

## Ion Exchange Characteristics of Rhodium and Ruthenium from a Simulated Radioactive Liquid Waste

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**Abstract**—Radioactive high-level liquid wastes contain significant quantities of platinum group metals (PGM) such as palladium [Pd(II)], rhodium [Rh(III)] and ruthenium [Ru(III)]. The PGM are produced as fission products in a nuclear reactor. In this study, batch and column experiments were carried out to investigate the ion exchange characteristics of Rh(III) and Ru(III) including the effects of the ionic group of ion exchangers, solution temperature, and the concentration of nitric acid by various ion exchangers such as IRN 78 and Dowex 1×8; the elution characteristics of Rh(III) and Ru(III) by various eluents were also investigated. Anion exchangers such as Dowex 1×8 with the ionic group of quaternary methyl ammonium had a higher capacity than anion exchanger such as IRN 78 with amine group for the adsorption of Rh(III) and Ru(III) from a simulated liquid waste. The optimal nitric acid concentration for the adsorption of Rh(III) and Ru(III) by anion exchangers was shown to be about 3 M and 2-3 M, respectively.

Key words: Rhodium, Ruthenium, Ion Exchangers, Recovery, Elution, Platinum Group Metals

### INTRODUCTION

The PGM, such as Pd(II), Rh(III), and Ru(III), are produced as the fission products in nuclear reactors. The demand for noble metals continues to grow steadily. The PGM are valuable and important as noble metals, but their natural resources are rather limited. Due to the increase in utilization of PGM in the automotive and dental industries, in electronic and electrical devices, in the production of ultrapure hydrogen, and as an industrial catalyst, the demand for PGM continues to grow in a steady manner. As the number of nuclear power plants increases, amounts of these metals in irradiated nuclear fuels are expected to become comparable to those of the natural resources in the world. The noble metals generated by the fission can thus be recognized as an important alternative resource to meet the increasing need of noble metals [Kondo and Kuboto, 1992].

In order to separate the PGM from high-level radioactive liquid waste (HLLW), many recovery methods for PGM have been studied, for example, the lead oxide extraction method, liquid-liquid extraction method with tri-butylphosphate (TBP), adsorption method with active carbon, ion exchange method, and precipitation methods by formic acid, hydrazine, hypo-phosphorous acid, and ascorbic acid etc. [Smith and McDuffie, 1981; Jensen, 1984; Beamish, 1960; Carlin et al., 1975; Nito et al., 1986; Rizvi et al., 1996; Lee et al., 1994, 1999, 2000]. Among these methods, precipitation and ion exchange methods would be most practical way because of the economy and simplicity.

In the present work, ion exchange was chosen as an alternative method for separation and recovery of Rh(III) and Ru(III) from HLLW by ion exchangers. One of the first attempts to use ion exchange methods for the separation of PGM was recorded by Stevenson et al. [1953]. Recently, Bazi and Gaita [1995] investigated ion

exchange characteristics for selective separation of PGM from the solution obtained by the leaching automotive catalytic converters and Marina et al. [1997] investigated anion exchange separation procedures for the PGM and gold by Dowex 1×8 resin. Navratil also studied ion exchange technology in spent fuel reprocessing [Navratil, 1989]. Ion exchange characteristics of Pd(II) by anion exchangers and precipitation characteristics of Pd(II) by ascorbic acid have been already investigated [Lee et al., 1999, 2000]. Pd over 99.5% was selectively precipitated at ascorbic acid concentration above 0.06 M. In general, trivalent rhodium may be adsorbed on Dowex 50 W cation exchanger from a weak acid solution and subsequently eluted with moderate or strong concentrations of hydrochloric acid. Rh(III) is only slightly adsorbed onto the anion exchanger and is typically eluted from the column first with a dilute acid or salt solution, and can be separated from palladium and platinum [Wei et al., 1996; Faris and Buchanan, 1964].

In this work, to determine the optimal separation conditions of Rh(III) and Ru(III) from HLLW, batch and column experiments were carried out to investigate the ion exchange characteristics including the effects of the ionic group of ion exchangers, solution temperature, and the concentration of nitric acid. The optimal separation conditions and the elution characteristics of Rh(III) and Ru(III) by various eluents were also studied.


### EXPERIMENTAL

Commercial anion and cation exchangers such as IRN 78, Dowex 1×8 and Dowex 50 W were used for these experiments. Table 1 shows the properties of the ion exchange resins used. The resins were pretreated with 10% sodium hydroxide solution, washed with distilled water, converted into nitrate form with nitric acid, and dried overnight at 50 °C in a vacuum dry oven. Reagent grade nitric acid was diluted with distilled water to obtain a desired concentration varying from 0.1 to 7 M. The nitric acid solution of Rh(III) and Ru(III) was prepared by dissolving 10 wt% Rh(NO<sub>3</sub>)<sub>3</sub> solution and ruthenium

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**Table 1. The properties of ion exchangers**

Ion exchangers	Ionic functional groups
- IRN 78	- $\text{N}^+(\text{CH}_3)_3\text{OH}^-$
- Dowex 1×8-400	- $\text{CH}_2-\text{N}^+(\text{CH}_3)_2\text{CH}_3\text{Cl}^-$
- Dowex 50 W×4-100	- $\text{SO}_3^- \text{H}^+$
- AR-01	

nium(III) nitrosyl nitrate  $[\text{Ru}(\text{NO})(\text{NO}_3)_x]$  into the nitric acid solution.

In batch experiments, 1 g of an ion exchanger and 20 ml of a PGM containing solution were put in a glass flask and the flask was set in a mechanically shaken water bath kept at 20 or 60 for 24 hours. It was then taken out and centrifuged for 5 minutes at 3,000 rpm, and the metal concentration in the solution was analyzed by inductively coupled plasma atomic emission spectroscopy (ICP, Model: Jobin Yvon JY38 plus, polychromator, JYOCY).

The sorption kinetic studies of Rh(III) and Ru(III) by ion exchangers were carried out in a 200 ml metal solution with 1 g of dried resin. Samples were taken periodically from the suspension and centrifuged immediately to remove resins. The residual metal content in supernatant liquor was analyzed by ICP spectroscopy for residual metal contents. Elution characteristics were also studied by various eluents such as thiourea hydrochloric and nitric acid solutions.

The distribution coefficient ( $K_d$ ) of metal is defined as the ratio of the metal concentration in the resin of the ion-exchanger to that in the solution [Helfferich, 1962]. Thus, the  $K_d$  value was calculated by the following equation:

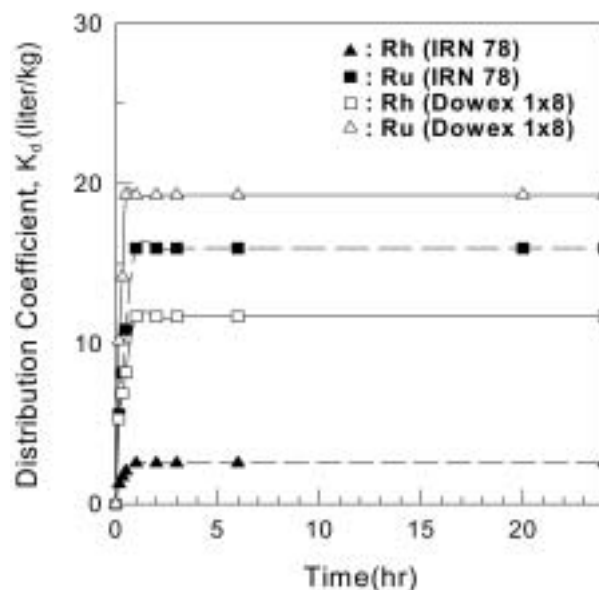
$$K_d = \frac{C_1}{C_2}$$

where  $C_1$  is the content of metal in 1 g of resin and  $C_2$  is the content of metal of 1 ml in the solution.

The column experiments were carried out in a glass column of 1.5 cm internal diameter and 30 cm length filled with 5 g of ion exchange resin. Feed solution was percolated through the packed column at a flow rate of 1.0 ml/min controlled by a peristaltic pump (EYELA SMP-21, Japan). The effluent samples were collected at regular intervals by the fraction collector (Model: Adventec SF-2100) and analyzed for Pd(II) and Ru(III) concentrations by ICP.

## RESULTS AND DISCUSSION

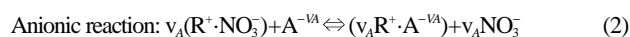
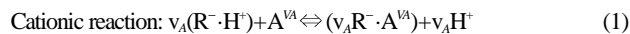
The adsorption kinetics of Rh(III) and Ru(III) by anion exchangers such as IRN-78, Dowex 1×8 are shown in Fig. 1. The results show that the rate of ion exchange of Rh(III) and Ru(III) by an anion exchanger was very rapid and reached an equilibrium state within 1 hr. Considering the cationic and anionic exchange reaction of Rh(III) and Ru(III) in nitrate media of Eqs. (1) and (2), the ionic groups of ion exchangers act as metal ion exchange sites. Therefore, the rate of ion exchange may be very rapid. Ru(III) is strongly



**Fig. 1. Adsorption kinetics of Rh(III) and Ru(III) on various anion exchangers [Nitric acid concentration: 0.1 M, Temperature: 20 °C].**

adsorbed from dilute nitric acid solutions, and this is considered to result from the complex formation between Ru(III) and the anion exchanger. However, Rh(III) is slightly adsorbed onto the ion exchangers.

The ion exchange reaction of cation and anionic complexes in nitrate medium is generally expressed as [Wei et al., 1996],



where  $\text{R}^+/\text{R}^-$ , A, and  $v_A$  denote the fixed ionic group, the counter ion, and the charge number of the counter ion, respectively.

Fig. 2 shows the effect of ionic groups on the adsorption of Rh(III) and Ru(III) from nitric acid solution onto the several ion exchangers. From these experimental results, the selectivity of Rh by anion exchangers was very low. Also, the capacity of Rh adsorption by ion exchange resins was different. This result can be explained by the difference in the chemical structures of ionic groups of ion exchangers in Table 1. Dowex 1×8 with an ionic group of quaternary methyl ammonium has higher selectivity than IRN 78 with the con-

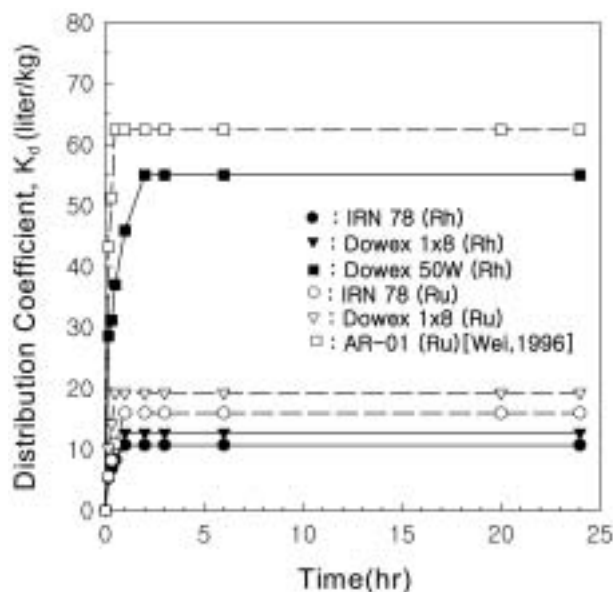


Fig. 2. Effect of ionic group on the adsorption of Rh(III) and Ru(III) on various ion exchangers [Nitric acid concentration: 0.5 M (Rh), 1 M (Ru), Temperature: 60 °C].

ventional amine group for the adsorption of Rh from nitric acid solutions. Particularly, the cation exchanger, Dowex 50 W, with the sulfonic group shows significantly strong Rh adsorption at a diluted nitric acid solution. From the results, Rh cations such as  $\text{Rh}^{+3}$  or  $\text{Rh}^{+2}$  may be dominant ions in diluted nitric acid concentrations below 0.5 M. Therefore, Rh is more adsorbed by the cation exchanger, Dowex 50 W, than by anionic exchangers such as IRN 78 and Dowex 1×8.

The results on the adsorption of Ru(III) from nitric acid solution onto the several conventional anion exchangers such as IRN 78 and Dowex 1×8 were compared with those from the anion exchanger named AR-01 with quaternary and tertiary benzimidazole groups

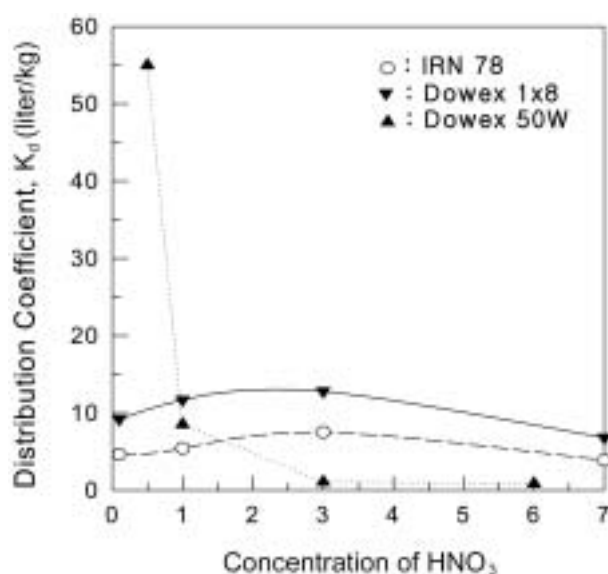


Fig. 3. Effect of nitric acid concentration on the adsorption of Rh(III) on various ion exchangers [Temperature: 20 °C].

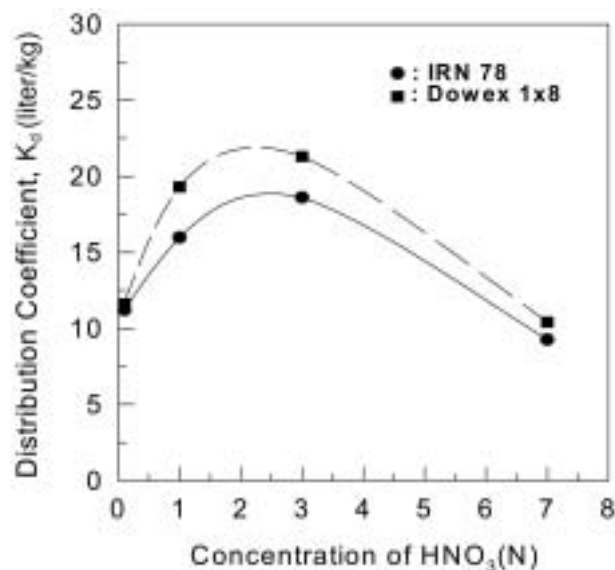


Fig. 4. Effect of nitric acid concentration on the adsorption of Ru(III) on various anion exchangers [Temperature: 20 °C].

cited in the literature [Wei et al., 1996]. As shown in Fig. 2, anion exchangers such as Dowex 1×8 with an ionic group of quaternary methyl ammonium have higher ion exchange capacity than anion exchangers such as IRN 78 with a conventional amine group. Wei and coworker reported that the anion exchanger AR-01 with a benzimidazole group especially showed strong adsorption of Ru(III) from nitric acid solution. These results can be explained by the difference in the chemical structures of the ionic groups of anion exchangers in Table 1.

Fig. 3 and Fig. 4 show that the effect of the nitric acid concentration on the adsorption of Rh(III) and Ru(III) in the range of 0.1 to 7 M by various ion exchangers, respectively. As shown in the figures, the optimal nitric acid concentration for the adsorption of Rh(III) was shown to be about 3 M for anion exchangers, the optimal  $K_d$  value was measured at 7.5 for IRN 78 and 12.8 for Dowex 1×8, respectively. These results coincide with the results from the literature [Navratil, 1989]. However, the cation exchanger, Dowex 50 W, with the sulfonic group shows significantly strong Rh(III) adsorption at a diluted nitric acid solution. The optimal nitric acid concentration for the adsorption of Rh(III) was shown to be about 0.5 M for the cation exchanger; the  $K_d$  value was measured at 55 for Dowex 50. Based on the results, Rh cations such as  $\text{Rh}^{3+}$  or  $\text{Rh}(\text{NO}_3)^{+2}$  may be dominant ions in diluted nitric acid concentrations below 0.5 M. Therefore, the cation exchanger, Dowex 50 W had a higher capacity than anion exchangers such as IRN 78 and Dowex 1×8 for the adsorption of Rh(III) in diluted nitric acid concentrations below 0.5 M. However, as the concentration of nitric acid increases, Rh(III) may be anionic complexed with nitrate ions ( $\text{NO}_3^-$ ) in the nitric acid solution, and may mainly exist as anions such as  $\text{Rh}(\text{NO}_3)_4^-$ . As shown in Fig. 5, in case of Ru(III), the optimal nitric acid concentration was also shown to be in 2–3 M. the optimal  $K_d$  value was measured at 18.6 for IRN 78 and 21.3 for Dowex 1×8, respectively.

The effect of solution temperature for the adsorption of Rh(III) and Ru(III) by IRN 78 and Dowex 1×8 is shown in Fig. 5 and Fig. 6, respectively. As shown in the figures, the ion exchange capacity

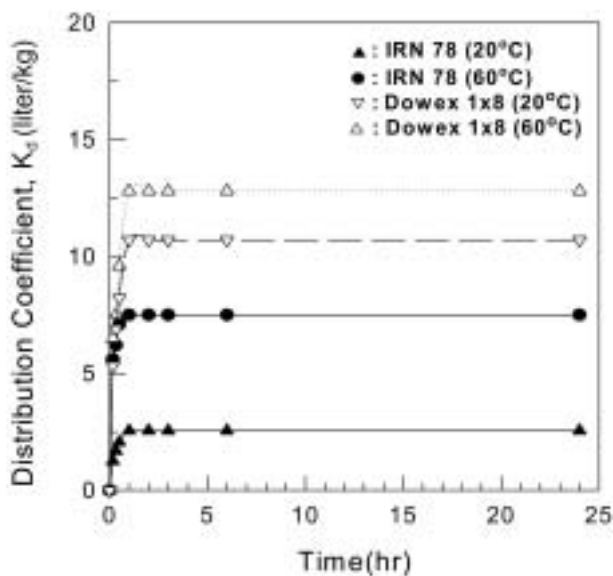


Fig. 5. Effect of solution temperature on the adsorption of Rh(III) on anion exchangers [Nitric acid concentration: 0.1 M, Rh concentration: 95 ppm].

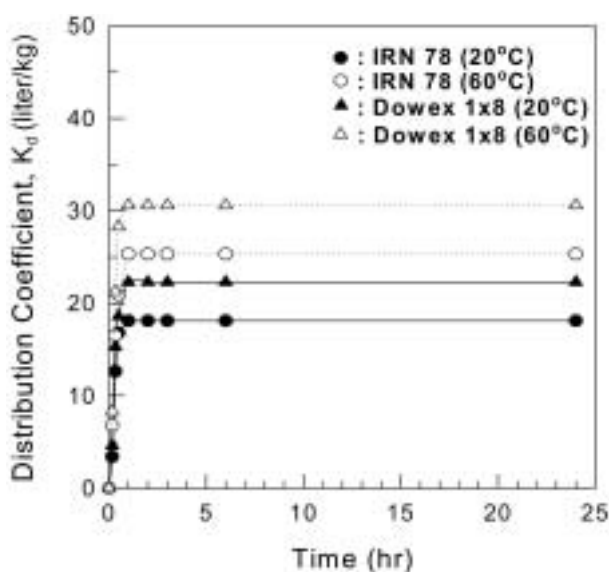


Fig. 6. Effect of solution temperature on the adsorption of Ru(III) on anion exchangers [Nitric acid concentration: 2 M, Ru concentration: 50 ppm].

of Rh(III) and Ru(III) at a high solution temperature (60 °C) is higher than that at a low temperature (20 °C).

Fig. 7 shows the elution characteristics of Rh(III) by various eluents in the batch experiment. As shown in Fig. 7, the capacity for the elution of Rh(III) by 6 M HCl was very high. However the elution capacity of Rh(III) by other eluents such as thiourea and nitric acid solutions was very low. Also, when the nitric acid was used as an eluent, the increase in nitric acid concentration did not play an important role in the elution capacity of Rh(III).

The ion exchange characteristics of Rh in a packed bed filled with 5 g ion exchange resins at 0.5 M nitric acid solution are shown in Fig. 8. The ion exchange capacity of Rh by the cation exchange

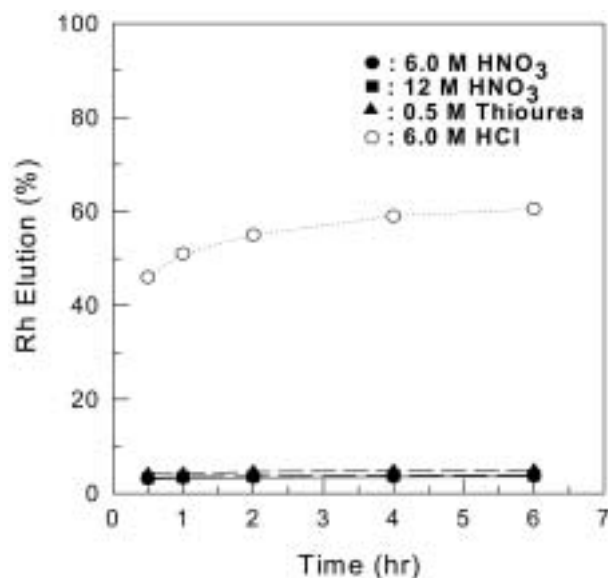


Fig. 7. Time evolution of Rh(III) elution with various eluents using saturated IRN 78 ion exchange resin.

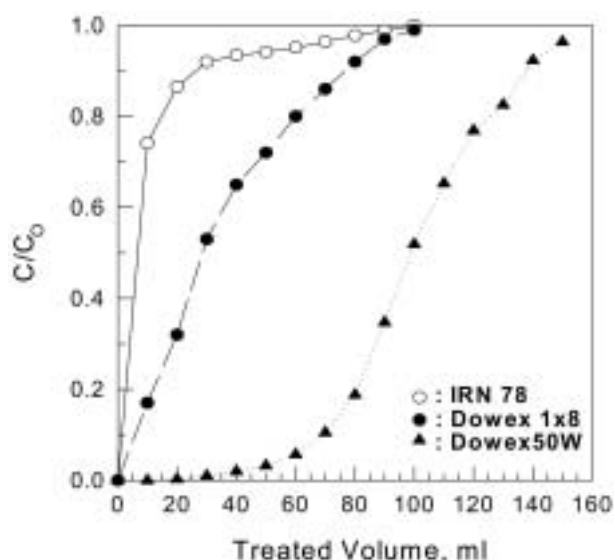


Fig. 8. Breakthrough curve for Rh(III) adsorption by anion exchangers [Rh(III) concentration: 177 ppm, nitric acid concentration: 0.5 M, feed rate: 1 ml/min].

resin (Dowex 50 W) was several times higher than that by anion exchange resins (Dowex 1×8 and IRN 78) at a dilute nitric acid solution. Breakthrough by Dowex 1×8 occurred at a 5 ml volume treatment and the bed was saturated at 100 ml volume treatment while breakthrough and saturation volume by Dowex 50 W increased 50 ml and 150 ml, respectively. Based on these experimental results, it is also confirmed that the majority of Rh(III) exist as cations in dilute nitric acid concentrations below 0.5 M. Fig. 9 shows the ion exchange characteristic of Ru(III) in the packed columns filled with 5 g of ion exchange resins in a 2.0 M nitric acid solution. Dowex 1×8 with ionic group of quaternary methyl ammonium has higher ion exchange capacity than IRN 78 with conventional amine group.

Fig. 10 shows the effect of feed rate on the adsorption of Rh(III)

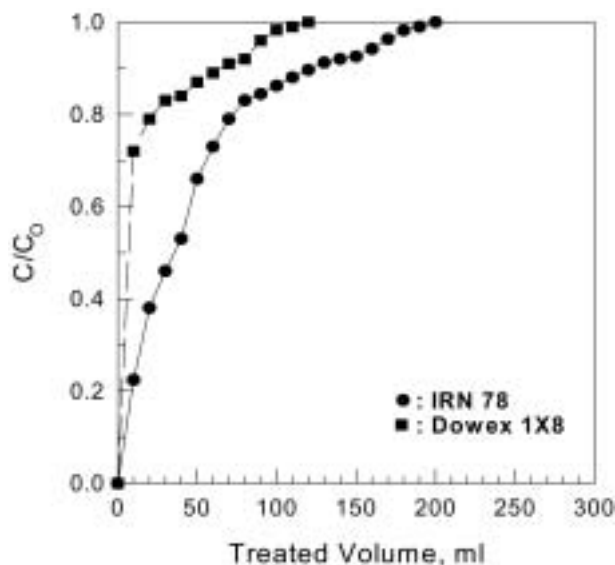


Fig. 9. Breakthrough curve for Ru(III) adsorption by anion exchangers [Ru concentraion: 160 ppm, nitric acid concentration: 2.0 M, feed rate: 1 ml/min].

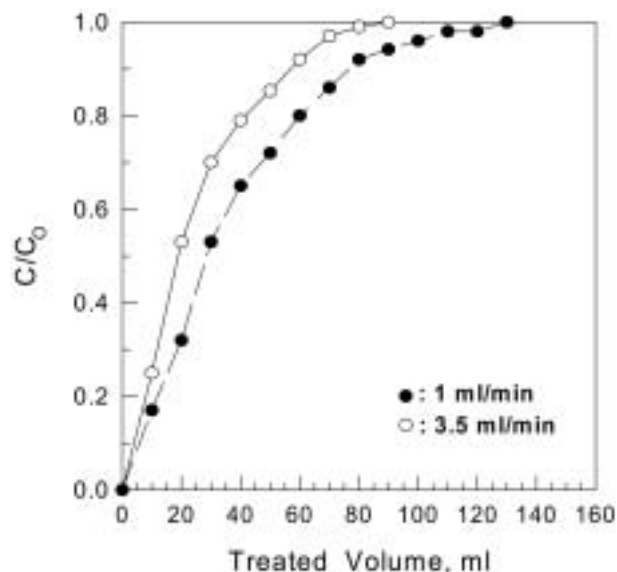


Fig. 11. Effect of feed rate on the adsorption of Ru(III) by Dowex 1×8 [Concentraion: 160 ppm, nitric acid concentration: 0.5 M].

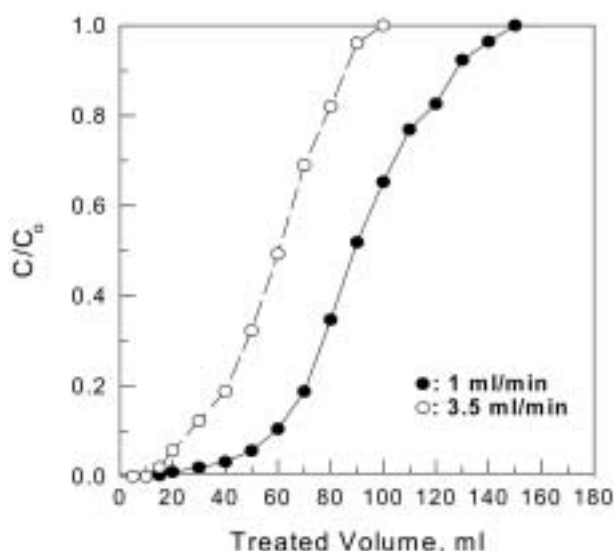


Fig. 10. Effect of feed rate on the adsorption of Rh(III) by Dowex 50 W [Rh(III) concentraion: 177 ppm, nitric acid concentration: 0.5 M].

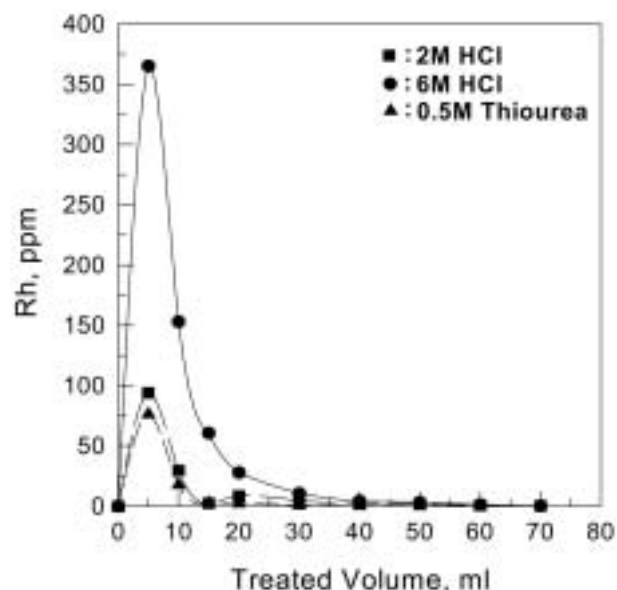


Fig. 12. Elution curves for Rh(III) saturated column by various eluents [Resin: 5 g Dowex 1×8, feed rate: 1 ml/min].

by Dowex 50 W in packed columns. As shown in Fig. 10, as the feed rate increased, the ion exchange capacity of Rh decreased. When the feed rate was 1 ml/min, the breakthrough occurred at 50 ml volume treatment and the bed was saturated at 150 ml volume treatment. But, when the feed rate increased 3.5 ml/min, the breakthrough and saturation volumes of Rh decreased to 20 ml and 110 ml, respectively.

Fig. 11 shows the effect of feed rate on the adsorption of Ru(III) in the packed columns by Dowex 1×8. The ion exchange capacity of Ru(III) decreased as feed rate increased. In the case of ion exchange reaction of Ru(III), when feed rate was 1 ml/min, the bed was saturated at 90 ml treatment. When the feed rate increased 3.5

ml/min, however, the bed was saturated at 130 ml treatment.

Fig. 12 shows the elution curve through a packed bed for Rh(III) adsorption by Dowex 1×8 using various eluents. As for the results of elution experiments in the batch, Rh was effectively eluted by 6 M HCl solution, while the elution capacity of Rh by other eluents such as thiourea was low. About 40 ml of eluent was necessary for the almost complete elution of Rh ions.

Fig. 13 shows the elution curves for Ru(III) saturation columns by various eluents. As shown, Ru(III) was effectively eluted by a 6 M HCl solution. The capacity for the elution of Ru(III) by 0.5 M thiourea and 0.1 M nitric acid mixed solution was also relatively low.

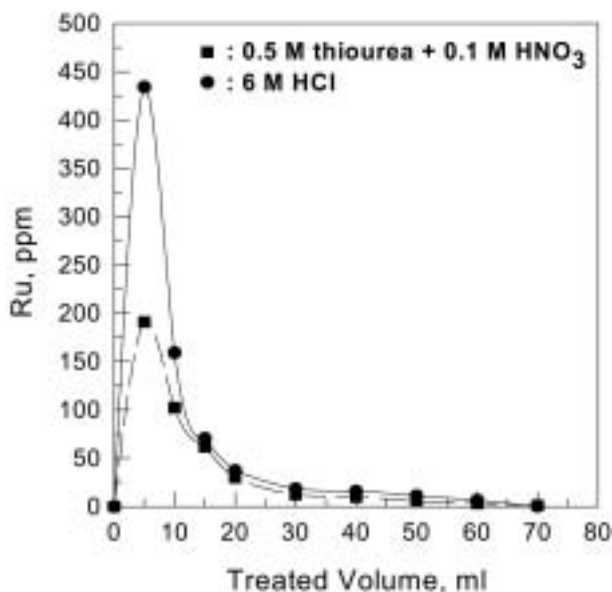


Fig. 13. Elution curves for Ru(III) saturated column by various eluents [Resin: 5 g Dowex 1×8, feed rate: 1 ml/min].

### CONCLUSIONS

Batch and column experiments were carried out to investigate the ion exchange and elution characteristics of Rh(III) and Ru(III) by various ion exchangers. Based on experimental results, the rate of ion exchange of Rh(III) and Ru(III) by various ion exchangers was very rapid and reached an equilibrium state within 1 hr. Rh(III) is slightly adsorbed onto the ion exchangers. The ionic groups of ion exchangers significantly affected the ion exchange capacity for the adsorption of Rh(III) and Ru(III) from nitric acid solutions. Anion exchangers such as Dowex 1×8 with the ionic group of quaternary methyl ammonium had a higher capacity than anion exchangers such as IRN 78 with amine group for the adsorption of Rh(III) and Ru(III) from nitric acid solution in the batch and column experiments. The optimal nitric acid concentration for the adsorption of Rh(III) and Ru(III) by anion exchangers was shown to be about 3 M and 2-3 M, respectively. However, Dowex 50 W with the sulfonic group shows significantly strong Rh(III) adsorption at a diluted nitric acid solution. Rh(III) and Ru(III) were effectively eluted by a 6 M HCl solution. About 40 ml of eluents was necessary for the almost complete elution. The capacity for the elution of Ru(III) by 0.5 M thiourea and 0.1 M nitric acid mixed solution was also relatively low.

Based on these experiments, to separate Rh(III) and Ru(III) effectively by the ion exchange method from radioactive liquid waste, the development of an ion exchanger with a high selectivity for Rh(III) and Ru(III) may be necessary.

### ACKNOWLEDGMENT

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