Article

Selective Sc Recovery from Rare Earths in Nitric Acid Medium by Extraction Chromatography

Sou WATANABE^{1*}, Hideya SUZUKI², Ichiro GOTO¹, Hirohide KOFUJI¹
and Tatsuro MATSUMURA²

¹Nuclear Fuel Cycle Engineering Laboratories, Japan Atomic Energy Agency, 4-33, Muramatsu, Tokai-mura, Naka-gun, Ibaraki, Japan

²Nuclear Science Research Institute, Japan Atomic Energy Agency, 2-4, Shirakata, Tokai-mura, Naka-gun, Ibaraki, Japan

(Manuscript received April 9, 2018; accepted June 19, 2018)

Abstract

Chemical compounds containing scandium (Sc) are widely applied to various fields such as catalysts, alloys, lamps and etc. Sc is found in mineral ore, and it is necessary to develop efficient Sc separation and recovery technology for the industrial applications. *N,N,N',N',N'',N''*-hexaoctylnitritoltriacetamide (HONTA) extractant has been shown to be promising for selective Sc extraction. In this study, applicability of the extraction chromatography technology using HONTA impregnated adsorbent for the selective Sc recovery from other rare earth elements (REs) was experimentally evaluated through batch-wise adsorption/elution studies and column separation experiments. Batch-wise experiments showed that distribution coefficient of Sc onto the HONTA/SiO₂-P adsorbent was far larger than those of other REs at acidity region with $0.001 < [\text{HNO}_3] < 4 \text{ mol dm}^{-3}$ and that the adsorbed Sc was efficiently eluted into 1 M H₂SO₄ solution. Appropriate experimental conditions for the column separation experiment were proposed based on those results, and performance of the flow-sheet was examined for laboratory scale column system. Only Sc in 4 mol dm^{-3} HNO₃ solution was adsorbed into a packed column with the adsorbent while other REs were discharged from the column with the feed solution, and then loaded Sc was properly eluted into 1 M H₂SO₄ solution. Purity of the Sc product solution obtained by the column separation experiment depended on Sc recovery ratio, and about 99.9 % purity was achieved with 97 % recovery ratio. The residual Sc was eluted from the column with other REs and did not remain inside the column, therefore repeated use of the column was shown to be possible. This process was shown to be promising for selective Sc recovery from mixture of REs in nitric acid.

Keywords: Scandium recovery, Rare earth elements, Extraction chromatography, HONTA

1. Introduction

Wide variety of compounds containing scandium (Sc) are recently attracted for various applications such as catalyst^{1,2)}, alloys^{3,4)}, lamp of laser⁵⁾ and etc. Rare earth elements (REs) involving 15 lanthanides, yttrium and Sc are chemically similar,

therefore the yield of scandium is not so large due to difficulty in separation from other REs. Effective and appropriate Sc extraction and purification procedures from mineral ore, which is main source of Sc, is essential for its commercial use. So far, several fundamental studies on recovery and purification

* Corresponding author

E-mail: watanabe.sou@jaea.go.jp

technologies of scandium have been carried out⁶⁻⁹⁾. However, an efficient process with releasing small amount of secondary wastes is desirable for practical operation. Our group is focusing on the extraction chromatography as a promising technology for separation and purification of Sc from chemically similar elements due to its simplicity in operation and compactness in equipment.

Japan Atomic Energy Agency has been developing the extraction chromatography technology for recovery of trivalent minor actinides (MA(III): Am and Cm) from spent nuclear fuel, and performance of the technology has been systematically investigated so far¹⁰⁻¹⁵⁾. The technology employs porous silica based adsorbent impregnating an extractant in the particle, and adsorption/elution reactions inside the packed column enable to separate and recover target elements involved in a feed solution. The porous silica particle with about 50 μm diameter and 50 nm pore diameter are coated by styrene divinyl benzene copolymer (referred as $\text{SiO}_2\text{-P}$), and various extractants can be utilized for the adsorbent. The extractant is adopted according to the target element, and an appropriate flow-sheet is designed based on fundamental adsorption/elution performance of the adsorbent. This technology can reduce amount of secondary wastes compared to the solvent extraction process since it does not require any diluent and the number of stages can be easily increased not by adding equipment but by simply lengthening the column. Small difference in distribution coefficient between elements onto the adsorbent is fully utilized for the separation of them by modifying operation conditions. These features are suitable for practical Sc recovery from REs mixtures.

Recent development in the extractant for MA(III) recovery has found that *N,N,N',N',N'',N''*-hexaoctylnitrilotriacetamide (HONTA, Fig. 1)¹⁶⁾ extractant which show selectivity for MA(III) over REs has strong affinity to Sc. In this study, HONTA impregnated adsorbent (HONTA/ $\text{SiO}_2\text{-P}$) was prepared, and applicability of the adsorbent to the extraction chromatography for Sc recovery was experimentally evaluated. Batch-wise adsorption/elution experiments were carried out to evaluate influence of acidity on the distribution coefficients of REs and to give an appropriate flow-sheet for column separation operation. Based on the fundamental adsorption/elution data, the flow-sheet was proposed and its performance was evaluated through recovery ratio and purity of Sc in a product solution obtained by a laboratory scale column separation experiment.

2. Experimental

2.1 Preparation of adsorbent

Porous silica particle with about 50 nm pore size and about 50 μm particle diameters were prepared by sol-gel method. Porosity of the particle was about 0.35. Styrene-divinyl benzene copolymer was applied on surface of the particle with about several hundred nanometers thickness¹⁷⁾. Degree of the cross

Fig. 1 *N,N,N',N',N'',N''*-hexaoctylnitrilotriacetamide (HONTA)

linkage of the copolymer was 15 %. HONTA extractant were impregnated into the polymer. Amount of extractants impregnated was fixed at 33 wt% of total weight of the adsorbent. Detail preparation procedure is described in a reference¹⁸⁾.

2.2 Batch-wise experiments

0.5 g of the adsorbent was mixed with 10 mL of the feed solution containing 20 mg/L of all rare earth elements (except for Pm(III)), and then shaken for 3 h at 298 K. Acidity of the feed solution was parametrically changed at $0.001 < [\text{HNO}_3] < 4 \text{ mol dm}^{-3} \text{ (M)}$. After separating solid and liquid phases, concentrations of the rare earth elements in the supernatant solution were analyzed by ICP-AES measurement.

Batch-wise elution experiments were also carried out using REs loaded adsorbent for DTPA, citric acid and sulfuric acid solutions as eluents. 0.2 g of the adsorbent after contacting with the feed solution was mixed with 4 mL of the eluents, and then shaken for 3 h at 298 K. Acidity of the feed solution was decided based on the results of the adsorption experiments. Elution ratios of REs were calculated by these experiments, and then an appropriate elution condition for the column separation experiment was determined.

2.3 Column separation experiments

Column separation experiments were carried out with a condition derived from the batch-wise experiments. Experimental setup consisted of a column, a pump for feeding solutions, a switching valve and a fraction collector. HONTA/ $\text{SiO}_2\text{-P}$ adsorbent was packed in a glass column with 1 $\text{cm}\phi \times 10 \text{ cm}$ height (1 Bed Volume (BV) = 7.85 cm^3). Feed solution, wash solution and an eluent were sequentially supplied into the column, and then effluent was fractionally collected at every 0.5 BV. Concentrations of REs in the fractions were analyzed by ICP-AES measurement. Elution curves of REs were obtained, and recovery ratio of Sc and purity of Sc in a product solution were calculated.

3. Results and discussion

3.1 Batch-wise experiments

Distribution coefficients K_d of REs onto HONTA/SiO₂-P adsorbent calculated by the following equation are shown in Fig. 2;

$$K_d = \frac{C_0 - C_s}{C_0} \times \frac{V}{W} \quad (1)$$

where C_0 and C_s are concentrations of cations in the solution before and after the adsorption, respectively, V is volume of the solution, W is weight of the adsorbent.

The HONTA/SiO₂-P selectively adsorbed Sc and K_d of Sc was far larger than those of other REs at any acidity region although K_d has local minimum at $[\text{HNO}_3] = 2$ M. Selective adsorption of Sc from nitric acid solution containing all REs should be possible. The distinct difference in the K_d between different RE elements might be caused by difference in ionic radii of them. Hydration behavior of Sc(III) is reported to be different from those of other REs due to its small size¹⁹⁾.

K_d for all REs drastically depended on acidity of the feed solution, and those variation might be attributed to contribution of NO_3^- ions for formation of complexes. These features have been observed also in the solvent extraction system¹⁶⁾, and selective MA(III) adsorption onto the HONTA/SiO₂-P is expected at $[\text{HNO}_3] = 0.1$ M according to the distribution behavior into the solvent. Design of MA(III) recovery flow-sheet from spent nuclear fuel is in progress, and performance of the flow-sheet will be examined in near future.

In order to achieve selective Sc adsorption with suppressing extraction of other REs by the HONTA, an appropriate acidity of the feed solution for the column separation operation was decided to be 4 M. In this condition, almost REs except for La and Ce were not loaded onto the adsorbent. The batch-wise elution experiments were carried out using the condition, and elution ratio of only Sc was evaluated. Figure 3 shows the elution ratios of Sc from the adsorbent onto various solutions. Complex reagents such as citric acid and DTPA in nitric acid solution effectively worked for Sc stripping, however sulfuric acid achieved the highest elution ratio. Elution ratio increased with increasing the acidity at low acidity region, whereas elution ratio decreased at $[\text{H}_2\text{SO}_4] > 1$ M. The ionic strength of the eluent is considered to influence on the elution behavior. An appropriate acidity of the eluent for the column separation was set to be 1 M.

3.2 Column separation experiments

Experimental conditions of the column separation are shown in Table 1, where concentration of each REs in the feed solution was 100 ppm. After conditioning the packed column with 4 M HNO_3 solution, 25 BV of the feed solution was fed into the column. Amount of the supplied Sc was one third of the adsorption capacity of HONTA/SiO₂-P packed column assuming that one HONTA molecule forms complex with one

Fig. 2 Distribution coefficient of RE(III) onto HONTA/SiO₂-P adsorbent.

Fig. 3 Elution ratio of Sc from HONTA/SiO₂-P into various solutions.

RE(III) ion¹⁷⁾. The wash solution was supplied to discharge non-extracted elements from the column, and then 1 M H_2SO_4 solution was supplied to discharge the loaded Sc. In this experiment, excess volume of the wash solution and the eluent were supplied to properly discharge REs from the column.

Elution curves of all REs obtained by the column separation experiment are shown in Fig. 4. All REs except for Sc were not adsorbed by the column and were eluted with the feed solution, and this feature was exactly expected from the K_d profile. Small amount of Sc leaked from the column after the mobile phase was switched from the feed solution to the wash solution. Since the amount of HONTA must be enough for adsorption of all supplied Sc, some part of impregnated HONTA might not contribute to Sc extraction. Adsorption/elution performance often influenced by the amount of impregnated extractant²⁰⁾, therefore composition of the adsorbent might be desirable to be improved for efficient use of the extractant.

Concentrated Sc solution was discharged from the column

just after supplying the eluent, and Sc was not detected in the effluent after supplying 30 BV of the eluent. If the product is set at initial few BV less than 25 BV after switching to the eluent, the concentration of Sc in the product will be larger than the feed solution. This result implies that the extraction chromatography process can achieve separation and concentration of Sc simultaneously.

All supplied Sc was recovered in fractions of the wash solution and the eluent, and 97 % was found in the first 30 BV of the eluent. Amount of the leaked Sc in the wash solution might possible to be reduced by optimizing in composition of the adsorbent and in volume of the feed solution. If some fractions of the wash solution is added to the final product solution, recovery ratio of Sc increases while some other REs mixed with the Sc product. **Figure 5** shows the purity of Sc plotted as function of the recovery ratio of Sc. About 97 % of Sc was recovered with 99.9 % purity, however the purity decreased to be about 98 % if the recovery ratio is required to be more than 99.5 %. An appropriate specification of the Sc product solution has to be determined by requirements from its application.

Material balances of all REs are 100 % and any elements did not remained inside the column after the operation, thus the column is possible to be used repeatedly. In order to evaluate application limit of the column precisely, not only repeated separation experiments but also investigation on durability of the HONTA/SiO₂-P adsorbent are required. As the adsorbent contacts with strong acids during the process, degradation of the adsorbent by decomposition and leaching of the HONTA extractant should be considered.

Table 1 Experimental condition of the column separation experiment.

	Flow velocity: 1 cm/min	
	Temperature of the column: 298 K	
	Solution	Amount
Conditioning	4 M HNO ₃	5 BV
Feed	RE(III) in 4 M HNO ₃	25 BV
Wash solution	4 M HNO ₃	10 BV
Eluent	1 M H ₂ SO ₄	50 BV

4. Summary

New selective Sc recovery process flow using combination of the extraction chromatography technology and HONTA extractant was designed and performance of the process was experimentally demonstrated. Sc in nitric acid solution containing all rare earth elements was selectively adsorbed by HONTA impregnated adsorbent and successfully recovered into sulfuric acid solution. About 97 % recovery ratio of Sc with 99.9 % purity was achieved by a column separation test, and

repeated use of the column must be possible. Further optimization in the adsorbent and in the flow-sheet are expected to improve the performance.

Fig. 4 Elution curves of REs obtained by the column separation experiment.

Fig. 5 Purity of Sc in the product plotted as function of recovery ratio.

References

- 1) M. Distaso and E. Quaranta, *J. Catalysis*, **253**, 278 (2008).
- 2) C. Wang, G. Luo, M. Nishiura, G. Song, A. Tamamoto, Y. Luo and Z. Hou, *Sci. Adv.*, **3**, e1701011 (2017).
- 3) J. Røyset, *Metall. Sci. Technol.*, **25**, 2, 11 (2007).
- 4) R. Sawell and C. L. Jensen, *Metall. Trans. A*, **21**, 421 (1990).
- 5) F. Rainer, W. H. Lowdermild, D. Milam, T. Tuttle Hart, T. L. Lichtenstein and C. K. Carniglia, *Appl. Opt.*, **21**, 3685 (1982).
- 6) B. Onghena, C. R. Borra, T. V. Ferven and K. Binnemans, *Sep. Purif. Technol.*, **176**, 208 (2017).
- 7) H. Nie, Y. Wang, Y. Wang, Z. Zhao, Y. Dong and X. Sun, *Hydrometallurgy*, **175**, 117 (2018).
- 8) Y. Chen, H. Wang, Y. Pei and J. Wang, *Sep. Purif. Technol.*, **178**, 261 (2017).

- 9) F. Basuki, N. Seko and M. Tamada, *J. Ion Exchange*, **21**, 3, 127 (2010).
- 10) Y. Koma, Y. Sano, K. Nomura, S. Watanabe, T. Matsumura and Y. Morita, *Proc. 11th IEMPT*, San Francisco, USA, November 1-4, 2010, IV-4 (2010).
- 11) S. Watanabe, I. Goto, K. Nomura, Y. Sano and Y. Koma, *Energy Procedia* **7**, 449 (2011).
- 12) S. Watanabe, K. Nomura, S. Kitawaki, A. Shibata, H. Kofuji, Y. Sano and M. Takeuchi, *Procedia Chemistry*, **21**, 101 (2016).
- 13) S. Watanabe, I. Goto, Y. Sano and Y. Koma, *J. Eng. Gas Turbines Power*, **132**, 102903 (2010).
- 14) S. Watanabe, Y. Sano, K. Nomura, Y. Koma and Y. Okamoto, *EPJ Nuclear Sci. Technol.* **1**, 9 (2015).
- 15) S. Watanabe, T. Senzaki, A. Shibata, K. Nomura, Y. Koma and Y. Nakajima, *Proc. Global 2011*, Chiba, Japan, December 11-16, 2011, 387433 (2011).
- 16) Y. Sasaki, Y. Tsubata, Y. Kitatsuji and Y. Morita, *Chem. Lett.*, **42**, 91 (2013).
- 17) Y. Wei, M. Kumagai and Y. Takashima, *Nucl. Technol.*, **132**, 413 (2000).
- 18) Y. Sano, S. Watanabe, H. Matsuura, K. Nagoshi and T. Arai, *J. Nucl. Sci. Technol.*, **54**, 10, 1058 (2017).
- 19) S.A. Cotton, *Polyhedron* **18**, 1691 (1999).
- 20) S. Watanabe, T. Arai, T. Ogawa, M. Takizawa, K. Sano, K. Nomura and Y. Koma, *Procedia Chemistry*, **7**, 411 (2012).