

Solvent extraction of scandium from chlorination system with EHPAEH

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Abstract. The extraction of scandium from hydrochloric acid media with EHPAEH is investigated. Fe³⁺ in synthesized solution would reduce the purity of scandium, therefore, N235 is selected as extractant for separating Fe³⁺ and Sc³⁺. Experimental results indicated that separation factor $\beta_{Fe/Sc}$ reached 5416.4 with the organic system consisting of 20 vol% trinoctylamine(N235), phase volume ratio(O/A) of 1:1, extraction stage of 3. Then mono(2-ethyl hexyl)-2-ethyl hexyl phosphonate(EHPAEH) is employed to extract Sc³⁺ from the leaching solution of Fe³⁺ free. With the organic phase containing 5 vol% EHPAEH, phase volume ratio O/A of 1:5, at pH 0.3, nearly 99% scandium is extracted. Finally, the scandium-loaded organic phase is stripped with 4.5N hydrochloric acid, under phase volume ratio of 1:1 at 65°C.

1 Introduction

Scandium, an important Rare Earth element, is widely used in advanced ceramics, electric lighting source, electronic and other high-tech fields due to its excellent physical and chemical properties. In nature, independent scandium deposits are rare, it is usually associated with other metals and mainly recovered as by-product from residues, tailings and waste liquors in the smelting process of some metals such as rare earths, uranium, titanium, tungsten, aluminium, tantalum and niobium[1,2]. In this experiment, raw material is the residue originated in TiCl₄ production by boiling chlorinating method (and the scandium compounds are enriched in it)[3].

Scandium in chlorination residue can be leached with hydrochloric acid. The methods of recovering scandium from synthesized solutions usually include solvent extraction[4-8]and ion exchange[4,9-11].

Solvent extraction with the characteristics of efficiency and economical is widely used in the enrichment and purification of many metals. Plenty of extractants can be used for scandium concentrate and separate it from other metal ions [2]. Acidic organophosphorus and neutral organophosphorus are two common types of extractants. Nearly 100% scandium is extracted from chloride solutions with 20 vol% di-2-ethylhexyl phosphoric acid(D2EHPA, in China used to call P₂₀₄)[5].

In this paper, Fe³⁺ is removed by N₂₃₅ before extracting Sc³⁺ with EHPAEH. Experimental parameters which affecting extraction process, such as concentration of

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extractants, phase volume ratio (O/A), temperature and extraction stages are investigated in detail and the optimal experimental conditions are carried out.

2 Experimental

2.1 Aqueous solution

Synthetic leaching solution for this experiment was prepared by dissolving chlorination dust with 1mol/L HCl, liquid to solid ratio (L/S) of 2:1, at 75°C holding for 3h. (The concentration of Sc^{3+} and Fe^{3+} were respectively 238.3mg/L and 3.1g/L). All aqueous solutions were made up using distilled water.

2.2 Organic reagents

Extractant Trinooctylamine (N235) and Mono(2-ethyl hexyl)-2-ethyl hexyl phosphonate (EHPAEH) were of industrial grade. Modifier Sec-Octyl alcohol analytical grade was of analytical grade. Diluent sulfonated kerosene was of industrial grade. All reagents were directly used without further purification.

2.3 Test produces

Extraction and stripping experiments were carried out in a 125 ml separating funnel by contacting the organic and aqueous phases under the given experimental condition including certain pH, composition of organic phase, phase volume ratio O/A and temperature. The funnel was immersed in a temperature controlled water bath to keep temperature constant (and ensure a well mixed model between organic and aqueous solution). When the reaction reached equilibrium, organic phase and aqueous phase was separated, then ion concentrations in aqueous solution was analyzed.

2.4 Test method and calculation formula

Each test, about 10mL aqueous solution was taken for chemical analysis. Inductively Coupled Plasma and Atomic Emission Spectroscopy (ICP-AES) was used to test the concentration of scandium. The model of 722s spectrophotometer was used to test the concentration of Fe^{3+} , and sulfosalicylic acid was served as chromogenic agent. Sartorius PHS-3 pH meter was employed to measure pH value in aqueous solution.

3. Results and discussion

3.1 Removal of Fe^{3+} by Trinooctylamine (N₂₃₅)

The main impurities in the synthetic leaching solutions are iron, aluminum, manganese, calcium, titanium, manganese, etc. Preliminary experiments have shown that the co-extraction rate of Mn^{2+} and Fe^{3+} were relatively high when extracted with acidic organophosphorus. It will pose interference to the purity of scandium. Mn^{2+} can be removed by hydrolysis precipitation method due to the big difference of precipitation pH. In this experiment, the effect of N₂₃₅ concentration, modifier concentration, extraction stage on and separation factor were studied.

3.1.1 The effect of N_{235} concentration

Different concentrations of N_{235} in sulfonated kerosene between 5 vol% and 40 vol% were employed in the preliminary experiment and kept phase volume ratio O/A of 1:1. The results shows that with the increase concentration of N_{235} , the extraction rate of Fe^{3+} gradually increased, while it presents very little effect on the Sc^{3+} with the extraction rate always less than 2 vol%. However, organic phase turns into a turbidity, when concentration exceeded 20 vol%. The extraction rate only increased by 3.31% with N_{235} concentration increasing from 20 vol% to 30 vol% and the change of extraction rate and separation factor are very small after over 40 vol%. The appropriate concentration of N_{235} in sulfonated kerosene is 20 vol% and it was set up in the following experiments.

Table 1. Effect of N_{235} concentration on extraction.

No.	N_{235} concentrations (vol%)	E_{Fe} (%)	E_{Sc} (%)	$\beta_{Fe/Sc}$
1	5	71.61	0.88	284.1
2	10	80.65	1.26	326.6
3	20	85.81	1.34	445.2
4	30	88.71	1.72	449.0
5	40	87.74	1.59	442.9

3.1.2 The effect of modifier concentration

Although N_{235} has a good property on separation of Sc^{3+} and Fe^{3+} , the separation rate of organic phase and aqueous phase is slow and easy to appear a third phase in organic phase. In order to solve this problem, a modifier Sec-Octyl alcohol was added into the organic phase. In this experiments, the concentration of Sec-Octyl alcohol was varied from 0 vol% to 25 vol% with other parameters constant.

Table 2. Effect of modifier concentration on extraction.

No.	Sec-Octyl alcohol concentration (vol%)	E_{Fe} (%)	E_{Sc} (%)	$\beta_{Sc/Fe}$	The third phase
1	0	85.65	1.34	445.2	existent
2	5	85.32	1.34	427.9	non-existent
3	10	85.16	1.30	435.7	non-existent
4	15	85.16	1.26	449.7	non-existent
5	20	80.00	1.28	308.5	non-existent
6	25	71.61	1.20	207.7	non-existent

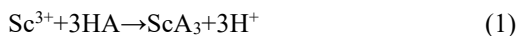
No difficulty was encountered in phase separation when adding Sec-Octyl alcohol. As shown in Table 2, the change of Fe^{3+} extraction rate is small with Sec-Octyl alcohol less than 15%, but sharply dropped when it exceeded 15%, while the change of Sc^{3+} is almost negligible. This may be due to the formation of complexation between Sec-Octyl alcohol and N_{235} thus reduce the effective concentration of extractant then prevented the combination of Fe^{3+} and N_{235} . Therefore, the concentration of Sec-Octyl alcohol should be no more than 15 vol%.

3.2 Solvent extraction of scandium

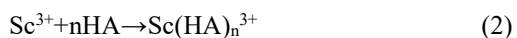
EHPAEH is a kind of organophosphorus acids extractant which is similar to DE2HPA. But EHPAEH is easier to be stripped owing to its weaker extraction ability. In addition, it is more suitable for extracting Sc^{3+} from high acidity solution[4]. In this experiment,

EHPAEH is employed to extract Sc^{3+} . The extraction principles are as follows[4]:

① in low acidity system:



② in high acidity system:



It can be seen from reaction Eq. (1) and (2) that cation exchange reaction exits in low acidity solution and solvation exits in high acidity solution[4,12].

The effects of experimental parameters, such as aqueous pH, EHPAEH concentration, and phase volume ratio are investigated to determine the optimum operating conditions.

Poor phase separation easily appears in the extraction process when organic phase contained only EHPAEH in sulfonated kerosene. After adding 15 vol% sec-Octyl alcohol as modifier, phase separation improves significantly.

3.2.1 Effect of pH

In the experiment, pH was regulated in the range of 0~2.0 (under the following conditions) with 5 vol% EHPAEH in sulfonated kerosene, phase volume ratio O/A ratio of 1:1 and the temperature of 25°C).

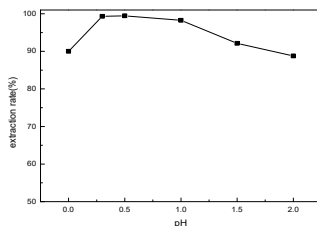


Fig. 1. Effect of solution pH on extraction rate.

It can be seen from Fig.1 that at beginning, with the increase of pH, the extraction rate of Sc^{3+} gradually increased then significantly decreased after pH greater than 0.9. The preferable pH range for scandium extraction is 0.3~1.0. The extraction rate gradually decreased with pH greater than 1.0, possibly caused by impurity irons hydrolysis. The initial pH 0.3 is in the appropriate range, so directly extraction without adjusting pH is feasible.

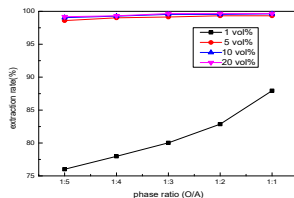


Fig. 2. Effect of phase ratio on extraction rate with different EHPAEH concentration.

3.2.2 Effect of EHPAEH concentration and phase volume ratio

Fig.2 shows the effect of phase volume ratio O/A on the Sc^{3+} extraction rate at different EHPAEH concentrations. Extraction rate increased with both increasing concentrations and increasing volume phase ratio. But lower O/A is beneficial to concentrating scandium in the organic phase[4]. Scandium has more charge and smaller ionic radius which shows the great electron affinity and extractability, therefore, the selectivity of scandium over other metals is increased with low EHPAEH concentration. Since extraction rate doesn't increase obviously with the concentration of EHPAEH over 5 vol% and O/A over 1:5, 5 vol% and 1:5 is the decent concentration and phase volume ratio, respectively.

3.3 Stripping of scandium

3.3.1 Effect of hydrochloric acid concentration and phase volume ratio

Lanthanide element has the characteristic of lanthanide contraction. It means the atomic radius of the sixth periodic element is smaller than the fifth. From lanthanum to lutetium with the increase of nuclear charge, the effective nuclear charge gradually increases, which cause the atomic volume reduced. Consequently the heavy rare earth elements with larger atomic number has more smaller radius. Scandium that located in the forth periodic is similar to heavy rare earth elements in terms of atomic radius. Therefore it requires high hydrochloric acid concentration in the stripping process[4].

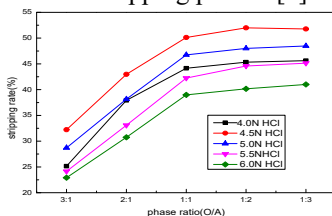


Fig. 3. Effect of phase ratio on stripping rate with different concentration of hydrochloric acid.

The effect of phase volume ratio O/A with different hydrochloric acid concentration on stripping rate of scandium was investigated. Fig.3 shows that at the outset the stripping rate of scandium gradually increased with the increasing acid concentration and it reaches the maximum of 50.13% with 4.5mol/L HCl then begin to drop. Similarly, with the increase of phase volume ratio(O/A), the stripping rate of scandium gradually increased, then stables in a certain range with phase volume ratio over 1:1.

3.3.2 Effect of temperature

Scandium was stripped from scandium-loaded organic phase at different temperatures with the fixed condition of 4.5N HCl, phase ratio O/A of 1:1. Fig.4 shows that at beginning with the increase of temperature, the stripping rate of Sc^{3+} gradually increased, but it only increased by 0.91% (from 80.36% to 81.27%) when temperature increased from 65°C to 85°C. Furthermore, high temperature easily led to the organics. To sum up, 65°C is appropriate.

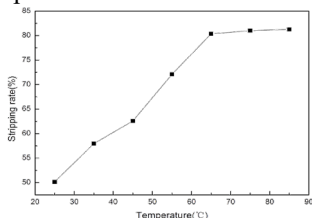


Fig. 4. Effect of temperature on stripping rate.

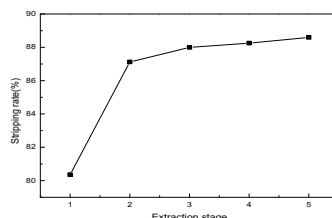


Fig. 5. Effect of stripping stage on stripping rate.

3.3.3 Effect of stripping stage

According to Fig.5, the stripping rate of scandium is improved by increasing stripping stage. After two stages, the stripping rate reached 87.12% then increased slowly. After certain treatment, the organic solvent is reused for extraction.

4 Conclusion

N₂₃₅ demonstrates better selectivity for Fe³⁺ and Sc³⁺. More than 99% Fe³⁺ in synthetic solution is extracted into organic phase while little scandium is co-extracted. The separation factor $\beta_{Fe/Sc}$ reaches 5416.4 with the organic system consisting of 20 vol% N₂₃₅+15 vol% Sec-Octyl alcohol+65 vol% sulfonated kerosene, phase volume ratio O/A of 1:1, temperature of 25°C, and extraction stages of three.

EHPAEH has a high scandium extraction ability, even small amount can acquire good results. The extraction rate of Sc³⁺ reaches 98.59% with the organic system consisting of 5 vol% EHPAEH, 15 vol% sec-Octyl alcohol+80 vol% sulfonated kerosene, phase volume ratio (O/A) of 1:5, at pH 0.3.

Finally the Sc extracted complexes is stripped by hydrochloric acid. With increasing of temperature and hydrochloric acid concentration, the stripping rate of Sc³⁺ increases quickly but tend to be smooth finally. Under the conditions of hydrochloric acid concentration 4.5N, temperature of 65°C, stripping stages of two, 87.12% scandium in organic phase returns into aqueous phase.

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