## 4–12 Recovery of Valuable Rare Metals from High-Level Radioactive Waste — Separation of Rhodium with Ion-Exchange Resin —





 $HNO_3$  initial concentration,  $[HNO_3]_{init}$  (mol/ $\ell$ )

Experimental conditions

$$\label{eq:constraint} \begin{split} & [Rh(III)] = 0.10 \ mmol/\ell, \ [La(III)] = 0.072 \ mmol/\ell, \\ & [Sr(II)] = 0.12 \ mmol/\ell, \ [Cs(I)] = 0.075 \ mmol/\ell, \\ & [Na(I)] = 0.43 \ mmol/\ell, \ Solution \ volume = 1.0 \ m\ell, \\ & AMP03 = 0.099 \ g, \ Shaking \ time = 60 \ min. \end{split}$$

## Fig.4-24 Schematic formula of betaine resin, AMP03

Functional groups with ion exchangeability have been connected to the structure of cross-linked polystyrene, which is an amphoteric ionexchange resin having a positive and a negative charge in a functional group. The structure of the resin contains carbon, hydrogen, oxygen, and nitrogen.

## Fig.4-25 Adsorption behavior of metal ions with AMP03

Plots of the extraction rate (A.R., %) value against initial concentration of nitric acid for the adsorption of Rh(III), La(III), Sr(II), Cs(I), and Na(I).

High-level radioactive waste (HLW) from reprocessing process contains various elements. Some of these are valuable, such as rare metals. If the valuable rare metal in HLW is recovered for industrial usage, it may become an important resource. Rhodium (Rh) is a platinum-group metal that is necessary for the production of catalytic agents used in automobiles. The price of Rh is relatively high and will increase further with growing automobile demand. Relatively large amounts of Rh are generated as fission products. Although radioactive <sup>102</sup>Rh and <sup>102m</sup>Rh, with half-lives of 2.9 and 0.57 years, respectively, are present in minor amounts, almost all Rh generated in fission reactors is of the stable isotope <sup>103</sup>Rh. Therefore, after suitable storage, Rh can be used in industrial applications.

We examined Rh(III) adsorption using styrenedivinylbenzene copolymer functionalized with betaine (AMP03, Fig.4-24). AMP03 is generally used to separate sugar groups and salts. Consequently, AMP03 was found to successfully adsorb Rh(III) from the HNO<sub>3</sub> solution with pH 1.72. AMP03 is composed of C, H, O, and N and is favorable for reducing secondary radioactive waste. This point is advantageous for application to Rh(III) recovery from HLLW.



Experimental conditions  $[Rh(III)] = 0.10 \text{ mmol/}\ell$ , Solution volume = 1.0 m $\ell$ , AMP03 = 0.099 g, Shaking time = 60 min.

**Fig.4-26 Adsorption behavior of Rh(III) with AMP03** Plots of  $K_d$  versus TEA concentration in initial solutions. The Rh(III)-adsorption ability of AMP03 greatly increased after the additions of amine compounds, such as trimethylamine, TEA, to the aqueous phase.

The adsorption of Rh(III), La(III), Sr(II), Cs(I), and Na(I) from an HNO<sub>3</sub> solution was also studied by varying the HNO<sub>3</sub> concentration in the initial solution, [HNO<sub>3</sub>]<sub>init</sub>. The results are shown in Fig.4-25;Rh(III) and La(III) were adsorbed in the low-[HNO<sub>3</sub>]<sub>init</sub> range. The adsorption-ratio (AR) values of Rh(III) and La(III) decreased with increasing [HNO<sub>3</sub>]<sub>init</sub>. By contrast, AMP03 showed lower affinity for Sr(II), Cs(I), and Na(I) across the entire range of [HNO<sub>3</sub>]<sub>init</sub> values (AR < 10%). The order of the adsorption selectivity for AMP03 (Rh(III) > La(III) > Cs(I), Sr(II), Na(I)) is advantageous for the selective recovery of Rh(III).

The K<sub>d</sub> values of Rh(III) for AMP03 greatly increased with the addition of trimethylamine (TEA). To obtain detailed data for the efficient recovery of Rh(III), adsorption experiments were performed using 0.1–0.5M HNO<sub>3</sub> solution containing Rh(III) and TEA. Fig.4-26 shows plots of K<sub>d</sub> against the concentration of TEA contained in the initial solutions [TEA]<sub>init</sub>. All K<sub>d</sub> values in Fig.4-26 significantly increased with the addition of the amine compound. Effective Rh(III) adsorption with K<sub>d</sub> > 100 was also observed.

R&D activities aimed at establishing reasonable treatment processes for HLW will be conducted.

## Reference

Suzuki, T., Matsumura, T. et al., Recovery of Rhodium(III) from Nitric Acid Solutions using Adsorbent Functionalized with *N*,*N*,*N*- Trimethylglycine, Bulletin of the Chemical Society of Japan, vol.89, no.5, 2016, p.608-616.