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Removal of impurities from scandium chloride solution using 732-type resin☆

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ABSTRACT

The deep removal of Al, Fe(II/III), Ca, Zr, Ti and Si from scandium chloride solution was carried out by using 732-type strong acid cation exchange resin. The effects of pH value, contact time and complexing agents (EDTA) on the purification process are investigated. The results indicate that the 732-type resin have a good scandium selectivity and the adsorption order is Sc > Fe(III)>Al > Ca > Zr > Ti > Si in the pH range of 1–3. The separation of Sc and Zr, Si, Ti can be directly carried out because the resin have a good adsorption effect on Sc, Al and Fe(III) but poor adsorption effect on Zr, Si and Ti under the condition of pH = 2.5 and contact time 180 min. The Fe(II), Ca and Al are selectively adsorbed on the resin by adding reducing agent ascorbic acid and EDTA into the solution for reducing Fe(III) to Fe(II) and complexing Sc. By using two-step ion exchange adsorption separation method, the removal rates of Fe(III), Ti, Al, Ca, Zr and Si are 95.5%, 99.8%, 100%, 98.2%, 98.6% and 100%, respectively.

1. Introduction

Currently, the methods such as chemical precipitation, solvent extraction and ion exchange have been used in high purity scandium oxide preparation.[1] The chemical precipitation is the conventional method on separation and concentration of scandium. However, it is hard to obtain a high purity scandium compounds by using this method.[2,3] The solvent extraction is one of the most widely used method on purification and separation of scandium. This method provides advantages including high selectivity, large throughput and ease operation.[4] The extractant TBP could properly separate scandium from titanium, calcium, aluminum and other rare earth elements in the solution containing 9 mol/L Cl^{-}.[5] A process using methyl dioctyl phosphate (DIOMP) as synergic reagent in TBP was developed by Korovin[6] to improve the separation coefficient of scandium and impurities. Wang et al.[7] had proposed a process by that over 99% scandium was extracted and almost no iron and aluminum were co-extracted with the extractant consisting of D2EHPA and TBP. In this process, the $Sc(OH)_3$ product was obtained by using precipitation of Sc with sodium hydroxide solution from strip liquors. A selective extraction of Sc using Cyanex 923 as extractant from titanium white waste acid has been reported by Li et al.[8] The primary amine N1923 and tertiary amine N235 could be used as extractant to obtain 90% purity scandium, and 30% P507-70% kerosene could effectively separate Sc from Fe, Al, Ca, Y and so on.[9–11] Using P350-HCl system produces more than 99.99% purity of scandium as reported as well by Zhang.[12] Karve et al.[13] and Vibhute et al.[14] proposed a process in which Sc could be separated from Fe, Al, Mn, Ce, Th, etc. efficiently by 0.1 mol/L quaternary ammonium chloride Aliquat 336S. It is known that ion exchange exhibits great advantages in some difficult separation elements. Lin et al.[15] used 732-type resin 732-type to separate Sc from feed solution containing Ca, Mn, Fe, Ti, Al and Mg by selective elution with different strippants (NH_4SCN, HCl, NaCl, HCl). Sokolova[16] separated Zr from Sc by sorption with KRF-20t-60 cation exchanger effectively. Smirnov and Molchanova[17] used ampholite resins AFI-21 and AFI-22 to extract scandium and uranium from red mud resulting from alumina production. Herchenroeder et al.[18,19] have proposed a process that ion exchange chromatography were used to prepare kilogram quantities of Sc_2O_3 of ultrahigh purity which upgraded about 10 kg of Sc_2O_3 from 98% to 99.995% purity. Using extraction

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chromatography,[20,21] levextrel-type resin[22] and liquid membrane extraction[23–25] to purify scandium has been mentioned in some literature.

The purpose of this paper was to purify scandium chloride solution by using 732-type strong acid cation exchange resin. The adsorption behaviors of Sc and impurities such as Al, Fe(III), Ca, Zr, Ti and Si were investigated to explore the most appropriate experimental conditions and develop a novel process of the purification of scandium chloride solution. The process consisted of two ion exchange steps: the removal of Ti, Zr and Si from scandium chloride solution in the first step, and the removal of Fe(III), Ca and Al with the addition of ascorbic acid and EDTA in the second step.

2. Materials and methods

2.1. Materials

The 732-type strongly acidic cation exchange resin used in this study was made by Zhejiang Zhengguang industrial Co., Ltd. The feed solution was prepared by dissolving corresponding salts or oxide in hydrochloric acid. Specifically, a certain amount of Sc_2O_3 was added to the beaker containing 1–2 mol/L hydrochloric acid and stirred continuously until all dissolved on the electric stove at 150–200 °C, and then Fe_2O_3, $AlCl_3·6H_2O$, $Na_2SiO_3·9H_2O$, $ZrOCl_2·8H_2O$, $CaCO_3$, $TiCl_4$ were added to the prepared scandium chloride in proper order. The Sc_2O_3 was prepared by Sinopharm Chemical Reagent Co., Ltd. All chemicals used were of analytical grade. The typical compositions of feed solution are shown in Table 1.

2.2. Experimental methods

The static adsorption tests were carried out by mixing 100 mL feed solution and 10 mL 732-type resin in a conical flask immersed in a water bath and constant temperature oscillator at 25 °C for a certain time.

The column tests were carried out by using an ion exchange column with 6.4 mm diameter and 200 mm height. The dynamic ion exchange experimental device is shown in Fig. 1. The volume of 732-type of resin packed in the column was 10 mL. The feed solution was fed to the bottom of the ion exchange column by using a peristaltic pump. The ion exchanged liquid that outflowed from the top of the column was taken periodically by using the automatic sampling instrument. The saturated resins were washed with distilled water, and then 2 mol/L HCl solution was used as strippant. The concentrations of Sc and impurities in the solution were analyzed by using an inductive coupled plasma emission spectrometer (ICP). The concentration of Sc and impurities in resin and the adsorption rate of Sc and impurities were calculated based on mass balance.

3. Results and discussion

3.1. Effect of pH

Fig. 2 shows the effect of initial pH value on adsorption of Sc, Fe(III), Al, Zr, Ca, Ti and Si. It can be seen from Fig. 2 that the adsorption order was Zr > Sc > Fe(III) > Al > Ti > Si at pH ≤ 0.5, while it was Sc > Fe(III) > Al > Ca > Zr > Ti > Si at pH = 1–3. The adsorption rate of Sc, Fe(III) and Al changed a lot with the pH value. The adsorption rates of Sc, Fe(III) and Al which increased with the increase of pH value were 84.2%, 75.3% and 63.9%, respectively at pH 2.5. In contrast, the adsorption rate of Zr and Ti decreased with increase of the pH value and were 10.7% and 6.3%, respectively at pH 2.5. The pH value had a little influence on the adsorption of Ca which stabled at 40%. The Si was adsorbed on the resin which was probably caused by physical adsorption of colloidal silicic formed at a low pH value.

Table 1
Main compositions of the feed solution.

Elements	Sc	Fe(III)	Ti	Al	Ca	Si	Zr
Concentration/(g/L)	0.5	0.5	0.1	0.5	0.5	0.1	0.5

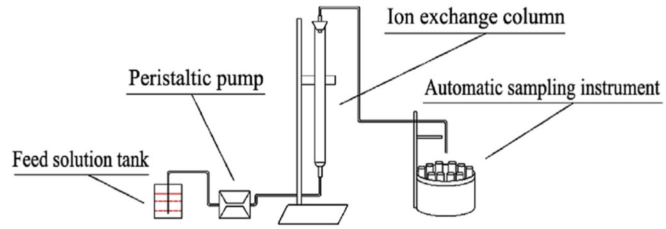

Fig. 1. Dynamic ion exchange experimental devices.

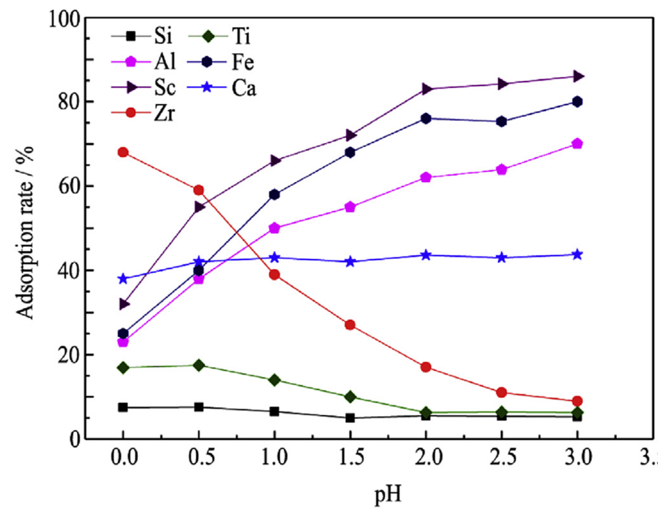

Fig. 2. Effect of initial pH value on adsorption of Sc, Fe(III), Al, Zr, Ca, Ti and Si (200 r/min, 25 °C, 180 min).

Table 2 shows the separation coefficients of Sc/impurity at different initial pH values. It can be seen from Table 2 that the separation of Sc and impurities can be carried out by controlling the pH of the solution. The separation coefficient of Sc/Ca, Sc/Zr, Sc/Ti and Sc/Si increased with the increase of the pH value. However, the pH had a little influence on the separation coefficient of Sc/Fe(III) and Sc/Al in the range from $[H^+]$ = 1 mol/L to pH = 3, which indicated that it is difficult to remove Fe and Al from the solution by controlling pH value. The hydrolysis of Fe(III) resulted in the presence of suspended matter when pH > 3. Therefore, a pH value of 2.5 was selected as optimum.

Table 2
Effect of initial pH value on the separation coefficients of Sc/impurities.

Separation coefficient	pH 0	pH 0.5	pH 1	pH 1.5	pH 2	pH 2.5	pH 3
$\beta_{Sc/Fe(III)}$	1.41	1.83	1.41	1.21	1.54	1.75	1.54
$\beta_{Sc/Ca}$	0.77	1.69	2.57	3.55	6.32	7.06	7.91
$\beta_{Sc/Al}$	1.58	1.99	1.94	2.10	2.99	3.01	2.63
$\beta_{Sc/Zr}$	0.22	0.85	3.04	6.95	23.84	43.12	62.11
$\beta_{Sc/Ti}$	2.31	5.76	11.92	23.14	72.62	79.26	91.36
$\beta_{Sc/Si}$	5.80	14.86	27.92	48.86	83.89	93.36	109.76