Recovery of Scandium from Hot Spring Water with Graft Adsorbent Containing Phosphoric Groups

Hiroyuki HOSHINA1*, Noboru KASAI 1, Haruyo AMADA1, Makikatsu TAKAHASHI 2, Kazuya TANAKA 3 and Noriaki SEKO 1

1 Environmental Polymer Group, Quantum Beam Science Center, Sector of Nuclear Science Research, Japan Atomic Energy Agency, 1233 Watanuki, Takasaki, Gunma, Japan
2 ERH Techno Research, Co., Ltd., 2030-5 Ishihara, Takasaki, Gunma, Japan
3 Anzai Co., Ltd., 3097-1 Nakanoya, Annaka, Gunma, Japan

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Abstract

Scandium (Sc) which is a kind of rare-earth element has dissolved at a low concentration into the Kusatsu Hot Spring, located in Gunma prefecture, Japan. If Sc can be recovered from hot spring water, it is possible to ensure a stable supply of Sc as a future resource. Therefore, an adsorbent for Sc recovery was developed with radiation-induced graft polymerization of phosphoric acids that have a high affinity for Sc onto a polyethylene fabric. Hot spring water in Kusatsu Town flows into the Yukawa River, so Sc is contained at the concentration of 17 μg dm⁻³ in the Yukawa River. The adsorption performance of Sc was evaluated with the Sc recovery equipment, consisting of 155 mm internal diameter columns and a pump that were set up near Yukawa River. The adsorbent (1.5 dm³) was packed into a column and water from the Yukawa River was pumped through the column at a space velocity of 250 h⁻¹. As a result of the adsorption test, approximately 60 mg of Sc was collected per column. In addition, to achieve a practical use of Sc recovery, the adsorbent needs to be able to be used repeatedly while maintaining its efficiency in terms of cost reduction. So, the reusability of the adsorbent was investigated by repeating adsorption and elution. The breakthrough curves of Sc adsorption showed similar behavior in all tests. The adsorbed Sc from the 19th adsorption test was 56 mg, which was a comparable capacity relative to the average. These results indicated that the adsorbent was used more than 19 times while maintaining high adsorption performance of Sc.

Keywords: Scandium, Fibrous adsorbent, Hot spring water, Radiation-induced graft polymerization

1. Introduction

The market size of rare-earth elements, which are used for mobile device batteries, liquid crystal televisions, and hybrid/electric car motors, has continued to expand in recent years. Therefore, rare-earth elements become indispensable materials for a high-tech industry. Scandium (Sc) which is a kind of rare-earth element has been used for metal halide lamps and sporting equipment. Even though the demand of Sc for batteries has been increasing in recent years, it is difficult to ensure a sufficient quantity of Sc for industrial application because Sc is produced as a slight byproduct of tungsten and uranium refining. Therefore Sc becomes very expensive and remains used in limited applications. A stable supply of rare-earth elements including Sc in Japan has become a concern because Japan relies on imported materials to satisfy its needs.

* Corresponding author
E-mail: hoshina.hiroyuki@jaea.go.jp
Many kinds of useful metals have dissolved into hot spring water which gushes from underground. Japan is dotted with 27,000 hot spring sources. The total emerging hot spring water in Japan amounts to 1.9 million tons per minute\(^2\). So, hot springs attract attention as a new supply source of rare-earth. Sc has dissolved at a low concentration into the Kusatsu Hot Spring, located in Gunma prefecture, which is one of the most famous hot springs in Japan\(^3\). At Bandai Source, which is one of the water sources of Kusatsu, Sc has dissolved at the concentration of approximately 40 \(\mu\)g dm\(^{-3}\) at 92°C under an acidic condition. Hot spring water flows into the Yukawa River which flows through Kusatsu town. The flow quantity amounts to about 70,000 tons per day. Since the Sc concentration dissolved in the Yukawa River is 17 \(\mu\)g dm\(^{-3}\), it is estimated that roughly 1.2 kg per day, or in other words 430 kg per year, flow down the river. If Sc can be recovered from hot spring water, it is possible to ensure a stable supply of Sc as a future resource. Hence, recovering Sc with a fibrous graft adsorbent from hot spring water has been being investigated\(^4\).

Radiation-induced graft polymerization (RIGP) is a superior technique to functionalize a polymer based material like polyethylene\(^5,6\). The advantage of RIGP is able to generate radicals in a base material, without using an initiator. In addition, functional groups can be introduced onto base material without changing its characteristic dramatically. To recover the dissolved Sc at low concentrations from hot spring water, an adsorbent that can adsorb Sc selectively with high capacity is needed. So, the adsorbent for recovering Sc was prepared with RIGP by introducing phosphoric acid groups that have a high affinity for Sc under an acid condition\(^7,8\), onto a thin diameter polyethylene coated polypropylene fiber.

In this study, the adsorption performance of a fibrous graft adsorbent containing phosphoric acid groups for Sc was investigated on a bench scale with the Sc recovery equipment set up near the Yukawa River in Kusatsu town (Fig. 1).

### 2. Experimental

#### 2.1 Preparation of the adsorbent for Sc

A non-woven fabric composed of polyethylene coated polypropylene fiber provided by Kurashiki Textile Manufacturing Co., Ltd. was used as a base material for the adsorbent of Sc. The fabric was packed into a stainless-steel cartridge and the inside of the cartridge was made into a vacuum state with pumping. It was then irradiated at 160 kGy with gamma-ray. After irradiation, the irradiated fabric was contacted with a deoxidized 20% monomer solution at 60°C for 5 h by passing through the monomer solution in the cartridge. In this graft polymerization, a phosphoric acid monomer (2-hydroxyethyl methacrylate phosphoric acid; Kyoeisha Chemical Co., Ltd.) was used as a grafting monomer, which was composed of the mixture of mono (50%) and diester (50%). The degree of grafting (Dg) was calculated by the following formula:

\[
\text{Degree of grafting} \% = \left( \frac{W_1 - W_0}{W_0} \right) \times 100
\]

where \(W_0\) and \(W_1\) were the weight of fabrics before and after graft polymerization.

The grafted fabrics of Dg around 90% were applied to the recovery of Sc as the adsorbents.

#### 2.2 Evaluation of the graft adsorbent for Sc

The adsorption performance of Sc was evaluated with an imitation hot spring water containing Sc on a laboratory scale and natural hot spring water on a bench scale. In the laboratory scale, the effect of flow rate on Sc adsorption was investigated with a 7 mm internal diameter column. 0.35 cm\(^3\) of adsorbent was packed into the column. The Sc solution, which was adjusted to 40 \(\mu\)g dm\(^{-3}\) by diluting 1000 mg dm\(^{-3}\) Sc standard

![Fig. 1 The method of Sc recovery with equipment on a bench scale.](image)
solution, was delivered to the column at the flow rate of space velocity (SV) 100, 250, 500 and 1000 h⁻¹. The pH of the Sc solution was adjusted to pH 1.5 with nitric acid. The solution flowed out from the column was collected with a fraction collector. The Sc concentration in the solution was measured with induced coupled plasma atomic emission spectroscopy [ICP-AES, Perkin Elmer Inc., Optima 4300DV]. To use the adsorbent repeatedly, elution tests were performed in batch. The adsorbents were soaked in 40 cm³ of eluting solutions, which were prepared by dissolving hydrochloric acid, nitric acid, oxalic acid, citric acid, ammonium citrate tribasic, trisodium citrate, sodium hydroxide, ammonium nitrate in pure water, respectively. In the bench scale, the reusability of the adsorbent was investigated with the Sc recovery equipment set up near the Yukawa River in Kusatsu. A 300 mm wide strip of adsorbent was rolled around the core, and placed into a 155 mm internal diameter column. Hot spring water was pumped up from the Yukawa River and passed through the adsorbent from the outside to inside at SV 250 h⁻¹. Water which passed adsorbent came out from the perforations in the core (Fig. 1). The water of the Yukawa River contains Sc at a concentration of 17 μg dm⁻³ at pH 2. After the Sc collecting, the recovered Sc was eluted by passing eluting solution through the column. Then, recovery and elution of Sc was repeated 19 times.

3. Results and Discussion

3.1 Evaluation of the adsorbent on the laboratory scale

Adsorption performance of Sc was studied with a Sc solution of 40 μg dm⁻³ concentration at SV 100, 250, 500 and 1000 h⁻¹. The breakthrough curves of Sc adsorption are shown in Fig. 2. The breakthrough curve was obtained by plotting C/C₀ which was the concentration of Sc in the solution outflow (C) divided by that of the solution inflow (C₀) versus bed volume (BV). The breakthrough point was determined when C/C₀ reached 0.05. The maximum value of BV at the breakthrough point was 3750 at SV 100 h⁻¹. The adsorption capacity of Sc up to the breakthrough point at SV 100 h⁻¹ was 12 mg g⁻¹. In the test of SV 250 h⁻¹, the breakthrough point was BV 3590, which was equivalent to the value of SV 100 h⁻¹. By increasing the flow rate to SV 500 h⁻¹, the BV at the breakthrough point was significantly decreased to 1143. These results indicate that the adsorbent can maintain maximum performance up to SV 250 h⁻¹. The optimum flow rate of Sc recovery was decided to be at a flow rate of SV 250 h⁻¹.

To know the suitable eluting solution, the elution ratio of Sc was evaluated as follows:

\[
\text{Elution ratio [\\%]} = \frac{A_1}{A_2} \times 100
\]

where \(A_1\) and \(A_2\) were the amounts of the eluted Sc and the adsorbed Sc, respectively.

The results of elution tests are presented in Table 1. The ammonium citrate tribasic solution adjusted to 1 mol dm⁻³ showed the highest elution ratio of 95%. The elution ratio was reduced to 83% by decreasing the concentration of ammonium citrate tribasic to 0.5 mol dm⁻³. Therefore, the 1 mol dm⁻³ ammonium citrate tribasic solution was employed to the eluting solution for Sc.

<table>
<thead>
<tr>
<th>Concentration [mol dm⁻³]</th>
<th>Elution ratio [%]</th>
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<tbody>
<tr>
<td>Hydrochloric acid</td>
<td>1</td>
</tr>
<tr>
<td>Nitric acid</td>
<td>1</td>
</tr>
<tr>
<td>Oxalic acid</td>
<td>1</td>
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<tr>
<td>Citric acid</td>
<td>1</td>
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<tr>
<td>Ammonium citrate tribasic</td>
<td>1</td>
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<tr>
<td>Trisodium citrate</td>
<td>0.5</td>
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<tr>
<td>Sodium hydroxide</td>
<td>1</td>
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<tr>
<td>Ammonium nitrate</td>
<td>1</td>
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3.2 Evaluation of the adsorbent on the bench scale

To evaluate the reusability of the adsorbent, the adsorption and the elution of Sc was carried out repeatedly with the Sc recovery equipment on the bench scale. Figure 3 shows the profile of adsorption and elution of Sc with natural hot spring water and 1 mol dm⁻³ ammonium citrate tribasic solution on a bench scale. The breakthrough point of Sc adsorption was BV 1000. The amounts of recovered Sc at BV 1000 and 5000 were 49 mg and 98 mg, respectively. In the elution test, the highest
value of C/Co was 1800, which was equivalent to the 30 mg dm\(^{-3}\) result. The adsorbed Sc was eluted by passing 1 mol dm\(^{-3}\) ammonium citrate tribasic solution through the column. Almost all of Sc was completely eluted within BV 10 rapidly. The breakthrough curves of Sc adsorption at SV 250 h\(^{-1}\) on repeated adsorption tests are shown in Fig. 4. The breakthrough curves showed similar behavior up to 19th adsorption test. The values of C/Co at BV 3000 were less than 0.5 in all the repeated tests, which means the adsorbent could still adsorb more than half of the Sc from hot spring water at BV 3000. In order to effectively recover Sc from hot spring water, the adsorbent should be changed before the C/Co exceeds 0.5. The amounts of the recovered Sc up to BV 3000 in each test are shown in Fig. 5. The 8th adsorption test had the maximum amount of recovered Sc, which was 68 mg. The minimum amount of the recovered Sc was 51 mg in the 5th test. The average amount of the recovered Sc during the 19 tests was 60 mg. Since the Sc concentration dissolved in the Yukawa River was 17 \(\mu g\) dm\(^{-3}\), the total amount of Sc contained in the hot spring water until the BV reached 3000 was 77 mg. Therefore, the adsorbent recovered 80% of total Sc from hot spring water. The recovered Sc from the 19th adsorption test was 56 mg, which was a comparable capacity relative to the average. It means that the adsorbent was able to be used repeatedly more than 19 times while maintaining high adsorption performance of Sc. These results lead to the cost reduction of the Sc recovery from hot spring water. In addition, hot spring was expected to be a future resource of Sc.

References