Extraction of Scandium from Red Mud Using ELM with P204 as Carrier

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Abstract: Scandium is an important rare earth element. Stacking of red mud has caused serious environmental and social issues. Red mud is rich in scandium. In this paper, recovery of scandium from red mud by emulsion liquid membrane (ELM) was studied. Composition of ELM is P204-Span80-sulfonated kerosene-HCl. Effects of mobile carrier and surfactant concentration, Roi, Rwe, internal and external aqueous phase acidity on the extracting rate of Sc^{3+} were studied. Results show that it is feasible for P204-Span80-Sulfonated Kerosene-HCl ELM System extracting Sc^{3+} from red mud leaching solution. The optimum condition is P204=12%, Span80=3%, Roi= 2:3, Rwe=6, the internal aqueous $c(HCl) = 4 mol/L$, the external aqueous phase $pH=2$, the time of making emulsion is 20 minutes, extracting time is 15 minutes. The extracting rate of $Sc³⁺$ can reach to 99.6% under optimal condition. The extracting rate of other impurities is lower than 5%.

Introduction

Rare earth element scandium has huge economic importance and important strategic significance.^[1] Independent deposits of scandium are very small in nature. Bauxite, which account for 70% to 80% Sc reserves, has not been used as raw material for extraction of scandium^[2]. 98% of scandium in the bauxite is enriched to red mud. At present, solvent extraction is chief method of extracting scandium, but for trace scandium solution, to achieve a higher enrichment ratio need more extraction stages and long process, which costs a $\text{lot}^{[3]}$. Therefore, general solvent extraction is not suitable for extracting scandium from red mud, which results in a large number of scandium resources can not be comprehensive utilization^[4].

Emulsion liquid membrane (ELM) is a new separating technology with high efficiency^[5]. Many scholars have done a lot of research on extracting rare earth with ELM and the extraction technology of the trace scandium from rare earth ore has made a relatively good result^[6]. However, research on extracting scandium from red mud with ELM is rarely reported. Therefore, research on extracting scandium from the red mud with ELM will accelerate the development of scandium extraction process and utilization of Sc resources in China.

Experimental section

Reagents and Instruments

Main reagents: phosphate dioctyl (P204), chemical pure; surfactant dehydration sorbitol monooleate (Span80); membrane solvent: sulfonated kerosene, industrial pure; hydrochloric acid (HCl), commercially pure.

Main instruments: CNC constant speed blender, emulsification device, high voltage electrostatic demulsifier, PHS-3C type pH meter, 722-type spectrophotometer.

Leaching Sc(III) from red mud

Red mud sample was taken from one certain alumina plant, using 6mol/L HCl as leaching agent, and liquid-solid ratio was 5:1, the leaching temperature was 60° C, leaching time was 1h. Then transferred to 100mL flask, fixed and mixed. Main metal ions in the leaching solution are Fe^{3+} , Al^{3+} , Sc³⁺, Ti⁴⁺, and their concentration are Sc³⁺ 6.5mg/L, Ti⁴⁺ 0.032 g/L, Fe³⁺ 7.8 g/L. Condition Experiment

In the experiment, composition of the ELM's oil film is P204 + Span80 + sulfonated kerosene. Oil phase and internal water phase (HCl solution) was put into emulsification device, and stirred with high-speed (the speed is greater than 2000 rpm) for 20 minutes, and the milky white liquid obtained is a kind of water in oil type (W/O) emulsion. Then a certain proportion of the emulsion and leaching solution of red mud were put into a constant mixing container and stirred at $250~300$ rpm for 15 minutes. The upper emulsion was transferred to a demulsifier after standing and stratifying, demulsified with high voltage electrostatic demulsifier. Then the oil emulsion was return to emulsify. The recovered Sc^{3+} was enriched in the water phase. The concentration of Sc^{3+} was determined by spectrophotometer, and $Fe³⁺$ was determined by complexometric titration.

Comprehensive Experiment

Comprehensive experiment of recovery of $Sc³⁺$ from red mud leaching solution was performed according to the optimum conditions from condition experiment.

Results and discussion

Effect of mobile carrier concentration on the extracting rate of Sc^{3+} .

Mobile carrier, a soluble compound that adds to the ELM, can transport components in the liquid membrane selectively and increase transfer rate of material to be separated (solute or ion). It plays a decisive role in the selectivity and flux of components. Mobile carrier is the critical mass fraction to achieve separation and mass transfer of liquid membrane. Effect of mobile carrier concentration on the extracting rate of Sc^{3+} is shown in Figure 1 (Span80%=4%, Roi =2:3, Rwe=6, 15min, the external aqueous phase $pH=2.0$, the internal aqueous $c(HCl)=3mol/L$.

Fig.1 Effect of P204% on the extracting rate of Sc^{3+} Fig.2 Effect of span80% on the extracting rate of Sc^{3+}

Fig.1 shows that extraction rate of Sc^{3+} increased when the volume fraction of P204 was lower than 12%, and decreased when the volume fraction of P204 was higher than 12%. This is because the stability of ELM will decrease and appear swelling when the mobile carrier concentration is too high, which resulted in the Sc³⁺ extraction rate decrease^[7]. Therefore, optimal concentration range of mobile carrier concentration is 8%-12%.

Effect of surfactant concentration on the extracting rate of Sc^{3+} :

Surfactant is an important component of ELM. It plays a role of stabilizing film form, fixing oil water interface and affecting the penetration rate of solute. Effect of surfactant concentration on the extracting rate of Sc^{3+} is shown in Figure 2 (P204%=8%, Roi =2:3, Rwe=6:1, 15min, the external aqueous phase $pH=2.0$, the internal aqueous $c(HCl)=3mol/L$.

Fig.2 shows that extraction rate of $Sc³⁺$ rised as the volume fraction of Span80 increased. But extraction rate of Sc^{3+} was little changed when the concentration of Span80 is higher than 3%. This is because, when the concentration of surfactant is too high, ELM is difficult to be demulsified $[8]$. Therefore, we chose surfactant concentration as 3%.

Effect of the internal aqueous phase acidity on the extracting rate of Sc^{3+} .

Migration of Sc^{3+} in mobile carrier follows the reverse mass transfer mechanism. A high H⁺ concentration difference between both sides of the membrane phase is a prerequisite to ensure the continued migration of Sc³⁺, so internal aqueous phase must have a high H^+ concentration^[9]. In this study, we use HCl solution as the internal aqueous phase, and effect of the internal aqueous phase acidity on the extracting rate of Sc^{3+} are shown in Figure 3 (P204%=8%, Span80%=3%, Roi =2:3, Rwe=6, 15min, the external aqueous phase pH=2.0).

Fig. 3 shows that, when the internal aqueous phase cHCl is lower than 4mol/L, the Sc³⁺ extraction rate increases with acidity. This is because as H+ concentration difference between both sides of the membrane phase is increasing, the mass transfer of Sc^{3+} is speeded up. If acidity is too high, the stability of ELM will decrease and appear swelling, Sc^{3+} extraction rate decrease. Therefore, we choose the internal aqueous phase acidity as 4mol/L.

Effect of the external aqueous phase acidity on the extracting rate of Sc^{3+} :

Effect of the external aqueous phase acidity on the extracting rate of scandium is shown in Figure 4 $(P204\% = 8\%, \text{Span } 80\% = 3\%, \text{Roi } = 2.3, \text{Rwe } = 6, 15 \text{min}, \text{ the internal aqueous } c(\text{HCl}) = 3 \text{ mol/L}.$

Fig.4 shows that the extraction rate of Sc increases with exaltation of the external aqueous phase pH. When pH=0.5~2.0, the Sc³⁺ extraction rate increase obviously. When pH=2.0, Sc extraction rate reaches to 98% and it alter little when pH is further increased. Therefore, we choose external aqueous phase $pH = 2.0$.

Effect of Roi on the extracting rate of $Sc³⁺$:

Roi is the volume ratio of oil phase and the internal aqueous phase volume. Roi effects the structure stability of ELM and the migration speed of material to be separated (solute or ion). Effect of Roi on the extracting rate of Sc^{3+} is shown in Figure 5 (P204%=8%, Span80%=4%, Rwe=6, 15min, the internal aqueous $c(HCl) = 3mol/L$, the external aqueous phase $pH=2$).

Fig.5 shows that, when Roi is between 2:3 and 1:1, Sc^{3+} extracting rate is higher than 96%. This is because viscosity of the liquid membrane will rise when Roi increases, which will result in decline of the mass transfer rate. Meanwhile the liquid membrane will be difficult to be break. On the other hand, the stability of the liquid membrane will be declined when Roi is too low[14]. Therefore, we choose Roi as 2:3 to 1:1.

Effect of Rew on the extracting rate of $Sc³⁺$:

Rwe is the volume ratio of the external aqueous phase and ELM. Rwe is an important economic and technical indicator of ELM. Lower Rwe is better as long as separating efficiency can be satisfied. Effect of Rwe on the extracting rate of Sc³⁺ as shown in Figure.4 ((P204%=8%, Span80%=4%, Roi= 2:3, 15min, the internal aqueous $c(HCl) = 3mol/L$, the external aqueous phase pH=2).

 $Sc³⁺$ decrease obviously when Rwe is higher than 8:1. This is because Rwe is too high, the stability of ELM decreased, while the contact area between the external phase and liquid membrane reduce. When Rwe is too low, consumption of liquid membrane and costs increase, which does not meet economical requirements. Therefore, we choose Rwe as 6~8.

Fig.5 Effect of Roi on the extracting rate of Sc^{3+} Fig.6 Effect of Rwe on the extracting rate of Sc^{3+}

Comprehensive experiment:

Condition of comprehensive experiment is P204=12%, Span80=3%, Roi= 2:3, Rwe=6, the internal aqueous $c(HCl) = 4 \text{mol/L}$, the external aqueous phase $pH=2$, the time of making emulsion is 20 minutes, extracting time is 15 minutes. The extracting rate of Sc^{3+} was up to 99.6% and the extracting rate of other impurities such as $Ti4+$ and $Fe³⁺$ are lower than 5%. This ELM can achieve separation of scandium and other impurities.

Conclusions

- (1) The optimum conditions for ELM extracting Sc^{3+} from the red mud is P204=12%, Span80=3%, Roi=2:3, Rwe=6, the internal aqueous $c(HCl) = 4$ mol/L, the external aqueous phase pH=2, the time of making emulsion is 20 minutes, extracting time is 15 minutes;
- (2) It is feasible for ELM extracting Sc^{3+} from the red mud. The extracting rate of Sc^{3+} reaches to 99.6% under optimal conditions. The extracting rate of other impurities is lower than 5%. This ELM can achieve effective separation of scandium and other impurities.

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