration of REE in aqueous phase. NMR spectra were recorded using an AVANCEIII 500 MHz spectrometer (Bruker).

Download English Version:

<https://daneshyari.com/en/article/7697849>

Download Persian Version:

<https://daneshyari.com/article/7697849>

[Daneshyari.com](https://daneshyari.com)