RARE EARTH RECOVERY

BY SUPPORTED LIQUID MEMBRANE[①]

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ABSTRACT

A supported liquid membrane(SLM) process was studied for rare earth recovery from dilute solutions. The SLM technique proved to be suitable for recovering and concentrating rare earth from the solutions containing NaCl or$(NH_4)_2SO_4$. The influences of various factors such as different carrier, concentration of carrier, pH value of the feed solution, rare earth concentration, HCl concentration of the strip solution and flow rate of the feed and strip solution on the rare earth flux were studied.

Key words: rare earth   recovery   dilute solution   SLM technique

1   INTRODUCTION

The oxalate precipitation is conventionally adopted for rare earth recovery from dilute solutions such as leaching solutions of low grade ores. However the method has obvious disadvantages. The flow sheet is long, the direct recovery is low and the cost is high. Oxalic acid is poisonous, and only mixed oxides can be yielded. It is necessary to transfrom mixed oxides obtained into chlorides for following treatment. It is better to yield rare earth chlorides from the leaching solutions directly. Solvent extraction technique can do it, but large solvent inventory due to great volume of the leach solution leads to high process cost. In the recent years, liquid membrane has been widely studied as a new technique for separating and concentrating metal ions from hydrometallurgical solutions.

Zhang Reihua, Lu Zhenfang and Wang Xande studied extraction of rare earth from leaching solution of low grade rare ores by means of emulsion liquid membrane (ELM)[1]. The leaching solution containing $3\%(NH_4)_2SO_4$ and 1. 47g/L rare earth was used as the feed solution, D2EHPA(its Chinese trade mark is P_{204})was used as carrier. The membrane phase consisted of 5% $P_{204}+4.5\%$ LMS-2 and 90. 5% kerosene, and 6 mol/L HCl solution was used as inner phase. Through one stage counter-current membrane extraction followed by distillation of yielded inner phase a mixture of rare earth chlorides of purity more than 98% was produced. The operation cost is only 1/3 of that for oxalate precipitation technique. The solvent inventory of SLM is less than 1/10 of that for ELM, SLM is operated without making and breaking emulsion, and the operation environment of SLM is much better than that of ELM. So SLM has more advantages over ELM for recovery of rare

earth from leaching solution. Some theoretical investigation on extraction of some single rare earth metals was made outside China. Recovery of mixed rare earth from leach solution of low grade ores has not been reported yet.

2   EXPERIMENTAL

The feed solution was synthetic rare earth chlorides solution containing NaCl or sulphate solution containing (NH_4)$_2SO_4$. Such composition of feed solution is similar to leaching solution of low grade rare earth ores. The strip solution was prepared from hydrochloride acid of analytical purity and deionized water. The microporous polypropylene hollow fibres"Accurel"(German,EN-KA) were used as substrates throughout the experiments. 2- ethylhexyl phosphonic acid mono-2-ethyl-hexyl ester (its Chinese trade mark is P_{507})and P_{204} were used as the carriers and sulphonating kerosene as the diluent.

A single fibre was used as substrate. The fibre was impregnated with solvent by soaking. Then the fibre was fitted into glass tube. The strip solution circulated through the fibre lumen at a measured flow rate while the feed solution circulated on the shell side of the hollow fibre through the glass tube.

The feed solution and the strip solution were circulated counter-currently at a measured flow rate from the respective reservoirs. The pH values of the feed solution was measured by pHS- 2 pH- measuremeter and controlled by additions of alkali(NaOH) or acid. The temperature was 18～25 C. The strip solution and the feed solution were sampled and analysed at intevals of time.

The permeability of the SLM is expressed by the overal flux of metals J :

$$J = C_{RE·st}V/(tA) \qquad (1)$$

where J —overal flux of metals; V —the volume of strip solution ; t —the time of the experiment; A — the area of the inner surface of fibre,m^2; $C_{RE·st}$ —the rare earth concentration in the strip solution at the time t , g/L.

3   RESULTS AND DISCUSSION

3. 1   *Chloride System*

Many solvents can be used for extraction of rare earth, in present investigation P_{507} and P_{204} were chosen. The experimental results show that P_{507} and P_{204} can be used as carriers of rare earth, but P_{204} is better. Zhang Reihua[1] compared five diluents and maintained that, for extraction of rare earth, the best of them is sulphonating kerosene which is cheap, and it was chosen as diluent in present investigation.

Zhang Rehua adopted HCl, HNO_3 and H_2SO_4 as strip solution in his ELM investigation, and the results showed that at the same ELM conditions the sequence of the ability to strip rare earth is $HCl > HNO_3 > H_2SO_4$. In addition HCl is cheap, so it was chosen as strip solution in present investigation. The influences of the various factors on the rare earth flux were studied and the results are shown in Fig. 1 to Fig. 3.

For the all Figs. $V_F = 500$ mL (V_F is volume of the feed solution), $V_s = 250$ mL (V_s is volume of the strip solution) , $t = 8$h, P_{204} was used as carrier except $J_{RE} - C_{P_{507}}$ curve of Fig. 1. The rare earth concentration in the feed solutions was 2. 65 g/L except the $J_{RE} - V$ curve in Fig. 3, and pH of feed solution was 3 except the $J_{RE} - $ pH curve of Fig. 2. For Fig. 1 to Fig. 3 $v_F = 200$ mL/min. (v_F is flow rate of the feed solution) $v_s = 120$ mL/min. (v_s is flow rate of the strip solution) , HCl concentration of

strip solution was 6 mol/L except Fig. 3.

Fig. 1 shows that P_{204} or p_{507} concentration over 30% will not affect the rare earth flux. With increasing P_{204} and P_{507} concentration the concentration of carrier of rare earth ions increases, the tendency of diffusion of rare earth-carrier complex molecules to the membrane phase-strip solution interface increases. While the viscosity of membrane phase increases also and diffusion rate of the rare earth-carrier complex molecules becomes slow. Due to the simultaneous action of two factors the rare earth flux do not increase with increasing carrier concentration in the high concentration range.
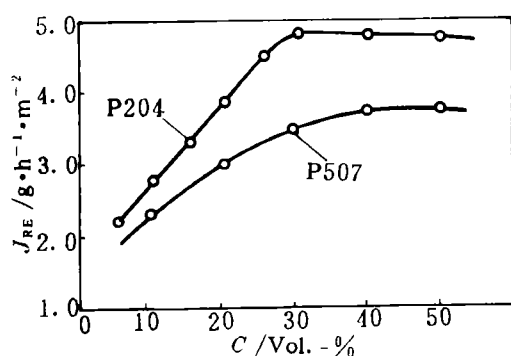

Fig. 1 Influence of P_{204} and P_{507} concentration on rare earth flux(J_{RE})

SEM micrographs of the supports used in the experiments of Guerriero $R^{[6]}$. showed that an increase in deterioration of the polymeric material with increasing D2EHPA concentration took place. As stated above the optimum conceneration of P_{204} or P_{507} in the membrane phase is 30%.

The extraction reaction of rare earth by use of P_{204} or P_{507} can be expressed as:

$$RE_{aq}^{3+} + 3H_2(R_2OP_4)_{2_M} =$$
$$3H_{aq}^{+} + RE(H(R_2PO_4)_2)_{3_M} \quad (1)$$
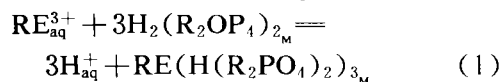
The distribution coefficient is:

$$\cdot K_d = [RE((HR_2PO_4)_2)_3]_M/[RE^{3+}]_{aq} \quad (2)$$

The equilibrium constant is:

$$K = \frac{[RE(H(R_2PO_4)_2)_3]_M[H^+]_{aq}^3}{[RE^{3+}]_{aq}[H_2(R_2PO_4)_2]_M^3} \quad (3)$$

In equations (2)and (3) M and $[\ ]$ stand for membrane phase and concentration respectively.

Combining Eqs. (2) and 3, Eq. (4) can be derived,

$$K_d = K [H_2(R_2PO_4)_2]_M^3/[H^+]_{aq}^3 \quad (4)$$

and $\lg K_d = 3\lg[H_2(R_2PO_4)_2]_M$
$$+ \lg K + 3pH \quad (5)$$

Eq. (5) shows that $\lg K_d$ increases with increasing pH of the feed solution at the same carrier concentration.

According to Danesi[7] P. R. the permeability coefficient can be expressed as

$$P = J/C = K_d/(K_d\triangle_a + \triangle_0) \quad (6)$$

where J stands for the flux, C is metal concentration in the feed solution, $\triangle_a = d_a/D_a$, D_a is the aqueous diffusion coefficient of the metal species, d_a is the thickness of aqueous boundary layer at the feed solution-membrane interface, $\triangle_0 = d_0/D_0$, D_0 is the membrane diffusion coefficient of the metal-containing species, and d_0 is the thickness of membrane.

From Eq. 6, Eq. (7) can be derived:

$$J = C \cdot K_d/(K_d\triangle_a + \triangle_0) \quad (7)$$

It is evident from Eq. 5 and Eq. 7 that the flux increases with increasing pH of feed solution. However as shown in Fig. 2 the flux of rare earth decreases with increasing pH in volume range more than 4.5 due to formation of $RE(OH)_n^{3-n}$. Fig. 2 also shows that the rare earth flux increases with increasing HCl concentration of the strip solution, but when HCl concentration is more than 3 mol/L the J vs[HCl] plot reaches a plateau, demostrating the independence of HCl concentration of the strip solution.

Variation of the concentration of the feed solution almost does not change $\triangle_a$ and $\triangle_0$, and it is evident from Eq. 3 that the flux of rare earth increases with increasing

rare earth concentration in the feed solution as shown in Fig. 3.
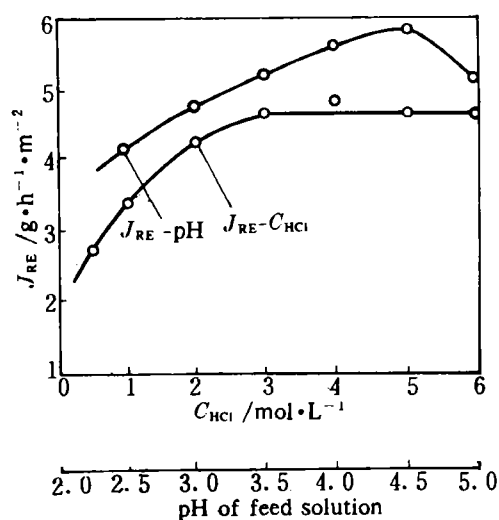
The point A in Fig. 3 expresses the flux

Fig. 2   Influence of feed solution pH and HCl concentration(C_{HCl}) of strip solution on RE flux
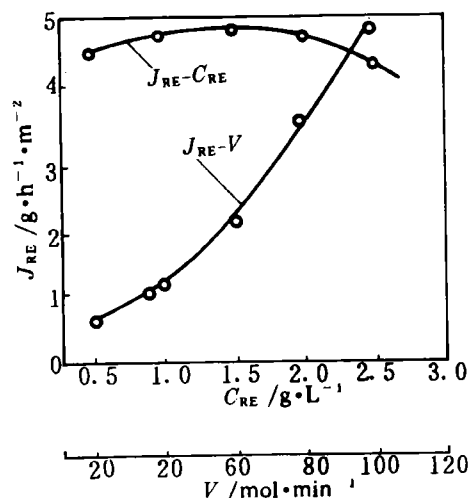

Fig. 3   Influence of RE conc. (C_{RE})and feed solution on flux.

for the feed solution containing NaCl 70 g/ L. It indicates that the NaCl concentration does not affect the rare earth flux.

With increasing flow rate of the feed solution the thickness of the aqueons boundary layer at the feed solution- membrane inter-

face decreases, so $\triangle_a$ decreases too, as the result the flux J increases.

At higher rate the organic film is probably lost to the aqueous phase.

3. 2   Sulphate System

Comparison between the results of SLM recovery of rare earth from sulphate and chloride solutions indicates that the effect of extraction from.sulphate solution containing $(NH_4)_2SO_4$ is better than that from chloride solution containing NaCl. The influence of the$(NH_4)_2SO_4$ concentration in the feed solution on the rare earth flux is shown in Fig. 4.
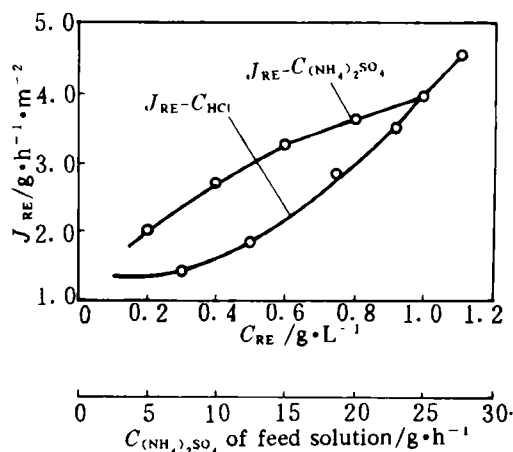

Fig. 4   Influence of $(NH_4)_2SO_4$ and RE conc. ($C_{(NH_4)_2SO_4}$ of feed solution/$g \cdot L^{-1}$) on RE flux

Fig. 4 also indicates that as for chloride system the rare earth flux increases with increasing rare earth concentration in the feed solution.

For Fig. 4 $V_F = 500\,mL$, $V_s = 250\,mL$, $v_F = 60\,mL/min$, $v_s = 120\,mL/min$, pH of solution was 3, HCl concentration of strip solution was $3\,mol/L$. Time interval of experiment was 8h, RE concentration of feed solution was $0.93\,g/L$ and $(NH_4)_2SO_4$ concentration was $15\,g/L$. The membrane

phase consisted of 30% $P_{204}+$ sulphonating kerosene.

4 CONCLUSIONS

The SLM technique has proved to be suitable for recovering and concentrating rare earth from leaching solutions of low grade ores .

At optimum conditions the rare earth flux can achieve 5 g/m^2. h, and this technique may hold some promise of commercial recovery of rare earth from dilute solutios, for example, from the leaching solution of low grade ores.

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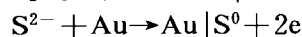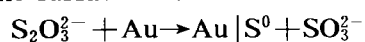
$(NH_3)_2^+$ acts as the intermediate speices in the process.

5 CONCLUSIONS

The anodic process of gold electrode in thiosulfate solution consists of an active dissolution reaction as

$$Au \rightarrow Au^+ + e$$
$$Au^+ + 2S_2O_3^{2-} \rightarrow Au(S_2O_3)_2^{3-}$$
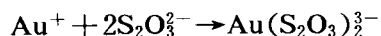
and a simultaneous passive reaction of formation and then adsorption of elemental sulfur on the surface of the electrode as

$$S_2O_3^{2-} + Au \rightarrow Au|S^0 + SO_3^{2-}$$
$$S^{2-} + Au \rightarrow Au|S^0 + 2e$$

By adding ammonia into thiosulfate system, the passivation of the electrode can be eliminated, and the process may described as

$$Au \rightarrow Au^+ + e$$
$$Au^+ + 2NH_3 \rightarrow Au(NH_3)_2^+$$
$$Au(NH_3)_2^+ + 2S_2O_3 \rightarrow Au(S_2O_3)_2^3$$
$$+ 2NH_3$$

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