A Study of Enrichment Process of Rare Earth Elements from Tamagawa Hot Spring Water

Kazutoshi HAGA^{*}, Masahiko BESSHO^{**}, Muniyappan Rajiv GANDHI^{*} and Atsushi SHIBAYAMA^{*}

^{*}Faculty of Engineering and Resource Science, Akita University, Akita 010-8502, Japan

^{**}International Center for Research and Education on Mineral and Energy Resources, Akita University, Akita 010-8502, Japan

E-mail : khaga@gipc.akita-u.ac.jp

Tamagawa hot spring water (Akita, Japan) is naturally acidic (pH 1.2) and concentration of rare earth elements (REEs) were found to be very low (1-70 µg/L). In this study, an effective enrichment for recovery of the REEs from the acidic hot spring water using adsorption and precipitation methods was investigated. Three polymers, namely Strata-X-C, TE-07 and TE-08 were used for adsorption of REEs from hot spring water, and adsorption and desorption of the REEs were carried out using a column type reactor. A strong cation exchange polymer (Strata-X-C, Phenomenex) was found to have very high adsorption of REEs. It was found that over 99% of REEs were adsorbed by Strata X-C within 1 min when the flow rate of hot spring water was 1 mL/min. Hydrochloric acid (6M-HCl) was used for desorption of REEs from polymeric resins, and results revealed that 70% of REEs could be recovered from the adsorbent by desorption. For further enrichment of REEs from the concentrated solution, NaOH was added in the solution to generate REEs as hydroxide precipitate. Consequently, the precipitate found to contain 1,100 g/t of REEs and we could enrich the over 5,700 times higher concentration of REEs compared to original Tamagawa hot spring water.

Key Words : Rare earth elements, Hot spring water, Adsorption, Precipitation

1 INTRODUCTION

Rare earth elements (REEs) indicate the fifteen lanthanides (with atomic number from 57 to 71) and scandium (Sc) and yttrium (Y). REEs have attractive physical and chemical properties. REEs are used as pigments, optical materials, magnetic materials and thermoelectric materials [1-6]. Tamagawa hot spring (Akita, Japan) is acidic in nature (pH 1.2) that contains very low concentration of REEs (1 to 70 µg/L) [7-9]. However, output water from Tamagawa hot spring is very high (ca. 9,000 L/min). Thus, generated REEs amount will be over 1 t/yr. The hot spring water does not have high REEs concentration for application to REEs refining process, but be used as REEs resources after enrichment process. However, other components in the hot spring water (e.g. iron (Fe), aluminum (Al) etc.) should be removed from hot spring water, because these are impurity in refining process. For the direct recovery and refining of REEs from hot spring water, an effective enrichment process is required. The current study was focused on the enrichment of REEs from Tamagawa hot spring water by adsorption and precipitation process. In this study, cation exchange resins were used for selective recovery of REEs and 6M HCl was used as stripping reagent from the resins. After, stripping REEs was concentrated by pH control using NaOH. In this study, we have achieved very high enrichment of REEs from Tamagawa hot spring water using adsorption and precipitation technique. Definitely this type of work would throw more light into the REEs recovery from hot spring water and new resource of REEs.

2 EXPERIMENTS

2.1 Hot spring water sample

Table 1 shows initial metals concentration of hot spring water from Obuki (which is located in Akita) used in this work. The hot spring water also contains many other metals. In this study, we also have focused iron (Fe), aluminum (Al), arsenic (As) which initially has a high concentration in the hot spring water. The hot spring water contains, Fe and Al ranged between 100 to 200 mg/L and 1 to 70 µg/L of REEs and also approximately 4,000 mg/L and 1,000 mg/L of chloride ion and sulfuric ion, respectively.

2.2 Adsorption and desorption

Separation and collection of dissolved REEs in hot spring water were carried out using adsorption in a column packed adsorbent (0.5 g of adsorbent in 6 mL cylinder, filled bed height: 17 mm). In this study, strata X-C (matrix constituent: styrene divinylbenzene, functional group: sulfonic acid, particle size: 33 µm, ion exchange capacity: 1 mmol/g, Phenomex), TE-07 and TE-08 (matrix constituent: Dibenzo-18-crown-6 chemically bonded silica gel, particle size: 150 to 300 µm, binding capacity: 0.1 to 0.3 mmol/g, IBC Advanced Technologies) were used for adsorption of REEs. For adsorption of REEs using 60 mL of hot spring water flowed into column which contains the resin (flow rate was 1 mL/min) from bottom side. The adsorption, desorption and precipitation rate (R) are calculated by equation (1).

Table 1 Typical element concentration in Tamagawa hot spring (Unit: $\mu\text{g/L}$)

Al*	Fe*	As*	Y	Ce	Pr	Nd	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu
186	122	2.9	63	40	6	27	8.1	1.9	10	1.8	12	2.5	7.2	1	6.4	1

(*: mg/L)

$$R(\%) = \frac{Ff - Ee}{Ff} \times 100 \quad (1)$$

where F is amount of feed solution, f is metal concentration in feed solution and E is amount of effluent, e is metal concentration in effluent.

After adsorption, the resin was rinsed by 5 mL of deionized water and adsorbed elements were removed by 6 mL of 6M HCl solution. The obtained solution was analyzed by ICP-OES and ICP-MS to monitor distribution of the metals and evaluated efficiency of adsorption and desorption process.

2.3 Precipitation

A process of metal recovery from solution by precipitation technique usually involves pH adjustment or sulfide addition to form solid products for separation. 50 mL of desorbed solution was adjusted to target pH by addition of NaOH (4M) and slowly stirred on magnetic stirrer. After pH adjustment, the solid precipitates were allowed to settle. This was followed by filtration and both solids and solution fraction were analyzed by ICP-AES to monitor distribution of the metals and evaluated efficiency of precipitation process.

3 Results and discussion

3.1 Adsorption

3.1.1 Adsorption behavior using strata X-C

Figure 1 shows adsorption behavior of metals in the hot spring water using strata X-C. Adsorption rates of REEs were almost similar, so adsorption rate of Nd was presented (as representative data of REEs) was in Figure 1. At first 5 min, over 98% of REEs and 90% of Fe and Al were adsorbed. Over 20 min passing,

adsorption rate decreased and Fe and Al could not adsorb on the resin. On the other hand, REEs kept the high adsorption rate 20 min after that REEs adsorption rate decreased. Adsorption of REEs onto Strata X-C resin was 99% until 20 min.

The chemical structure of strata X-C, TE-07 and TE-08 were shown in Scheme 1 and Scheme 2. A strata X-C has sulfonic acid as functional group. REEs and some metals were adsorbed by ion exchange reaction on strata X-C. Therefore, high REEs adsorption rate and was obtained by strata X-C.

3.1.2 Adsorption behavior using TE-07

Figure 2 shows adsorption behavior of metals in hot spring water using TE-07. At first 5 min, about 90% of Nd and 70% of Al were

Scheme 1 Chemical structure of Strata X-C

Scheme 2 Chemical structure of TE-07 and TE-08

Figure 1 Adsorption behaviors of metals in hot spring water using Strata X-C. (Conditions: Flow rate 1 mL/min, Temp. 20°C)

Figure 2 Adsorption behaviors of metals in hot spring water using TE-07. (Conditions: Flow rate 1 mL/min, Temp. 20°C)

adsorbed on TE-07. Fe and As could not adsorb in this condition. The breakthrough time of all metals is very fast compared with strata X-C and metals could not adsorb from over 20 min. From the results, TE-07 could recover only 90% REEs until 5 min elapsed time and total adsorbed amount of TE-07 is lower than strata X-C.

3.1.3 Adsorption behavior using TE-08

Figure 3 shows adsorption behavior of metals in hot spring water using TE-08. At first 5 min, about 85% of Nd and 70% of Al were adsorbed on TE-08. TE-08 was adsorbing small amount of Fe and As. The breakthrough time was 10 min, after that REEs were not adsorbed by TE-08. From the results, TE-08 adsorbing 85% of REEs until 5 min passing time, however the breakthrough time is earliest compared to other resins.

3.1.4 Desorption of metals from adsorbents

For recovery and/or enrichment of metals from adsorbent, we tried desorption of metals with high concentration of HCl. Metal concentration in desorbed solution are given in Table 2. According to Table 2, concentration of Nd was very high compared with original hot spring water using strata X-C polymer. The enrichment factor (I) is calculated by equation (2).

$$I = \frac{c}{f} \quad (2)$$

where c is metal concentration of enriched solution, f is metal concentration of feed solution in the process.

Enrichment factor (I) indicates upgrading ratio of concentrated material and efficiency of concentration process. The enrichment factor (I) of Nd on strata X-C polymer was 9.07. Desorption of Nd from TE-07 and TE-08 was carried out, but Nd could not be detected in desorbed solution. Desorption rate of Nd in strata X-C was 76%, while desorption of Nd from other two resin was not detected.

3.2 Precipitation

Desorption of REEs from strata X-C has concentrated more than 9 times compared to original hot spring water (Table 2). For recovery of REEs from desorbed solution from strata X-C polymer, we tried to generate precipitate by pH control using NaOH.

Figure 3 Adsorption behaviors of metals in hot spring water using TE-08. (Conditions: Flow rate 1 mL/min, Temp. 20°C)

Table 2 Metals concentration in desorbed solution obtained from several adsorbent. (Unit: mg/L)

Adsorbent	Al	Fe	As	Nd (T-REEs)	I_{Nd} (I_{REEs})
	(mg/L)				
Hot spring	186	122	2.9	0.027 (0.19)	-
Strata X-C	357	196	2.8	0.245 (1.50)	9.07 (7.90)
TE-07	89	177	2.1	N. D. (N. D.)	-
TE-08	101	145	1.3	N. D. (N. D.)	-

(T-REE: Total rare earth elements)

3.2.1 Precipitation behavior by pH control of hot spring water

Figure 4 shows recovery of metals dissolving in the hot spring water by precipitation process. These results revealed that precipitation rates of Al, Fe and Nd increased over the pH value of 4. At the pH value of 8, almost metals precipitation rates reached nearly 100 %. Based on these results, pH 8 was fixed for recovery of REEs from the desorbed solution.

3.2.2 Precipitation of desorbed solution at pH 8

We have studied the REEs recovery from desorbed solution obtained from strata X-C by precipitation at pH 8 using NaOH solution. Chemical composition of the precipitate from dissolved solution was shown in Table 3. The precipitate contained 22.9 mass%, 11.0 mass% and 114 g/t of Al, Fe and Nd respectively. This result supports that REEs was enriched in high concentration in the precipitate and indicates the possibility of REEs recovery from Tamagawa hot spring water in a large scale.

3.3 REEs enrichment process

Figure 5 depicts the proposal for enrichment of REEs from hot spring water, based on the current study. The process generally has the following stages; (1) adsorption to recover REEs from hot spring water via polymer type adsorbent, (2) desorption of REEs from adsorbent by acidic solution and (3) precipitation of REEs by addition of alkaline reagent.

In the first stage, the hot spring water elapsed strata X-C filled column for recovery of REEs. The adsorbent after elapsing was

Figure 4 Precipitation of metals in hot spring water as a function of pH.

Table 3 Typical composition of precipitate and enrichment factor of each element via adsorption – precipitation concentration process.

	Al	Fe	As	Y	Ce	Pr	Nd	Sm	Gd	Dy	Er	Tm
Precipitate (g/t(ppm))	22.9*	11.0*	156	270	551	36	114	37	45	31	34	2.3

(*: mass%)

treated in the second stage where desorption was performed by 1/10 volume of the spring water of 6M HCl solution. The concentrated solution contains above 1.5 mg/L of REEs concentration in total. In the third stage precipitation technique was performed to recover REEs as precipitate. The pH of this concentrated solution was controlled by NaOH from 1 to 8 for generation of REEs as hydroxide precipitate (precipitate 1), and the precipitate 1 is containing 1,100 g/t of REEs. The REEs in precipitate1 were further enrichment by hydrogen reduction. The obtained precipitate from hydrogen reduction (precipitate 2) is containing 5,600 g/t REEs. Some impurities in precipitate 2 such as Al and Fe can remove by conventional REE refining process. About 1 t/yr of REEs were generated with Tamagawa hot spring water. It was estimated that accordingly the REEs recovery process, 650 kg (65%) of REEs will recover from Tamagawa hot spring water per year.

4 Conclusion

The present work focused on feasibility studies of REEs enrichment of Tamagawa hot spring water via adsorption and precipitation is summarized below;

- 1) Adsorption of REEs using strata X-C up to 96% which is the

Figure 5 Flow sheet for REEs enrichment process from Tamagawa hot spring water.

highest adsorption percentage in this experiment. Adsorbed Nd could be desorbed by 6M HCl solution from strata X-C and their desorption rate was 74%. The desorbed solution contained 1.5 mg/L as total REEs and their enrichment factor of REEs was 7.90 compare to raw hot spring water.

- 2) In precipitation process, about 100% of REEs were precipitated at pH 8 by NaOH neutralization. Obtained precipitate contained 1,100 g/t of REE. This result shows that very high amount of REEs were enriched from hot spring water.

From this study, very low concentration of REEs resources of Tamagawa hot spring water was concentrated by adsorption-desorption and precipitation methods. These results showed new REEs resource and economic way to recover the REEs from hot spring water. The methods will leads to a larger scale REEs from hot spring water.

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