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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 nuclear reactors. In this study, batch and column experiments were carried out to investigate the ion exchange characteristics of Pd(II) and Ru(III), including the effects of the ionic group of ion exchangers, solution temperature, and the concentration of nitric acid by various anion exchangers such as IRN 78 and Dowex 1x8. The elution characteristics of Pd(II) and Ru(III) by various eluents were also investigated. The rate of ion exchange of Pd(II) and Ru(III) by an anion exchanger was very rapid and reached an equilibrium state within 1 hour. Anion exchangers such as Dowex 1x8 with the ionic group of quaternary methyl ammonium had a higher capacity than anion exchanger, such as IRN 78 with amine group,

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for the adsorption of Pd(II) and Ru(III). Pd(II) could be easily eluted by 0.5 M thiourea solution and 0.1-M nitric acid mixed solution. Ru(III) was effectively eluted by a 6-M HCl solution.

Key Words: Palladium; Ruthenium; Anion exchangers; Platinum group metals; Radioactive liquid waste.

INTRODUCTION

The irradiation of nuclear fuels in power reactors leads to the production of atoms of a wide range of fission products, ranging in atomic mass from 70 to 160. These fission products include three of PGM, i.e., Pd(II), Rh(III), and Ru(III). 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 ultra pure 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 fission can be recognized as the important alternative resource to meet the increasing demands.[2]

To separate the platinum group metals from high-level radioactive liquid waste (HLLW), many recovery methods for platinum group metals 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, hypophosphorous acid, and ascorbic acid.[3–8] Among these methods, precipitation characteristics of Pd(II) by ascorbic acid have been already studied.[9] Pd over 99.5% was selectively precipitated at ascorbic acid concentration above 0.06 M. In the present work, ion exchange method was chosen as an alternative method for separation and recovery of Pd(II) and Ru(III) from HLLW by anion exchangers. One of the first attempts to use ion exchange methods for the separation of PGM was recorded by Stevenson et al[10] Recently, Bazi and Gaita investigated ion exchange characteristics for selective separation of PGM from the solution obtained by the leaching automotive catalytic converters[11] and Marina et al investigated anion exchange separation procedures for the PGM and gold by Dowex 1x8 resin.[12] Wei and coworkers also reported that the anion exchanger AR-01 with a benzimidazole group especially shows significantly strong adsorption of Pd(II) from nitric acid solution.[7] Faris and Buchum investigated anion

exchange characteristics of the elements in nitric acid and nitrate solutions.[13] Navratil also studied ion exchange technology in spent fuel reprocessing.[14] In spite of numerous works concerned with PGM by various solvents, data on the use of sorption for the separation and recovery of PGM from HLLW are rather scarce.

In this work, to determine the optimal separation conditions of Pd(II) 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 Pd(II) and Ru(III) were also studied.

MATERIAL AND METHODS

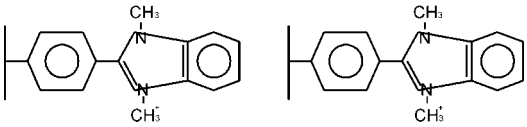
Commercial strongly basic anion exchangers, such as IRN-78 and Dowex 1x8, were used as anion exchangers for these experiments. Table 1 shows the properties of the anion exchange resins used. The resins were pretreated with 10% sodium hydroxide solution, washed with distilled water, converted into nitrate form with nitric acid, and dried overnight at 50°C in a convection 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 Pd(II) and Ru(III) was prepared by dissolving palladium(II) nitrate[Pd(NO3)2] and ruthenium(III) nitrosyl nitrate [Ru(NO)(NO3)x] into the nitric acid solution.

In batch experiments, 1 g of an anion exchanger and 20 mL of a platinum group metal containing solution were put in a glass flask and the flask was set in the mechanically shaking water bath maintained at 20°C or 60°C for 24 hours. It was then taken out and centrifuged for 5 minutes at 3000 rpm, and the metal concentration in the solution was measured by inductively coupled plasma atomic emission spectroscopy (ICP, Model: Jobin Yvon JY38 plus, polychromator, JYOCY). The sorption kinetic studies of Pd(II) and Ru(III) by anion 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. Supernatant liquor was analyzed by ICP spectroscopy for residual metal contents.

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.[10] Thus, the K_d value was calculated by the following equation:

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

Table 1. The properties of anion exchangers.

Ion exchangers	Ionic functional groups	K_d
IRN 78	$N^+(CH_3)_3OH^-$	16.9
Dowex 1x8-400	$CH_2\text{-}N^+(CH_3)_2\text{-}CH_3Cl^-$	25.1
Dowex 2x8-400	$CH_2\text{-}N^+(CH_3)_2\text{-}CH_2CH_2OHCl^-$	21.5
AR-01		167
IRA-93ZU	$N(CH_3)_2OH^-$	13.2
IRA-900	$N^+(CH_3)_3OH^-$	12.3

K_d: distribution coefficient values for the adsorption of Pd(II) (L/kg) under experimental conditions: nitric acid concentration = 6 N, temperature = 60°C.

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 Pd(II) and Ru(III) by anion exchangers such as IRN-78, Dowex 1x8 are shown in Fig. 1. The results show that the rate of ion exchange of Pd(II) and Ru(III) by an anion exchanger was very rapid and reached an equilibrium state within 1 hour. Considering the anionic exchange

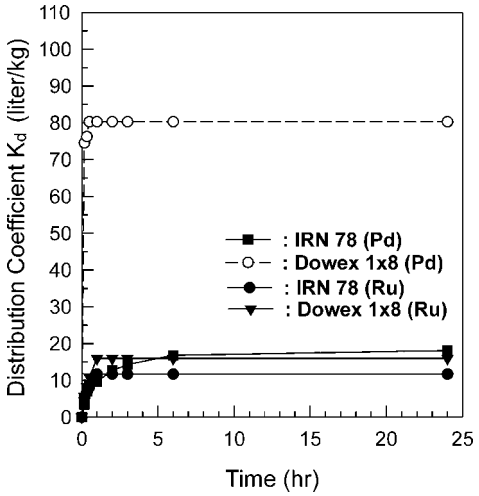


Figure 1. Adsorption kinetics of Pd(II) and Ru(III) on various anion exchangers. Nitric acid concentration: 0.1-M (Pd), 1-M (Ru), temperature: 20°C.

reaction of Pd(II) and Ru(III) in nitrate media of Eq. (1), the ionic groups of ion exchangers acted as metal ion exchange sites. Therefore, the rate of ion exchange may be very rapid.

The ion exchange reaction of anionic complexes in nitrate media is generally expressed as,[7]

$$v_A(R^+ \cdot NO_3^-) + A^{-vA} \Leftrightarrow (v_A R^+ \cdot A^{-vA}) + v_A NO_3^- \quad (1)$$

where R^+, A, and v_A denote the fixed ionic group, the counter ion (anionic complex), and the charge number of the counter ion, respectively.

Figures 2 and 3 show the effect of ionic groups on the adsorption of Pd(II) and Ru(III) from nitric acid solution onto the several anion exchangers, independently. These results were compared with those from the anion exchanger named AR-01 with quaternary and tertiary benzimidazole groups and the several conventional anion exchangers, such as IRA 900 and IRA-93ZU cited in the literature.[7] As shown in the figures, anion exchangers, such as Dowex 1x8 and Dowex 2x8, with an ionic group of quaternary methyl ammonium have higher ion exchange capacity than anion exchangers, such as IRN 78 and IRA-93ZU, with a conventional amine group. Wei and coworkers reported that the anion exchanger AR-01 with a benzimidazole group especially showed significantly strong adsorption of Pd(II) from nitric acid solution. The distribution coefficient (K_d) value for the adsorption of Pd(II)

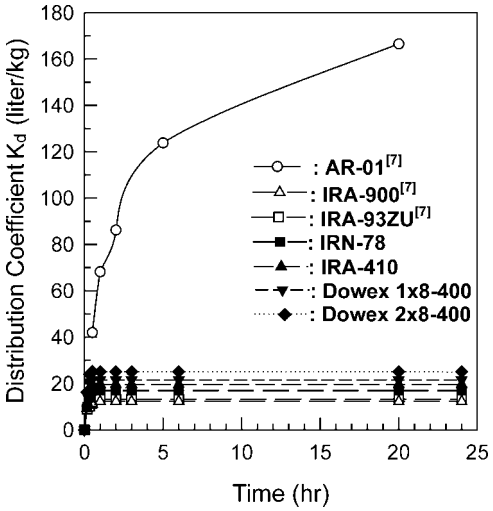


Figure 2. Effect of ionic group on the adsorption of Pd(II) on various anion exchangers. Nitric acid concentration: 6 M, temperature: 60°C.

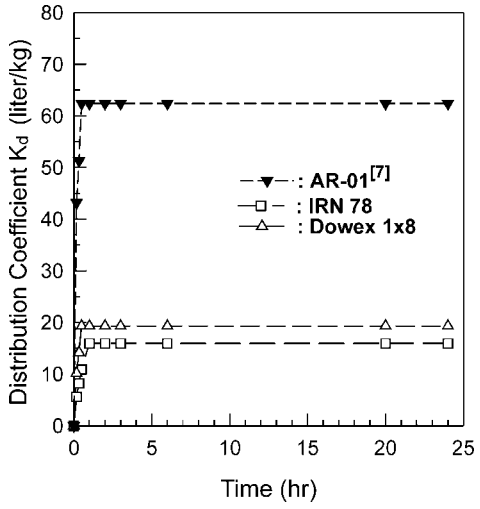


Figure 3. Effect of ionic group on the adsorption of Ru(III) on various anion exchangers. Nitric acid concentration: 1 M, temperature: 60°C.

was about 2000 ~ 3000 at 0.1 M of nitric acid solution.[7] These experimental results can be explained by the difference in the chemical structures of the ionic groups of anion exchangers in Table 1.

Figure 4 shows the effect of the nitric acid concentration on the adsorption of Pd(II) and Ru(III) in the range of 0.1 to 7 M by Dowex 1x8 and IRN 78. As shown, the optimal nitric acid concentration was shown to be in 2 ~ 3 M for Pd(II) and Ru(III). These experimental results coincide with the results from the literature (Navratil, 1989). Figures 5 and 6 illustrate the effect of solution temperature on the adsorption of Pd(II) and Ru(III) by IRN-78 and Dowex 1x8. As shown in the figures, the ion exchange capacity of Pd(II) and Ru(III) at high solution temperature (60°C) is higher than that of low temperature (20°C). The effect of co-ions for adsorption of Pd(II) by IRN 78 was studied in the mixed solutions (Pd, Ru, Rh). As shown in Fig. 7, the co-ion effect of Rh(III) for the adsorption of Pd(II) was negligible. However, in the presence of Ru(III), some reduction for the adsorption of Pd(II) was observed. Based on these results, Rh(III) ions may not be a stronger competitive ion than Ru(III) ions for the adsorption of Pd(II). Figure 8 shows the elution characteristic of Pd(II) by various eluents in batch experiments. As shown in Fig. 8, the capacity for the elution of Pd(II) by 0.5-M thiourea and 0.1-M nitric acid mixed solution was very high. However, the elution capacity of other eluents,

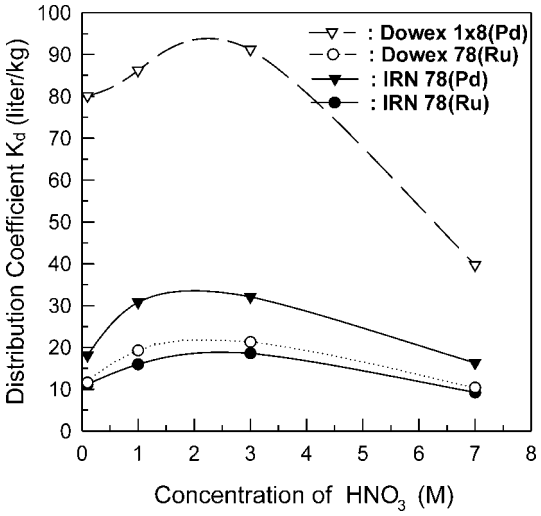


Figure 4. Effect of nitric acid concentration on the adsorption of Pd(II) and Ru(III) onto various anion exchangers. Temperature: 20°C.

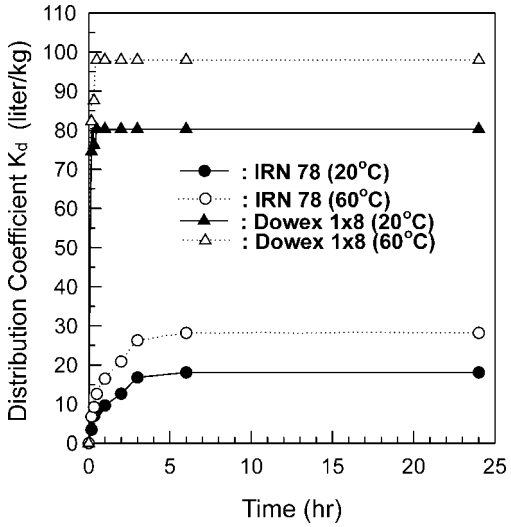


Figure 5. Effect of temperature on the adsorption of Pd(II). Nitric acid concentration: 0.1 M, Pd concentration: 95 ppm.

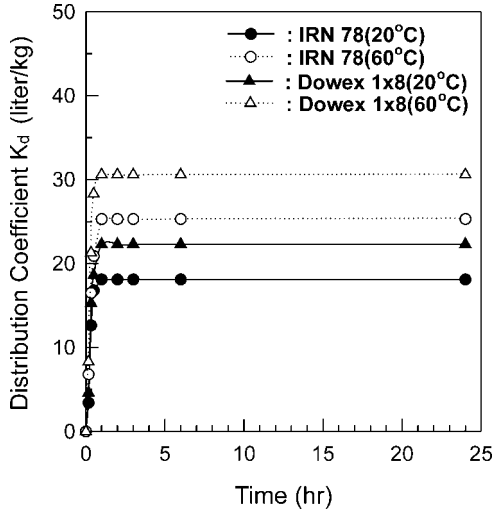


Figure 6. Effect of temperature on the adsorption of Ru(III). Nitric acid concentration: 2 M, Ru concentration: 50 ppm.

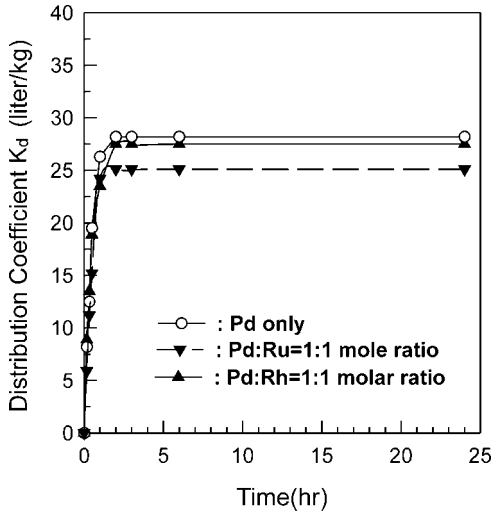


Figure 7. Effect of co-ions on the adsorption of Pd(II) by IRN 78. Nitric acid concentration: 0.1 M, temperature: 60°C, Pd, Rh, and Ru concentration: 95 ppm, 200 ppm, 50 ppm.

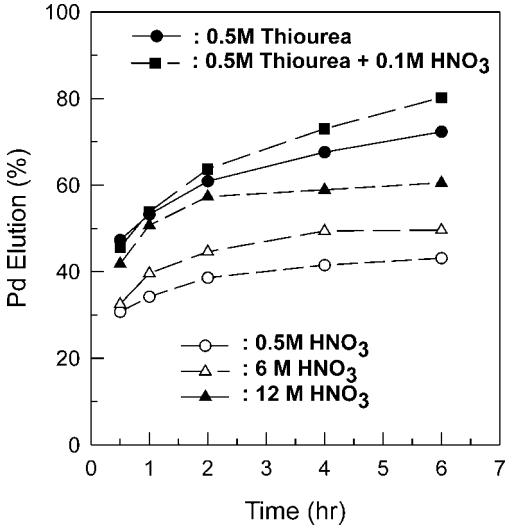


Figure 8. Time evolution of Pd(II) elution with various eluents using saturated IRN 78 ion exchange resin.

such as nitric acid solutions, was low. Also, when the nitric acid was used as an eluent, the elution capacity increased as the nitric acid concentration increased.

The ion exchange characteristics of Pd(II) and Ru(III) in a packed column filled with 5-g anion exchange resins at 2.0-M nitric acid solution are shown in Fig. 9. From the results, the ion exchange capacity of Pd(II) by Dowex 1x8 was higher than that by IRN 78 at 2.0-M nitric acid solution. Breakthrough by IRN 78 occurred at 40-mL volume treatment when Pd concentration was 172 ppm, while breakthrough volume by Dowex 1x8 was 100 mL. This result shows a similar trend to the results in batch experiments, Dowex 1x8 with ionic group of quaternary methyl ammonium has higher ion exchange capacity than IRN 78 with conventional amine group. In case of Ru(III), similar trend to the results in the ion exchange characteristics of Pd(II), Dowex 1x8 with ionic group of quaternary methyl ammonium has higher ion exchange capacity than IRN 78 with conventional amine group. Figure 10 shows the effect of feed rate on the adsorption of Pd(II) and Ru(III) in the packed columns by Dowex 1x8. The ion exchange capacity of Pd(II) and Ru(III) decreased as feed rate increased. In case of ion exchange reaction of Pd(II), when feed rate was 1 mL/min, breakthrough point occurred at 100-mL

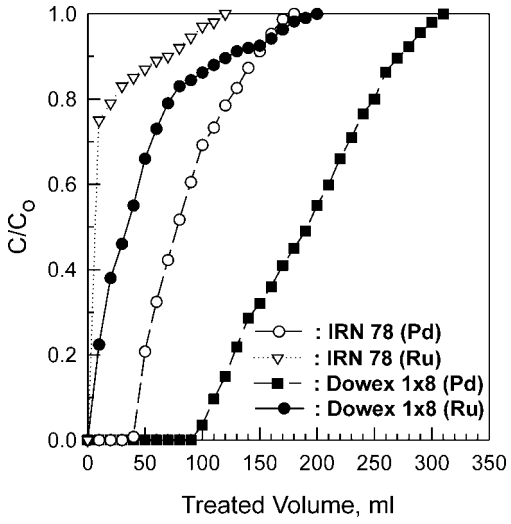


Figure 9. Breakthrough curve for Pd(II) and Ru(III) adsorption by anion exchangers. Pd and Ru concentration: 172 ppm, 160 ppm, nitric acid concentration: 2 M, feed rate: 1 mL/min.

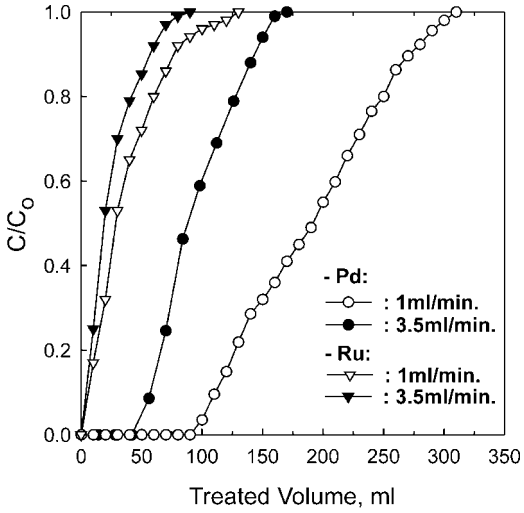


Figure 10. Effect of feed rate on the adsorption of Pd(II) and Ru(III) by Dowex 1x8. Pd and Ru concentration: 172 ppm, 160 ppm, nitric acid concentration: 2.0-M (Pd), 0.5-M (Ru).

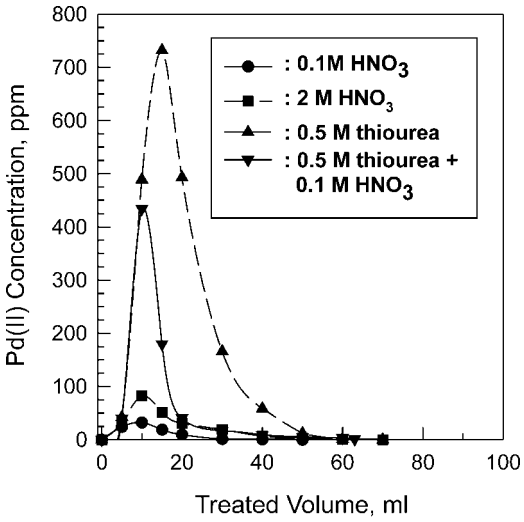


Figure 11. Elution curves for Pd(II) saturated column by various eluents. Resin: 5 g Dowex 1x8, feed rate: 1 mL/min.

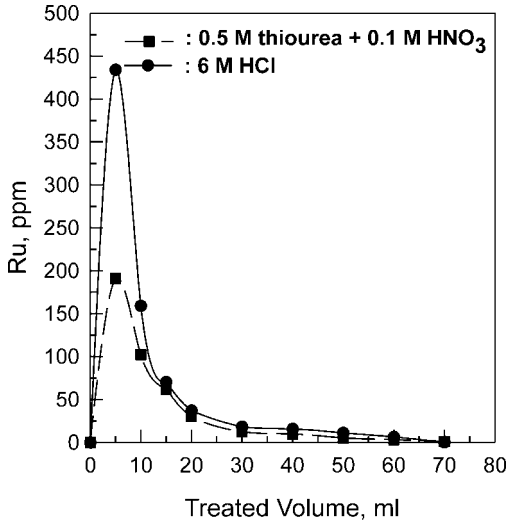


Figure 12. Elution curves for Ru(III) saturated column by various eluents. Resin: 5 g Dowex 1x8, feed rate: 1 mL/min.

treatment and the bed was saturated at 310-mL treatment. When the feed rate increased 3.5 mL/min, however, the breakthrough volume for Pd(II) adsorption decreased to 48 mL and the bed was saturated at 150 mL treatment.

The elution characteristics of Pd(II) in packed bed filled with 5-g Dowex 1x8 saturated with Pd(II) by various eluents are shown in Fig. 11. As shown, the capacity for the elution of Pd(II) by 0.5-M thiourea and 0.1-M nitric acid mixed solution was high. Pd was easily and perfectly eluted by 0.5-M thiourea and 0.1-M nitric acid mixed solution. The capacity for the elution of Pd(II) by 0.5-M thiourea was also relatively high. However, the elution capacity of Pd(II) by low concentration of nitric acid was very low. Figure 12 shows the elution curves for Rh(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.

CONCLUSION

Ion exchange and elution characteristics of Pd(II) and Ru(III) by several anion exchangers in the batch and column were investigated. Based on

experimental results, the ionic groups of anion exchangers affected the ion exchange capacity for the adsorption of Pd(II) and Ru(III) from nitric acid solutions significantly. Anion exchangers such as Dowex 1x8 with the ionic group of quaternary methyl ammonium had a higher capacity than anion exchanger, such as IRN 78 and IRA-93ZU, with amine group for the adsorption of Pd(II) from nitric acid solution in the batch and column experiments. Especially, new type anion exchanger, AR-01 with quaternary and tertiary benzimidazole groups showed very strong adsorption of Pd(II) and Ru(III) compared with other conventional anion exchangers.

The elution characteristics of Pd(II) in the batch and packed column showed that the capacity for the elution of Pd(II) by 0.5-M thiourea solution and 0.1-M nitric acid mixed solution was high compared with the other eluents such as nitric and hydrochloric acid solutions. Pd could be easily eluted by 0.5-M thiourea solution and 0.1-M nitric acid mixed solution. 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.

Based on these experiments, to separate Pd(II) and Ru(III) effectively by the ion exchange method from radioactive liquid waste, the development of an ion exchanger with a high selectivity for Pd(II) and Ru(III), such as AR-01 with quaternary and tertiary benzimidazole groups, may be necessary.

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