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Extraction and Group Separation of Rare Earths by a Combined Extraction/Electrostatic Pseudo Liquid Membrane from Simulated Rare Earths Mine Water

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Abstract

A new approach to extraction and separation of multi-metals by a combined extraction/electrostatic pseudo liquid membrane (ESPLIM) process is proposed. The ESPLIM set-up was modified in such a way that a hydrochloric acid concentration gradient stripping could be easily applied. The principle of separation is described. A simulated rare earth ore leachate containing some 1.0 g/L mixed REEs, 10 g/L $(NH_4)_2SO_4$, 5 g/L NH_4Cl and 0.6 g/l of non-RE ions such as Ca, Al, Si, Fe and Pb was used as the feed solution, which passed through the extraction cell at a flow rate of 1 L/h in once-through mode, while the stripping solution (0.32-6M HCl) passed through the stripping cell in recirculation mode. 20% (v/v) di-(2-ethylhexyl) phosphoric acid (HDEHP) in kerosene was employed as the organic membrane phase. The influences of feed pH value, flow rate of feed, stripping and organic phases, stripping acid concentration, and operation time were investigated. A RE extraction percentage of > 95% and preliminary group separation and pre-concentration of RE from the simulated rare earths mine water were achieved.

1 Introduction

Southern China provinces are rich in ion-adsorbed type rare earth (RE) mineral resources. For such kinds of RE ores, rare earth elements (REEs) can be leached by electrolyte solutions [e.g. $(NH_4)_2SO_4$, NH_4Cl, and/or NaCl]. The traditional methods for extracting and concentrating RE from such leachate is precipitation with oxalic acid at pH 1.5-2.5. The resulting rare earths oxalates are calcined into RE oxides (RE_2O_3) and dissolved with hydrochloric acid for the preparation of feed stock solution in the solvent extraction separation and purification plant. This oxalate precipitation method is complicated, time-consuming and reagent-consuming (2-3 kg oxalic acid/1 kg rare earth oxides). In addition, the RE yield of this method is low (about 75%). Therefore, this traditional method is uneconomic for producing RE_2O_3 . Methods of improving the RE yields, simplifying the process and lowering the production costs are under development in order to replace the current oxalate precipitation method. Recovery of rare earths from the leachate solutions by solvent extraction techniques can be a problem due to low rare earths concentration in the solutions.

The liquid membrane process has attracted increasing attention due to its potential capability in the field of separation and pre-concentration from dilute streams. Laboratory studies and pilot plant tests on the extraction of REE from RE ore leachates by emulsion liquid membrane (ELM) have been reported [1]. Before the RE concentrates, obtained from the leachate solution are introduced into the solvent extraction separation and purification plant for the further separation and purification of individual REs, a preliminary separation of the RE concentrates is preferred. Therefore, recent attention has been paid to this preliminary separation of RE when considering the extraction efficiency. A scheme for the extraction and group separation of RE from the leachate solutions has been reported [2], using 8 stages of emulsion liquid membrane separation, giving products of > 95% light RE (La, Ce, Pr, Nd) and heavy RE (Tb, Dy, Ho, Er, Tm, Yb, Lu, Y) and an intermediate RE concentrate. However, the stability of the emulsion liquid membrane (membrane swelling and leakage) is still not satisfactory for routine use. Furthermore, the necessary emulsification and demulsification processes make the process complicated.

In this work, the extraction and group separation of RE from simulated rare earth ore mine water was carried out by a novel hydrometallurgical process: a combined extraction/electrostatic pseudo-liquid membrane.

2 Principle of the process for multi-metal separation

Figure 1 shows a schematic diagram of the ESPLIM setup. A grounded electrode coated with polyethylene film is mounted at the sides of the extraction and stripping cells in the rectangular reaction tank, respectively, and a high voltage electrode (polyethylene coating) is wound on the perforated baffle-plate separating the extraction and stripping cell. The upper part of the reaction tank is filled with organic solution containing a specific extractant for the metal ions to be extracted and separated. The lower part of the tank is an aqueous phase settler and divided by a blank plate. The basic structure of the baffle plate is Λ-shape and is made of hydrophobic polypropylene. The function of the baffle-plate is to provide a passageway for the continuous organic phase and to isolate the feed and stripping solutions in extraction and stripping cells, respectively. When a high voltage electrostatic field is applied to the reaction tank, the aqueous drops (feed and stripping) in the organic continuous phase disintegrate into numerous smaller droplets under the action of the electrostatic field. The resulting aqueous droplet diameters can be less than 0.2 mm under suitable conditions [3]. As a result, a huge contact area between the aqueous phase and the continuous organic phase is produced for metal extraction and stripping in the tank. Under gravity, the feed and stripping droplets in the continuous oil phase sink in their own cells to form cross-current extraction and back-extraction. When they sink into the settler region of the tank, where no electrostatic field is applied, the aqueous droplets coalesce and separate from the organic phase. The extractant dissolved in the continuous organic phase acts as a shuttle to transport metal ions from the extraction cell to the stripping cell. Therefore, the extraction and stripping steps are coupled in the tank by means of the baffle-plate, and the continuous organic phase behaves like a bulk liquid membrane.

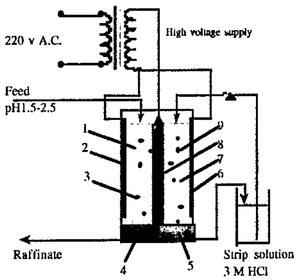

Figure 1: Schematic of the ESPLIM set-up. 1, extraction cell; 2, grounded electrode in the extraction cell; 3, feed droplet; 4, extraction settler; 5, stripping settler; 6, grounded electrode in the stripping cell; 7, stripping cell;, 8, baffle-plate wound with high voltage electrode; 9, stripping droplet

In this work, di-(2-ethylhexyl) phosphoric acid (HDEHP) was used as the extractant. The extraction and stripping reactions for trivalent RE (III) transport in an ESPLIM process using HDEHP as carrier can be generally expressed by the following equations:

$$\text{Extraction: } RE^{3+} + \overline{3(HDEPH)_2} \rightarrow \overline{REH_3(DEHP)_6} + 3H^+ \tag{1}$$

$$\text{Stripping: } 3H^+ + \overline{REH_3(DEHP)_6} \rightarrow \overline{3(HDEPH)_2} + RE^{3+} \tag{2}$$

where $(HDEHP)_2$ represents the dimer of HDEHP in the organic phase, and the overbar denotes the species in the organic phase. At an appropriate pH value (1.5-2.5) of feed solution, HDEHP selectively extracts RE to form a complex, which is the only solute in the organic phase, and Al is not (or only slightly) extracted by HDEHP, and left in the raffinate. The RE-HDEHP complex diffuses across the channels of the baffle plate into the stripping cell. The stability of the complex $REH_3(DEHP)_6$ is usually controlled by the pH value (acidity) of the aqueous phase. At a given acidity, the extraction of RE generally increases with increasing atomic number of REEs. Light, middle and heavy REs can be sequentially stripped from their complexes with HDEHP by a gradient HCl concentration. This separation process is, however, batch-type. An integrated multi-cell ESPLIM set-up (Fig. 2) was used for the continuous extraction and group separation of RE where a series of suitable HCl concentrations of stripping solutions were simultaneously applied to strip a bleed stream of the organic phase so as to maintain a continuous steady-state process. A similar multi-cell ESPLIM has been successfully used for yttrium recovery from waste water in a pilot-scale with a treatment capacity of 30-45 L/h [4].

3 Experimental

3.1 Apparatus

An integrated multi-cell ESPLIM set-up (Fig. 2) was used for the continuous extraction and group separation of REs. The reaction tank was divided by baffle-plates into 20 cells, in which the first cell was employed as the extraction cell and the other 19 as stripping cells. The first 8 stripping cells were used for the stripping of LRE using 0.32-0.5 M HCl, the second 8 for MRE using 0.83-1.2 M HCl, and the last 3 for HRE using 6 M HCl. The baffle-plates were arranged in parallel at intervals of 8-10 mm and wound with electric wires with a 0.25 mm thickness polyethylene film coating, which acted as high voltage and grounded electrodes separately. The inner dimension of the tank was 300 mm deep, 350 mm long and 200 mm wide. The electrode spacing was 8 mm. The settler cells were 35 mm deep.

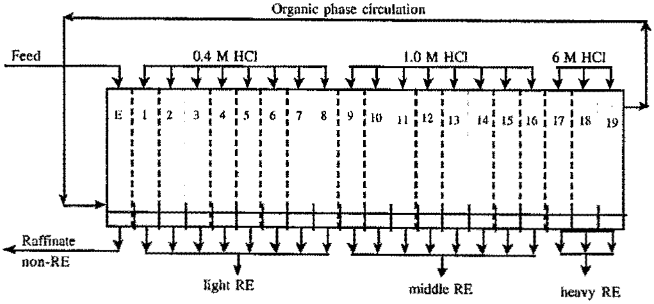

Figure 2: Schematic diagram and flow sheet of the integrated multi-cell ESPLIM set-up

3.2 Reagents and solutions

The organic phase used in this work consisted of 20% di-(2-ethylhexyl) phosphoric acid (HDEHP, industrial purity) and 80% kerosene. The main chemical components of the ion-sorbed rare earth ore leachate solution are given in Table 1. The simulated rare earth ore mine water was prepared by dissolving mixed RE oxides (90% purity) and reagent grade $AlCl_3$, $Ca(NO_3)_2$, $Fe_2(SO_4)_3$, $Pb(NO_3)_2$, NH_4Cl and $(NH_4)_2SO_4$ in concentrated hydrochloric acid and diluting to the corresponding concentration according to Table 1 with de-ionized water.

Components	RE_2O_3	Al_2O_3	Fe_2O_3	CaO	SiO_2	PbO	NH_4Cl	$(NH_4)_2SO_4$
Content (g/L)	1.3-1.5	0.3-0.6	0.05-0.1	0.3-0.5	0.02-0.05	0.01-0.03	5	10

Table 1: The main chemical components of the ion-sorbed RE ore mine water (pH 1.5-2.5)

3.3 Experimental procedure

First, 5.0 kV of high voltage electrostatic field was applied across the electrodes immersed in the organic solution and then the feed solution was pumped to the top of the extraction cell and passed through the extraction cell in once-through mode at a flow rate of 1.0 L/h, while all of the stripping solutions were recycled at a flow rate of 0.5 L/h. The electric current was between 2.4-3.6 mA. 0.32 - 0.4, 0.83 - 1.7, and 6 M HCl were used as the stripping solutions for stripping LRE, MRE, and HRE, respectively.

4 Results and discussion

In general, the parameters affecting the extraction efficiency of the ESPLIM process include the applied electrostatic field strength (this determines the degree of dispersion of aqueous phases in the continuous organic phase), the flow rate of feed and stripping solutions and the carrier concentration in the organic phase. For a specific metal extraction system, the pH value and metal ion concentration of the feed solution, and stripping solution concentration (most commonly the HCl concentration) are important parameters. For the present ESPLIM set-up (0.25 mm thickness of polyethylene film coating for the electrode wire and 8 mm distance between the high voltage and the grounded electrodes), 4.5-5 kV of applied voltage is suitable. A higher voltage causes emulsification of the aqueous phases, which would lead to the unwanted communication of aqueous phases in the extraction and stripping cells as well as difficulty in the phase separation. The feed concentration and flow rate and the extractant concentration of the organic phase play important roles in the extraction efficiency. For a high feed concentration, e.g. >1000 mg/L, the volume flow rate of feed should be kept low in order to obtain suitable extraction efficiency. In this work, the flow rate of the feed solution was fixed at 1 L/h and that of stripping at 0.2-0.5 L/h. The experimental process was usually run for between 12-36 h. The experimental data presented below were at 8-10 h intervals, unless, otherwise specified.

Operation time	Extraction (%)			
(h)	Al	La	Sm	Y
6	33.49	90.22	99.47	99.95
12	6.67	84.35	99.10	99.76
18	5.00	47.83	97.17	99.74
24	3.33	33.70	91.00	97.74
30	0	0	89.17	95.29

Table 2: The dependance of extraction efficiency of La, Sm and Y on the operation time - single ESPLIM. (feed pH 2.6, flowrate=1 L/h; strip 3 M HCl, flowrate=0.5 L/h)

In order to obtain satisfactory extraction efficiency of RE, a sufficiently high concentration of free extractant should be maintained in the organic phase of the extraction cell. In other words, the metal complexes diffusing from the extraction cell through the baffle-plate in the stripping cell should be stripped out by the stripping solution as quickly as possible. This requires a fast back-extraction reaction rate and large enough stripping solution flow rate. The free extractant can be replenished by the back-diffusion of free extractant through the baffle plate from the stripping cell to the extraction cell, which is the only way in a single two-cell ESPLIM setup. Table 2 shows the extraction efficiency of La, Sm and Y as a function of operation time using a single ESPLIM set-up with 3 M HCl for stripping LRE + MRE; the extraction efficiency of La decreased drastically and this was caused by the accumulation of HRE in the organic phase and, as a result, the free extractant concentration in organic phase decreased gradually. In this case, the feed solution loading was stopped and the organic phase was stripped by 6 M HCl for Y. Therefore, for the continuous extraction and separation, a multi-cell ESPLIM set-up was used as shown in Fig. 2 so that stripping using different HCl concentrations could be applied simultaneously and the organic phase could be recycled by a pump. The extraction efficiency of Al, La, Sm and Y as a function of operating time is given in Table 3. Compared with Table 2, the extraction of La was over 94% during 36 h of continuous operation, but it still decreased gradually. This implies that a slight accumulation of Y in the organic phase still occurred. Therefore, in such a case, the organic phase flow rate should be controlled carefully or the cell length increased to ensure long enough contact time between the organic phase and the stripping phase of 6 M HCl for the stripping of HRE and to obtain a suitable separation efficiency

Operation time	Extraction (%)			
(h)	Al	La	Sm	Y
6	38.36	97.60	99.80	99.91
12	37.70	97.24	99.82	99.93
24	35.22	96.13	99.80	99.96
36	33.30	94.54	99.75	99.94

Table 3: Extraction of Al, La, Sm and Y as a function of operation time – Multi-cell ESPLIM. (organic phase flow rate = 0.6 L/h; feed pH 2.6; strip HCl 0.32 M for LRE, 0.83 M for MRE, 6 M for HRE)

HCl	Light RE		Medium RE		Heavy RE		Separation factor	
conc. (M)	Purity	Partition	Purity	Partition	Purity	Partition	Nd/Sm	Gd/Tm
0.32	97.95	35.60		3.31		0.39	5.81	
0.83		48.50	5.21	14.04		1.30		4.72
6.00		15.90		82.65	47.5	98.30		
0.36	96.26	59.07		9.04		0.49	5.93	
1.20		33.76	13.96	61.07		8.51		3.50
6.00		7.27		29.89	70.99	91.00		
0.40	96.35	77.50		14.58		2.77	3.81	
1.70		19.04	27.44	49.56		31.27		1.97
6.00		3.46		35.86	81.84	67.96		
0.50	80.56	82.97		16.74		7.83	1.80	
1.70		16.74	24.48	41.18		34.94		1.64
6.00		0.29		34.94	95.88	57.23		
Feed	58.99		11.96		29.06			

Table 4: Group separation of RE as a function of HCl concentration – Multi-cell ESPLIM

Table 4 summarises the group separation of RE using various HCl concentrations as the stripping solution. 0.32 M HCl stripping acid can raise the purity of light RE from 58% in the feed to 97% in the product, but only 35% in proportion of light RE was stripped out under this condition. Increasing the HCl concentration from 0.32 to 0.50 M can enhance the proportion of light RE from 35% to 82%, but at the cost of decreasing the purity. By controlling the concentration of stripping acid for light and middle REs, over 95% purity light RE, over 95% purity heavy RE, and an intermediate RE concentrate were obtained. 0.4 M and 1.2-1.7 M HCl may be suitable for the stripping of light RE and middle RE, respectively. As the stripping solutions were recycled the concentrations of RE in the stripping solutions increased with time and a very high concentration factor can be obtained.

5 Conclusions

The extraction, rough group separation, and pre-concentration of REEs from a simulated RE ore leachate solution were performed in one continuous run by the proposed process. The main results obtained in this work are as follows: for the simulated ion-sorbed RE ore mine water containing about 1.0 g/L mixed REEs, 10 g/L (NH4)2SO4, 5 g/L NH4Cl and other non-RE ions such as Ca, Al, Si, Fe and Pb, the extraction percentage of total RE was over 95%; the separation factors (SF) were 5.9 and 4.7 for Nd-Sm and Gd-Tb, respectively. A light RE (from La to Nd) product with > 95% purity of light RE, a heavy RE (from Tb to Lu plus Y) products with > 95% purity of heavy RE, and an intermediate RE concentrate were obtained (the purity of light RE and heavy RE in the feed were 57% and 31%, respectively).

References

[1] J.H. Yu, Extraction of rare earths from ion-sorbed rare earth ore by emulsion liquid membranes, Rare Earth (in Chinese), 1 (1987) 1.

[2] J.Z. Luo, and X.J. Zhang, Studies on the three group rare earths separation by liquid membranes, Annual Report of Liquid Membranes in China, p21, 1992.

[3] Z.M. Gu, A new liquid membrane technology — electrostatic pseudo-liquid membrane, J. Membrane Sci., 52 (1990) 77.

[4] Z. Gu, Q. Wu, Z. Zheng, X. Li, Y. Jiang, C. Tang, P. Lin, Laboratory and pilot plant test of yttrium recovery from waste water by electrostatic pseudo liquid membranes, J. Membrane Sci., 93 (1994) 137-147.