Rare earth extraction from wet process phosphoric acid by emulsion liquid membrane

ZHANG Lichang (张利昌), CHEN Qianlin (陈前林)*, KANG Chao (康 超), MA Xin (马 昕), YANG Zunliang (杨尊良)

(School of Chemistry and Chemical Engineering, Guizhou University, Guiyang 550025, China)

Abstract: The recovery of rare earths (RE) during the wet processing of phosphoric acid is very important, the method of emulsion liquid membrane (ELM) with di(2-ethylhexly) phosphate (D2EHPA) as carrier has the high selectivity while cannot provide a satisfactory extraction rate. Here novel method of emulsion liquid membrane (ELM) using Aniline as carrier to extract RE from the feed solution was proposed. The method could increase the extraction rate of RE in the real sample to 93%. The effects of different parameters such as type and concentration of carrier and surfactant, hydrochloric acid concentration, organic to internal phase volume ratio, membrane to external phase volume ratio on extraction of RE^{3+} were investigated. Quantitative extraction (>93%) of RE^{3+} was observed with 6 vol.% Aniline and 4 vol.% T154 liquid membrane at external to internal phase volume ratio of 10 for the feed solution. The proposed method of ELM using Aniline as carrier can be expected to provide a practical, efficient, and economical method for extracting RE from phosphate leach solution with high acidity in the industry of wet process phosphoric acid.

Keywords: phosphate ore; emulsion liquid membrane; extraction; rare earths

The rare earths or rare-earth elements (REEs) are a group of 17 chemically similar metallic elements (15 lanthanides, plus scandium and yttrium). They are becoming increasingly important in the transition to a green, low-carbon economy. This is due to their essential role in permanent magnets, lamp phosphors, rechargeable NiMH batteries, catalysts and other applications[1].

The phosphorite ores-deposits rich in rare earth resource in Zhijin, Guizhou province, China is the most oversize mining area. The reserve of rare earths is more than 1.44 million tons, the content of rare earth oxides (REO) is 0.09%–0.27%[2,3]. Up to now, many kinds of recycling processes were proved to be effective in rare earth recovery[4–8]. Hydrometallurgical process such as leaching is a very common method to recover the rare earth metals from various rare earth metal bearing sources (primary/secondary) leading to the dissolution of said metal(s) into the respective lixiviant phase along with undesired other metal/impurities[9]. In hydrometallurgy, the separation process namely solvent extraction is employed to separate and purify rare earths from numerous aqueous solutions[10–13]. Wet-process phosphoric acid has been extensively used in industrial production to separate rare earths from low-grade phosphate ores[14], where organic extractants like D2EHPA, PC-88A, Cyanex301, Cyanex302, Cyanex272, and CA-12 were adopted to extract rare earth ions (RE^{3+}) respectively or synergistically[15–19]. Heterocyclic nitrogen compound was used to extract RE^{3+} from sulfate leach solution[20]. However, some negatives were found that complicated technology, by-products were inseparable and high-cost, etc. in the process of separation of rare earth elements by solvent extraction. Liquid membrane has the advantages of high efficiency, time-saving, high selectivity, and energy-saving. According to the membrane structure, different liquid membranes could be sorted into emulsion liquid membrane (ELM), supported liquid membrane and electrostatic quasi (pseudo) liquid membrane[21]. ELM has been highly applied in some fields such as hydrometallurgy and waste water treatment[22–29]. The ion transport through an ELM plays a major role in simulating biological membrane functions and separation technologies[30]. Xie et al.[31] have done the research about extracting the RE^{3+} from feed solution by ELM with D2EHPA as carrier, and the extraction rate was up to 76.46%. The synergistic extraction of the Nd(Ⅲ) has been studied using mixtures of di-nonyl phenyl phosphoric acid (DNPPA) and tri-n-octylphenyl phosphine oxide (TOPO) as the carrier in the ELM by Anitha et al.[32], and the quantitative extraction rate of Nd(III) is about 97%. ELM processes are those involving a selective liquid membrane phase in which simultaneous extraction/ stripping occurs. Separation is achieved by permeation of solute through this liquid phase from a feed phase to a

---

* **Corresponding author:** CHEN Qianlin (E-mail: cql1018@163.com; Tel.: +86-851-83658252)

receiving phase[33]. An ELM consists of three phases: the external phase, membrane phase and the internal aqueous phase. In the extraction process of the RE^{3+} by ELM, the feed is often referred to as the external phase and the membrane phase is the extractant in suitable diluents containing a surfactant. The internal aqueous phase is often an aqueous phase such as hyrochloric acid. The RE^{3+} forms a complex with the extractant at the interface of the emulsion globule and the external phase. The complex is transported through the membrane phase to the interface of the membrane phase and the internal phase, and the RE^{3+} is stripped into the internal phase from the complex. After the separation process, the membrane phase and the aqueous phase are separated in a settling step.

In this study, the removal of RE^{3+} with an ELM containing different regents as carriers, T154 and Span80 as surfactant to improve the extraction rate were investigated. The effects of the RE^{3+} extraction like type and concentration of carrier, type and concentration of surfactant, the concentration of the HCl as the internal aqueous phase, the volume ratio of the organic phase to internal phase (R_{oi}), the volume ratio of the emulsion phase to the feed solution (R_{ew}) were studied. The extraction rate of RE^{3+} could be raised as high as 93.53% from the phosphate leach solution by the ELM with optimal liquid membrane formulation.

1 Experimental

1.1 Materials

Lanthanide oxides was of regent grade and used without further purification. All aqueous solutions were prepared with deionized water. Carrier 2-ethylhexyl phosphonic acid mono-2-ethylhexyl ester (PC-88A, purity≥ 95%, Laiya, Shanghai, China), di(2-ethylhexyl) phosphoric acid (D2EHPA, purity≥95%, Laiya, Shanghai, China), Aniline (purity≥99.5%, Chendu Jinshan, Chendu, China) were used without further purification. Sorbitan monooleate (Span80, chemical grade) and polyisocrotyl succinimide (T154, chemical grade) were used as surfactants. The extractants were diluted with sulfonated kerosene. Other reagents such as HCl and Chlorophosphonazo mA (Shanghai Yuanye, Shanghai, China) were used without further purification.

1.2 Analytical measurements

The pH of aqueous solution was measured using PHS-3C pH-meter (Jinmai, Shanghai, China). The content of rare earth oxides (REO) was determined with a visible spectrophotometer 722 (Yoke, Shanghai, China) according to the method of GB/T 6730.24—2006[34]. The concentration of conventional metal elements such as Ca, Mg, Al, and Fe were judged by an atomic absorption

spectrophotometer INESA 4530F (INESA, Shanghai, China). The content of rare earth elements (REE) was determined with an inductively coupled plasma mass spectrometry (ICP-MS) ELAN DRC-e (PerkinElmer, Canada).

1.3 Procedures

1.3.1 Rare earth solution preparation

Solutions of rare earths (100 mg/L) were prepared by dissolving their oxides (La_2O_3, CeO_2, Y_2O_3, and Nd_2O_3), with a purity of larger than 99.9% in hydrochloric acid and diluted with distilled water, and the pH values of the solution were adjusted as 1.0, 0.5, 0.1, −0.1, and −0.5 respectively.

1.3.2 Feed solution preparation and analysis

The phosphorite ores used in this paper were chosen from Zhijin, Guizhou, and the samples were normally powder (<0.150 mm). After taking the powder of phosphorite, HCl solution (12 mol/L) was added and the reaction lasted for 2 h at 60 ℃ water bath, and stand for 2 d, then filtrated. The feed solution had a high acidity (pH–1.66).

The concentration of Ca, Mg, Al, and Fe in the feed solution are shown in Table 1.

Table 1 shows that the alkaline earth metal ions content in the feed solution is far more beyond that of rare earths. The concentration of Fe^{3+} and Al^{3+} to the concentration of REO was more than 15 times.

The content of rare earth elements (REE) was determined by ICP-MS. The feed solution have a high acidity and a large concentration of REO, then the feed solution needs to be diluted, the acidity needs to be reduced to pH 1.0. The content of REE analysis results are shown in Table 2.

Table 2 shows the distribution of main REE in the feed solution. It was determined by ICP-MS. It is clear that elements like La, Ce, Y, Nd take up 78.98% of the REE.

1.3.3 ELM preparation

The stability of the ELM is one of the critical factors affecting the removal of RE^{3+}. The primary emulsion was formed by adding the organic phase (O) and internal aqueous phase (I) in a 0.25 L glass under an intense stirring (4000 r/min at 298 K) by means of a motor-driven

Table 1 Concentrations of major metal cations in leaching solution

Metal cations	REO	Ca^{2+}	Mg^{2+}	Fe^{3+}	Al^{3+}
Concentration/(g/L)	0.328	55.78	7.90	4.14	1.02

Table 2 Distribution of rare earth elements in phosphate ore (wt.%)

Sc	Y	La	Ce	Pr	Nd	Sm	Eu
1.18	25.96	19.83	16.09	4.32	17.10	2.96	0.72
Tb	Dy	Er	Tm	Yb	Lu	Ho	Gd
0.54	2.90	1.76	0.19	1.07	0.12	0.64	3.92