The Extraction Separation of Sc(III) from a Simulated Solution of Waste Water by Using $O,O'$-bis(2-ethylhexyl) Hydrogen Thiophosphate

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No primary scandium (Sc) ore exists on the earth and therefore securing a stable supply of Sc is required. The authors reported previously that a hexane solution containing 0.1 mol dm$^{-3}$ of $O,O'$-bis(2-ethylhexyl) hydrogen thiophosphate (MSP-8®) could extract Sc(III) quantitatively from an aqueous solution containing 1.0 mol dm$^{-3}$ of zirconyl (ZrO(II)) and 0.10 mol dm$^{-3}$ of tripotassium citrate as a masking reagent. The present study was carried out in order to establish the liquid-liquid extraction separation of Sc from a simulated waste water produced in the zirconium (Zr) refinery by using MSP-8 as the extractant.

1. Introduction

Recently, Sc is attracting the interest of the electric utility industry as a material for the electrolyte used in solid fuel cells because of its high performance. Several routes for the recovery of Sc from various sources, such as uranium (U) ores, aluminum (Al) ores, Zr ores and nickel (Ni) ores have been developed [1]. Among these sources, the recovery of Sc from the waste water produced in a Zr refinery has not been utilized much to date because of difficulties compared to the recovery from other sources.

Solvent extraction separation of Sc(III) has been reported with several organophosphorus compounds, such as bis(trimethylpentyl) dithiophosphinic acid (Cyanex 301) [2], trialkyl phosphine oxides (Cyanex 923 and Cyanex 925) [3], 2-ethylhexyl phosphonic acid mono-2-ethylhexyl ester (PC88A) [3], di(2-ethylhexyl) phosphoric acid (HDEHP) [4], tributyl phosphate (TBP) [5], and bis(trimethylpentyl) monothiophosphinic acid (Cyanex 302) [6,7]. There are two difficulties in the solvent extraction separation of Sc(III) from ZrO(II). The first is that most of the above extractants combine strongly with Sc(III) to form stable complexes, so that the stripping efficiency from the loaded organic phase by acid is often poor although the extraction efficiency is excellent. The second is the separation performance of the extractant. The waste
water contains high concentrations of ions such as, Fe(III), Al(III), ZrO(II) and it is fairly difficult to isolate Sc(III) from these hard acid metal ions. Some of the above extractants cannot separate Sc(III) from these metals. Shibata et al., recently reported that mixed extractants containing 9,9-dimethyldecanoic acid (Versatic acid10) and tri-n-butyl phosphate (TBP) gave good separation between Sc(III) and Zr(IV) [8,9]. However, it has not been reported whether this extraction system can be used to recover Sc(III) from the waste water with such a complicated composition.

*O*-*O*-bis(2-ethylhexyl) hydrogen thiophosphate (MSP-8®) was found to extract Sc(III) quantitatively and to separate it successfully from ZrO(II) in the previous studies [10,11]. Therefore, the extraction separation of Sc(III) from the simulated solution of a waste water produced in a Chinese zirconium refinery was carried out by utilizing MSP-8 as an extractant.

### 2. Experimental

#### 2.1 Reagents

MSP-8 was purchased from Daihachi Chemical Industry Co., and used without further purification. All other reagents were purchased from Kanto Chemical Co., as analytical-grade reagents.

#### 2.2 Extraction of the metal ions

The extractions were carried out by the usual batch system at 25°C ± 1°C. Synthesized Zr waste-water was prepared with a similar composition to the Zr waste-water produced in a Zr refinery and was diluted appropriately to use as the aqueous phase while keeping the concentration of tripotassium citrate (TPC) at 0.10 mol dm⁻³ as a masking reagent. Equal volumes (10 cm³) of the aqueous phase and organic phase (0.10 mol dm⁻³ MSP-8 toluene solution) were shaken together vigorously for 1 h. Back extraction was carried out 2 times as follows: after separating the phases by using a centrifuge at 2000 rpm for 20 min, 8 cm³ of the organic phase was transferred to a new vial and shaken with the same volume of 0.5 mol dm⁻³ hydrochloric acid (HCl) to strip foreign metal ions from the loaded organic phase. Next, 5 cm³ of the organic phase was transferred to another vial after phase separation and followed by being equilibrated with an equal volume of 4 mol dm⁻³ HCl to back extract the Sc³⁺. All back extraction and centrifugal conditions such as shaking speed, run time and so on were the same as for the extraction procedure. The 3 aqueous phase solutions so obtained were subjected to metal ion determination by ICP-OES.

The percentage of extraction (𝐸%) and recovery (𝑅%) were obtained by the following equations.

\[
E\% = \frac{[M]_\text{init} - [M]_\text{aq}}{[M]_\text{init}} \times 100 \tag{1}
\]

\[
R\% = \frac{[M]_\text{aq} + [M]_\text{b}}{[M]_\text{init}} \times 100 \tag{2}
\]

where [M]ₐq, [M]₀ and [M]ₐₐ refer to the concentration of metal ion remaining in the aqueous phase after
extraction, the amount extracted into the organic phase after extraction and that in the original solution, respectively.

3. Results and Discussion

3.1 Extraction separation of Sc(III) from ZrO(II)

MSP-8 toluene and n-hexane solutions gave almost the same results in the values of E% and R% and, in the optimum pH range for the extraction of Sc(III), there is little to choose between these two solvents. However the R% values obtained with the MSP-8 toluene solution were slightly better (~1%) than that with the n-hexane solution, and, therefore, toluene was mainly used as the MSP-8 diluent in this study although n-hexane was used in the previous study [11].

The pH at which the hydroxides of Sc(III) and ZrO(II) in the 1.0 mmol dm\(^{-3}\) solution precipitate due to hydrolysis can be calculated to be pH 4.5 and 2.0, respectively, from the relationship between the pH and the solubility product published elsewhere [12] by using the solubility of 1.3 × 10\(^{-6}\) g dm\(^{-3}\) for Sc(OH)\(_3\) and 9.9 × 10\(^{-9}\) g dm\(^{-3}\) Zr(OH)\(_4\) [13]. Then, the addition of TPC was necessary to mask Sc(III) and ZrO(II) in order to extract these ions in a pH range greater than 2.0.

The effect of the hydrogen ion concentration on the extraction of Sc(III) and ZrO(II) is shown in Figure 1. Sc(III) was strongly extracted in the pH range of 1.05 – 3.93 with an E% value of 99.6 ± 0.92% and the E% value of Sc(III) dropped sharply at the higher pH range of 3.93. While, the E% value for ZrO(II) was a maximum of 84.4% at pH 1.05 and gradually decreased with the increment of pH value in the pH range of 1.05 – 3.44 to 0.81 ± 1.61% at the higher pH range of 3.44. This extraction behavior of ZrO(II) and Sc(III) may be ascribed to the above-mentioned tendency that the metal ions hydrolyze in the pH range of 2.5 – 4.0 and the pH dependence of dissociation of the carboxyl group in citric acid (pK\(_{a1}\) = 2.90, pK\(_{a2}\) = 4.35, pK\(_{a3}\) = 5.70) [14]. After all, Sc(III) can be satisfactorily separated from ZrO(II) in this pH range.

Furthermore, as can be seen in Figure 1, Sc(III) was effectively back extracted with 3 mol dm\(^{-3}\) HCl solution with an R% value of 99.6 ± 6.08% from the loaded organic phase. On the other hand, the R%
value of ZrO(II) decreased in accordance with the increment in the $E\%$ value of ZrO(II) at the lower pH region. This means that the ZrO(II) loaded into organic phase is difficult to be back extracted. Based on these results, it was decided that 4 mol dm$^{-3}$ HCl solution was used for the recovery of Sc(III) from the simulated Zr waste water.

### 3.2 Effect of the citrate concentration

Zr, Sc, Al, iron (Fe), titanium (Ti) and lanthanides are classified as lithophile elements by the Goldschmidt classification in geochemistry [15], and these elements usually occurred together in ores. Because of the similarity in their chemical properties, Al(III), Fe(III), Ti(IV) and Y(III) are common co ions in most Zr waste waters, although the composition of these metals in the Zr waste water is different depending on the Zr refinery. Therefore the removal of these 4 ions was mainly examined in this study. In the MSP-8 extraction method, the addition of citrate salt was essential to mask ZrO(II) for separating Sc(III) from ZrO(II), so the masking effect of citrate salt on the extraction of these 4 ions was examined. Figure 2 shows that the extraction behavior of Al(III), Fe(III) and Sc(III) in the hydrogen ion(H$^+$) concentration range of the of 0.1 mol dm$^{-3}$ – 5 mol dm$^{-3}$. At 0.5 mol dm$^{-3}$ H$^+$ concentration, the $E\%$ value for Al(III), Fe(III) and Sc(III) were 0%, 13.8% and 97.7%, respectively. This result suggests that Al(III) and Fe(III) can be back extracted by washing the loaded organic phase with 0.5 mol dm$^{-3}$ HCl but Sc(III) would remain in the organic phase without being stripped. Figure 3 shows the extraction behavior of Al(III) and Fe(III) in the presence of 0.01 mol dm$^{-3}$ and 0.1 mol dm$^{-3}$ TPC, respectively. TPC was fairly effective for the separation of these metals.

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**Figure 2.** Effect of the concentration of hydrogen ion on the extraction of Al(III), Fe(III) and Sc(III). 
[MSP-8]$_o = 0.10$ mol dm$^{-3}$, [TPC]$_{aq} = 0.10$ mol dm$^{-3}$, [M$^{3+}$] = 1.0 mmol dm$^{-3}$. Back extractant: 3 mol dm$^{-3}$ HCl.

**Figure 3.** Effect of the concentration of TCA on the extraction of Al(III) and Fe(III). 
[MSP-8]$_o = 0.10$ mol dm$^{-3}$, [TPC]$_{aq} = 0.10$ mol dm$^{-3}$, [M$^{3+}$] = 1.0 mmol dm$^{-3}$. Back extractant: 3 mol dm$^{-3}$ HCl.
in suppressing the extraction of Al(III). When 0.1 mol dm\(^{-3}\) TPC was used, Al(III) was not extracted at all in the pH range of 3.37 – 5.39 as well as in all the range of H\(^+\) concentrations examined (Figure 2). Judging from the results shown in Figures 1 and 3, Sc(III) can be easily separated from Al(III) by extracting in the pH range of 3.4-4.2 and Al(III) in the loaded organic phase can be easily removed by stripping with dilute acid if Al(III) was extracted together with Sc(III). However, the masking effect of citrate on the extraction of Fe(III) was a little regardless of the concentration of citrate. The \(E\%\) value of Fe(III) was at maximum in the pH range of 2 – 3 and thereafter decreased to 0% with increasing pH. By adjusting the pH value of the aqueous phase to 3.8 – 4.1, the extraction of Fe(III) with MSP-8 toluene solution can be suppressed to \(E\%\) values of less than 20%. However, if Fe(III) was extracted into the organic phase, the removal of Fe(III) by stripping Fe(III) with 0.5 mol dm\(^{-3}\) HCl can be expected to some extent (Figure 2). As for Ti(IV) and Y(III), when 0.01 mol dm\(^{-3}\) of TPC was added to the aqueous phase, both ions were extracted fairly well (Figure 4). However when 0.1 mol dm\(^{-3}\) of TPC was used, the extraction of Ti(IV) was dramatically suppressed. While, for Y(III), increasing the TPC concentration had little effect. Here, at pH 1, the \(E\%\) value for Y(III) was very low irrespective of the citrate concentration (Figure 4), and this result strongly suggests that the Y(III) in the loaded organic phase could be removed by washing the organic phase with 0.1 mol dm\(^{-3}\) HCl solution prior to the back extraction of Sc(III) with 4 mol dm\(^{-3}\) HCl. Based on this hypothesis, a 0.5 mol dm\(^{-3}\) HCl solution was used for removing Y(III) in the case of the simulated Zr waste water.

### 3.3 Recovery of Sc(III) from the simulated Zr waste water

As mentioned above, since the composition and contents in Zr waste water vary from refinery to refinery, the Zr waste water produced in a Chinese refinery was arbitrarily chosen. A simulated Zr waste water having a similar composition to the actual waste water was prepared and diluted 2 times, 5 times and 10 times, respectively, and the synthesized solutions were subjected to extraction with MSP-8.

The percentage of extraction and stripping of the metal ions obtained with 10 times diluted synthesized Zr waste water is shown in Figure 5 and that with 5 times is given in Figure 6 and that with 2

![Figure 4. Effect of the concentration of TPC on the extraction of Y(III) and Ti(IV).](image-url)
times is shown in Figure 7, respectively. Here, the stripping percentage was calculated by equation (3).

$$BE\% = \frac{[M]_{\text{HCl}}}{[M]_{\text{init}}-[M]_{\text{aq}}} \times 100$$  \hspace{1cm} (3)

where $[M]_{\text{HCl}}$ indicates the metal ion concentration in the back extractant, 0.5 mol dm$^{-3}$ HCl or 4 mol dm$^{-3}$ HCl. The concentration and composition of the metal ions in the back extractant obtained with 10 times diluted synthesized Zr waste water is summerized in Table 1-a and that obtained with the 5 times diluted waste water is shown in Table 1-b and that obtained for 2 times diluted waste water is summerized in Table 1-c, respectively. In Figures 5 – 7, the black bar is the percent extraction, and the lattice pattern bar is the
stripping percentage for the 1st back extraction by using 0.5 mol dm$^{-3}$ HCl. The horizontal stripes bar is the stripping percentage for the 2nd back extraction by using 4 mol dm$^{-3}$ HCl. As seen in Figures 5 – 7, only Sc(III), Y(III) and Yb(III) were extracted effectively and the other metal ions were hardly extracted at all. In particular, Sc(III) gave 100% extraction in all cases. Y(III) and Yb(III) also gave good $E\%$ values, but almost all of the extracted Y(III) and Yb(III) in the organic phase was removed by the 1st back extraction. Therefore, the mixing of these ions into 4 mol dm$^{-3}$ HCl was negligibly small (Table 1-a, -b, -c). As for the 10 times and 5 times diluted synthesized Zr waste waters, Sc(III) in the starting solution of which the content percentages were 0.26% and 0.21% were concentrated to a percentage of 39% and 36% in the 4 mol dm$^{-3}$ HCl solution, respectively, i.e. Sc(III) was concentrated 150 times in a single extraction (Table 1-a and 1-b). In the 2 times diluted synthesized Zr waste water, which is the most concentrated solution, the $E\%$ values for Al(III) and Fe(III) were less than 5% (Figure 7), but their concentrations in the starting solution were very high, and, as can be seen in Figure 7, the removing efficiency from the organic phase by rinsing with 0.5 mol dm$^{-3}$ HCl solution was not very high, i.e. 29% for Al(III) and 60% for Fe(III). Then, their quantity in 4 mol dm$^{-3}$ HCl became relatively large, and consequently the percentage content of Sc(III) in 4 mol dm$^{-3}$ HCl became fairly low, 7.9%. However the $E\%$ and $BE\%$ values of Sc(III) are very high, at 100% and 90%, respectively (Table 1-c). Incidentally, the $E\%$ values for Y(III) and Yb(III) were comparatively low, 76% and 84%, respectively (Figure 7). The total amount of the extracted metal ions was 156.2 μmol (Table 1-c) and the required amount of MSP-8 to form the 1 : 3 chelate complex was 468.6 μmol. The amount of MSP-8 used (1 mmol) was enough for Y(III) and Yb(III). These low $E\%$ values may be ascribed to the shortage of MSP-8 for complex formation with Y(III) and Yb(III) in the case of the 2 times diluted synthesized Zr waste water. Incidentally, the pH of all simulated Zr waste waters was adjusted
to be 4.2, but only the equilibrated pH of 2 times diluted synthesized Zr waste water became fairly low, at pH 2.98. Judging from the $E\%$ value for Fe(III) at pH 2.98 in Figure 3, Fe(III) should have been more than 80% extracted. However, the $E\%$ value for Fe(III) was surprisingly low compared to the expected $E\%$ value (Figure 7). This may also be attributed to the shortage of MSP-8 as mentioned above.

Table 1-a. Recovery of Sc(III) from the synthesized Zr waste water diluted 10 times.

| Component | Composition of the starting solution (mg dm$^{-3}$) (Content by percentage) | Composition in 0.5 mol dm$^{-3}$ HCl solution (mg dm$^{-3}$) | Composition in 4 mol dm$^{-3}$ HCl solution (mg dm$^{-3}$) (Content by percentage) |
|-----------|-------------------------------------------------|-------------------------------------------------|-------------------------------------------------|
| Al        | 368 (24%)                                       | 4 (5.5%)                                        | 0.5 (5.5%)                                      |
| Fe        | 760 (50%)                                       | 20 (50%)                                        | 4.3 (50%)                                       |
| Sc        | 4 (0.26%)                                       | 0 (0%)                                          | 3.4 (39%)                                       |
| Ti        | 25 (1.6%)                                       | 0 (0%)                                          | 0.2 (2.7%)                                      |
| Y         | 57 (3.8%)                                       | 54 (0%)                                         | 0.0 (0%)                                        |
| Yb        | 212 (14%)                                       | 186 (1.1%)                                      | 0.1 (1.1%)                                      |
| Zr        | 92 (6.0%)                                       | 0 (1.9%)                                        | 0.2 (1.9%)                                      |
Table 1-b. Recovery of Sc(III) from the synthesized Zr waste water diluted 5 times.

| Component | Composition of the starting solution (mg dm$^{-3}$) (Content by percentage) | Composition in 0.5 mol dm$^{-3}$ HCl solution (mg dm$^{-3}$) | Composition in 4 mol dm$^{-3}$ HCl solution (mg dm$^{-3}$) (Content by percentage) |
|-----------|------------------------------------------------------------------------------|-------------------------------------------------------------|--------------------------------------------------------------------------------|
| Al        | 874 (26%)                                                                    | 8                                                           | 1.9 (11%)                                                                    |
| Fe        | 1681 (50%)                                                                   | 35                                                          | 8.2 (45%)                                                                    |
| Sc        | 7 (0.21%)                                                                     | 1                                                           | 6.5 (36%)                                                                    |
| Ti        | 54 (1.6%)                                                                     | 1                                                           | 1.3 (7.1%)                                                                   |
| Y         | 120 (3.6%)                                                                    | 114                                                         | 0 (0%)                                                                       |
| Yb        | 431 (13%)                                                                     | 386                                                         | 0 (0%)                                                                       |
| Zr        | 192 (5.7%)                                                                    | 0                                                           | 0 (0%)                                                                       |

Table 1-c. Recovery of Sc(III) from the synthesized Zr waste water diluted 2 times.

| Component | Composition of the starting solution (mg dm$^{-3}$) (Content by percentage) | Composition in 0.5 mol dm$^{-3}$ HCl solution (mg dm$^{-3}$) | Composition in 4 mol dm$^{-3}$ HCl solution (mg dm$^{-3}$) (Content by percentage) |
|-----------|------------------------------------------------------------------------------|-------------------------------------------------------------|--------------------------------------------------------------------------------|
| Al        | 2482 (27%)                                                                   | 31                                                          | 78 (43%)                                                                      |
| Fe        | 4640 (50%)                                                                   | 114                                                         | 76 (42%)                                                                      |
| Sc        | 22 (0.24%)                                                                   | 3                                                           | 15 (7.9%)                                                                     |
| Ti        | 146 (1.5%)                                                                   | 4                                                           | 14 (7.4%)                                                                     |
| Y         | 326 (3.5%)                                                                   | 247                                                         | 0 (0%)                                                                        |
| Yb        | 1114 (12%)                                                                   | 934                                                         | 0 (0%)                                                                        |
| Zr        | 511 (5.5%)                                                                   | 0                                                           | 0 (0%)                                                                        |
4. Conclusion

According to the MSP-8 extraction method, the recovery of Sc(III) was successfully achieved by a single extraction with 10 times and 5 times diluted synthesized Zr waste waters. Most of the Y(III) and Yb(III) and more than 80% of the Al(III) and Fe(III) extracted together with Sc(III) was removed by washing the organic phase with 0.5 mol dm\(^{-3}\) HCl solution. However, the decontamination technique employed in this study, in which the masking effect using 0.10 mol dm\(^{-3}\) TPC and washing the loaded organic phase with 0.5 mol dm\(^{-3}\) HCl solution were combined, could not satisfactorily remove Al(III) and Fe(III) for the 2 times diluted synthetic Zr waste water. The present study verified that the MSP-8 extraction system would be useful for the recovery of Sc(III) from dilute Zr waste water produced in the Zr refinery, however a multi-step extraction would be preferable for the concentrated Zr waste water.

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