*Korean J. Chem. Eng.*, **16**(5), 571-575 (1999)

# Ion Exchange Characteristics of Palladium from Nitric Acid Solution by Anion Exchangers

**Sung Ho Lee†, Kwang Rag Kim, Chong Hun Jung and Hongsuk Chung**

Korea Atomic Energy Research Institute, P.O. Box, 105, Yusong, Taejon 305-600, Korea
(*Received 12 April 1999 • accepted 12 July 1999*)

**Abstract**–Radioactive high-level liquid wastes contain significant quantities of platinum group metals (PGM) such as Pd(II), Rh(III) and 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), 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 1×8 and also the elution characteristics of Pd(II) by various eluents for the determination of optimal separation conditions. Anion exchangers such as Dowex 1×8 with the ionic group of quaternary methyl ammonium showed a higher capacity than anion exchangers such as IRN 78 with amine group for the adsorption of Pd(II) from nitric acid solution. The optimal nitric acid concentration was shown to be in 2-3 M. The adsorbed Pd(II) was effectively eluted out by 0.5 M thiourea and 0.1 M nitric acid mixed solution.

Key words : Palladium, Ion Exchangers, Adsorption, Elution, Separation

## 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., palladium (Pd), rhodium (Rh) and ruthenium (Ru). 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 fission can be an important alternative resource to meet the increasing demand [Kondo and Kuboto, 1992].

Various processes such as lead extraction, solvent extraction, precipitation, adsorption and ion exchange methods were studied for separation and recovery of PGM from high-level radioactive liquid waste (HLLW) [Smith and Mcduffie, 1981; Jensen, 1984; Beamish, 1960; Carlin et al., 1975; Nito et al., 1986; Rizvi et al., 1996; Lee et al., 1999]. Among these methods, precipitation and ion exchange methods were first considered because of the economy and simplicity of these processes for recovery of high purity of Pd(II). The separation characteristics of Pd(II) by precipitation method using ascorbic acid have been studied [Lee et al., 1999]. Pd(II) over 99.5% was selectively precipitated at ascorbic acid concentration above 0.06 M. In the present work, the ion exchange method was chosen as an alternative method for separation and recovery of Pd(II) from HLLW by anion exchangers because of the simplicity of the adsorption and elution process. 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. Marina et al. [1997] investigated anion exchange separation procedures for the PGM and gold by Dowex 1×8 resin. Wei and coworkers [1996] also reported that anion exchanger AR-01 with a benzimidazole group especially shows significantly strong adsorption of Pd(II) from nitric acid solution. In spite of numerous works concerned with PGM by various sorbents, data on use of sorption for separation and recovery of PGM from HLLW are rather scarce.

In this work, to determine the optimal separation conditions of Pd(II) 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 and also the elution characteristics of Pd(II) by various eluents.

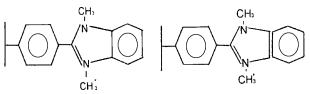
## EXPERIMENTAL

Commercial strongly basic anion exchangers such as IRN-78 and Dowex 1×8 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) was prepared by dissolving $Pd(NO_3)_2$ into the nitric acid solution.

In batch experiments, 1 g of an anion exchanger and 20 ml

†To whom correspondence should be addressed.
E-mail : shlee6@nanum.kaeri.re.kr

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

| Ion exchanges | Ionic groups | $K_d^*$ |
|---|---|---|
| -IRN78 | $-N^+(CH_3)_3OH^-$ | 16.9 |
| -Dowex 1×8-400 | $-CH_2-N^+(CH_3)_2-CH_3Cl^-$ | 25.1 |
| -Dowex 2×8-40 | $-CH_2-N^+(CH_3)_2-CH_2CH_2OHCl^-$ | 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), (liter/kg) under experimental conditions: nitric acid concentration= 6 N, temperature= 60 °C

of a platinum group metal containing solution were put in a glass flask and the flask was set in a mechanically shaken water bath maintained at 20 °C or 60 °C 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 measured by inductively coupled plasma atomic emission spectroscopy (ICP, Model : Jobin Yvon JY38 plus, polychromator, JYOCY).

The sorption kinetic studies of Pd(II) 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 [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 Pd 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 concentration by ICP.

## RESULTS AND DISCUSSION

The adsorption kinetics of Pd(II) 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 Pd(II) by an anion exchanger was very rapid and reached an equilibrium state within 1 hr. The ionic groups of ion exchangers acted as metal ion exchange sites. Pd(II) was strongly adsorbed from dilute nitric acid solutions.

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

$$v_A(R^+\cdot NO_3^-)+Pd(NO_3)_3^-\Leftrightarrow(v_AR^+\cdot Pd(NO_3)_3^-)+NO_3^-$$

where $R^+$, $Pd(NO_3)_3^-$, and $v_A$ denote the fixed ionic group, the counter ion (anionic complex of Pd), and the charge number of the counter ion, respectively.

Fig. 2 and Fig. 3 show the effect of ionic groups on the adsorption of Pd(II) from nitric acid solution onto the several anion exchangers. These results were compared with those from the anion exchanger named AR-01 with quarternary and

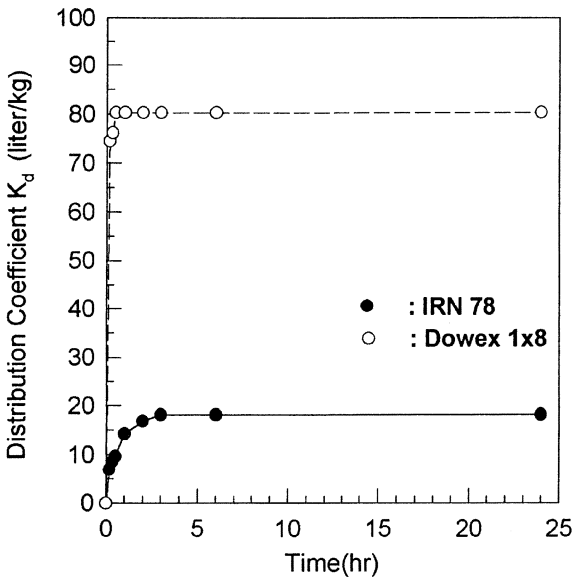



**Fig. 1. Adsorption rate of palladium onto anion exchangers.**
[Nitric acid concentration : 0.1 kmol/m$^3$, temperature : 20 ]

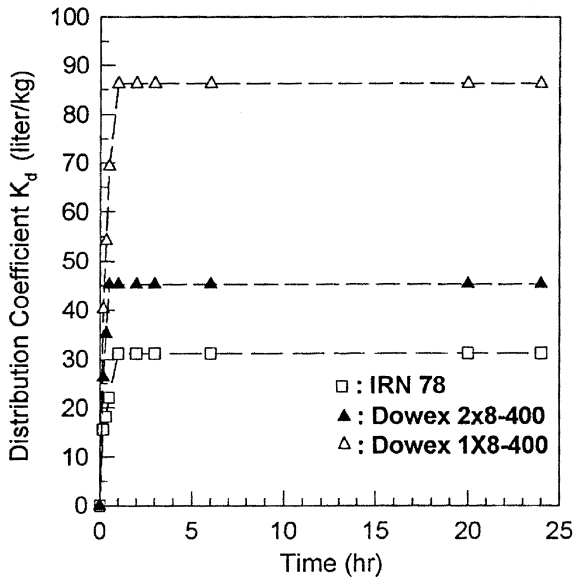



**Fig. 2. Effect of ionic group on the adsorption of Pd(II) onto various anion exchangers.**
[Nitric acid concentration : 1 kmol/m$^3$, temperature : 20 °C]

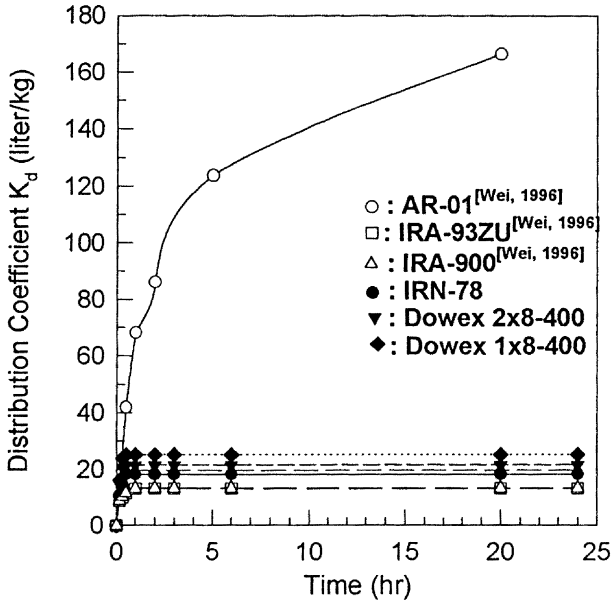



**Fig. 3. Effect of ionic group on the adsorption of Pd(II) onto various anion exchangers.**
[Nitric acid concentration : 6 kmol/m$^3$, temperature : 60 °C]

tertiary benzimidazole groups and several conventional anion exchangers such as IRA 900 and IRA-93ZU cited in the literature [Wei et al., 1996]. As shown in the figures, anion exchangers such as Dowex 1×8 and Dowex 2×8 with an ionic group of quaternary methyl ammonium have higher adsorption capacity than anion exchangers such as IRN 78 and IRA-93ZU with a conventional amine group. The anion exchanger AR-01 with a benzimidazole group especially shows significantly strong adsorption of Pd(II) from nitric acid solution. The distribution coefficient ($K_d$) value for the adsorption of Pd(II) was about 2000-3000 at 0.1 M of nitric acid solution [Wei, 1996]. These results can be explained by the difference in the chemical structures of the ionic groups of anion exchangers in Table 1.

The effect of solution temperature on the adsorption of Pd(II) by IRN-78 and Dowex 1×8 is shown in Fig. 4. As shown, the ion exchange capacity of Pd(II) at high solution temperature (60 °C) is higher than that of low temperature (20 °C).

Fig. 5 shows the effect of the nitric acid concentration on the adsorption of Pd(II) in the range of 0.1 to 7 M by Dowex 1×8 and IRN 78. The optimal nitric acid concentration was shown to be in 2-3 M. These experimental results coincide with the results from the literature [Navratil, 1989]. Fig. 6 shows the elution characteristic of Pd(II) by various eluents in batch experiments. As shown, the capacity for the elution of Pd(II) by

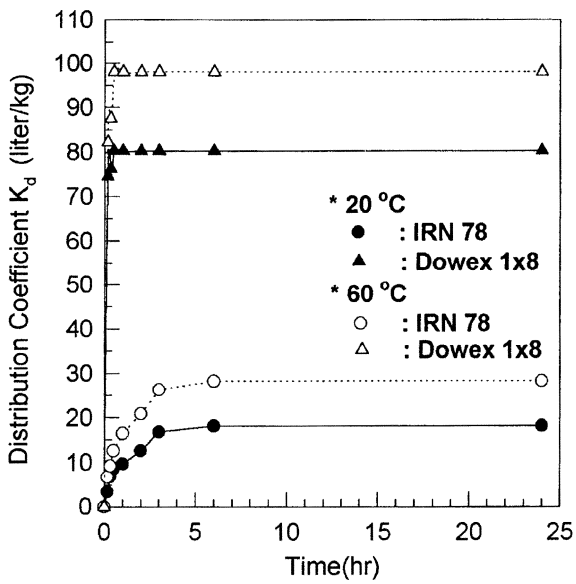



**Fig. 4. Effect of temperature on the adsorption of Pd(II) onto anion exchangers.**
[Nitric acid concentration : 0.1 kmol/m$^3$]

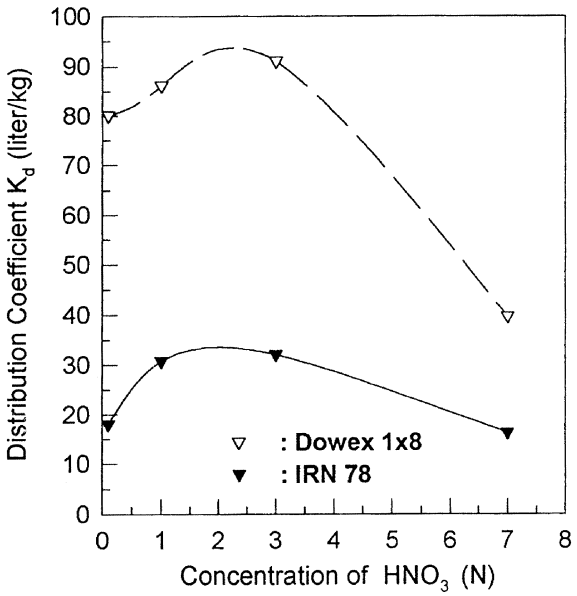



**Fig. 5. Effect of nitric acid concentration on the adsorption of Pd(II) onto anion exchangers.**
[Temperature : 20 °C]

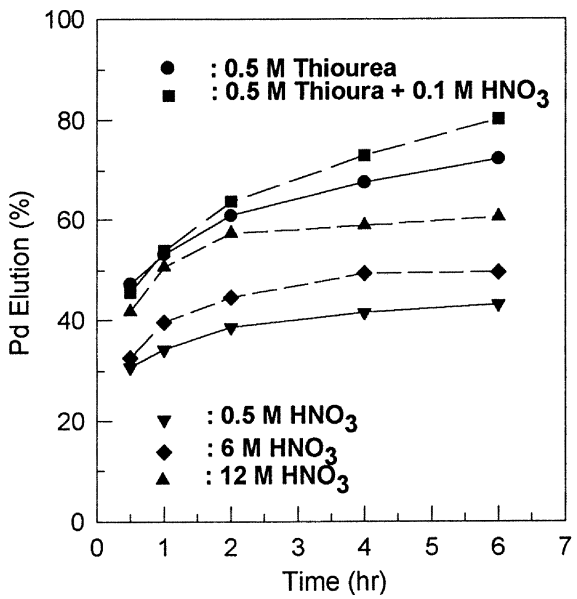



**Fig. 6. Time evolution of Pd(II) elution using IRN 78 ion exchangers by various eluents.**

0.5 M thiourea and 0.1 M nitric acid mixed solution was very high. However, the elution capacity of other eluents 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) in packed column filled with 5 g of anion exchange resin at 2.0 M nitric acid solution are shown in Fig. 7. The ion exchange capacity of Pd(II) by Dowex 1×8 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 1×8 was 100 ml. This result shows a similar trend to the results in batch experiments. Dowex 1×8 with ionic group of quaternary methyl ammonium has higher adsorption capacity than IRN 78 with conventional amine group.

Fig. 8 shows the effect of feed rate on the adsorption of Pd (II) in the packed columns by Dowex 1×8. As shown, the adsorption capacity of Pd(II) decreased as feed rate increased. When feed rate was 1 ml/min, breakthrough point occurred at 100 ml treatment and the bed was saturated at 310 ml treat-

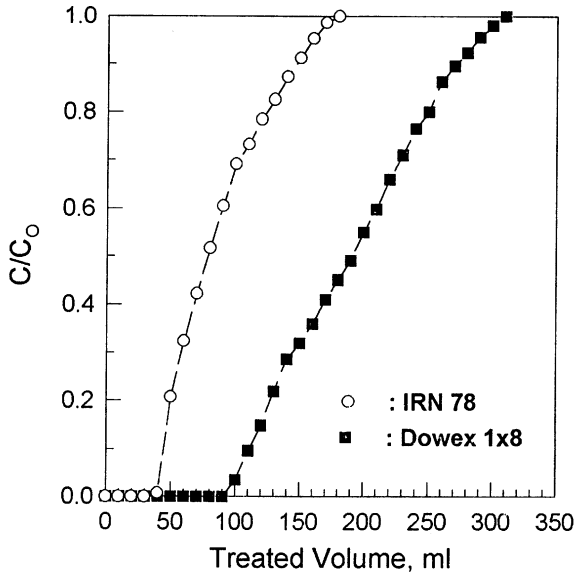



**Fig. 7. Breakthrough curve for Pd(II) adsorption by anion exchangers.**
[Pd concentration : 172 ppm, nitric acid concentration : 2.0 M, feed rate : 1 ml/min]

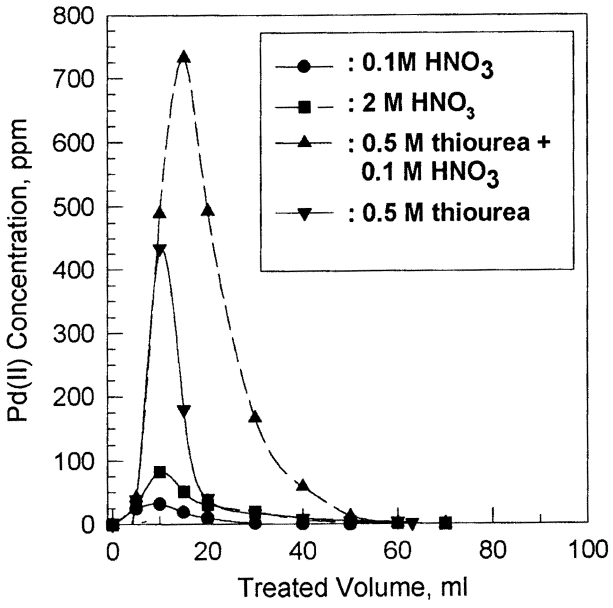



**Fig. 9. Elution curves for Pd(II) saturation column by various eluents.**
[Feed rate : 1 ml/min, resin : 5 g Dowex 1×8]

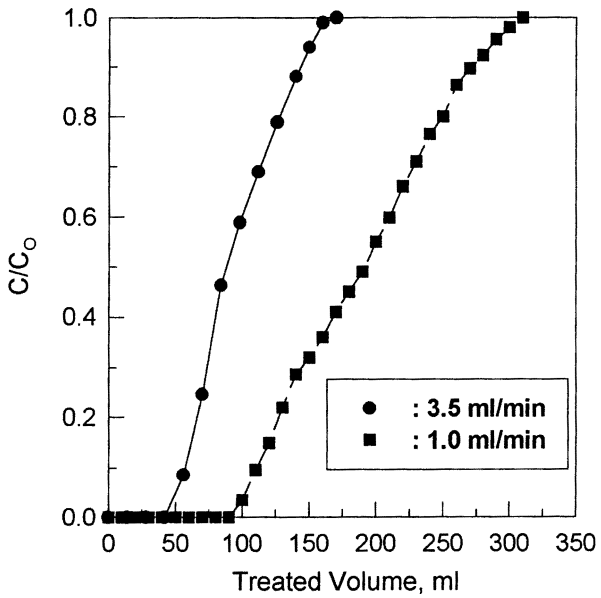



**Fig. 8. Effect of feed rate on Pd(II) adsorption by Dowex 1×8.**
[Pd concentration : 172 ppm, nitric acid concentration : 2.0 M]

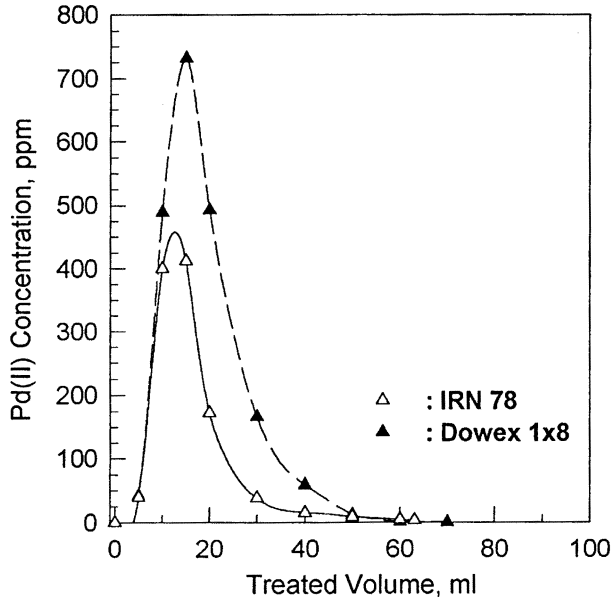



**Fig. 10. Elution curves for Pd(II) saturation column by 0.5 M thiourea and 0.1 M HNO$_3$ solution.**
[Feed rate : 1 ml/min, resin : 5 g ]

ment. 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 P(II) in a packed bed filled with 5 g Dowex 1×8 saturated with Pd(II) by various eluents are shown in Fig. 9. 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. However, the elution capacity of Pd(II) by low concentratration of nitric acid was very low. Fig. 10 shows the elution curves for Pd(II) saturation columns by 0.5 M thiourea and 0.1 M $HNO_3$ solution. As shown, the elution curve for IRN 78 saturated with Pd(II) had a similar trend to that for Dowex 1×8 by 0.5 M thiourea and 0.1 M nitric acid mixed solution. About 50 ml of eluent was necessary for the almost complete recovery of Pd(II) ions.

## CONCLUSIONS

Ion exchange and elution characteristics of Pd(II) 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) from nitric acid solutions significantly. Anion exchangers such as Dowex 1× 8 with the ionic group of quaternary methyl ammonium had a higher adsorption capacity than anion exchangers 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. In particular, a new type of anion exchanger, AR-01 with quaternary and tertiary benzimidazole groups, showed very strong adsorption of Pd(II) compared with other conventional anion exchangers. The optimal nitric acid concentration was shown to be 2-3 M. The elution characteristics of Pd(II) in the batch and packed column showed that Pd(II) could be effectively eluted out 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 and 0.1 M nitric acid mixed solution was high compared with the other eluents such as nitric acid solutions.

## ACKNOWLEDGEMENT

This project has been carried out under the Nuclear R&D Program by MOST.

## REFERENCES

Beamish, F. E., "A Critical Review of Methods of Isolating and Separation the Six Platinum Metals," *Talanta*, **5**, 1 (1960).

Carlin, W. W. and Darlinton, W. B., "Recovery of Fission Products from Acidic Waste Solutions," U. S. Patent 3891741 (1975).

Faris, J. R. and Buchum, R. F., "Anion Exchange Characteristics of the Elements in Nitric Acid and Nitrate Solutions and Application in Trace Element Analysis," ANL-6811 (1964).

Gaita, R. and AL-Bazi, S. J., "An Ion Exchange Method for Selective Separation of Palladium, Platinum and Rhodium from Solutions Obtained by Leaching Automotive Catalytic Converters," *Talanta*, **42**(2), 249 (1995).

Helfferich, F., "Ion Exchang," McGraw-Hill, New York (1962).

Jensen, G. A., Platt, A. M., Mellinger, G. B. and Bjorklund, W. J., "Recovery of Noble Metals from Fission Products," *Nucl. Technol.*, **65**, 305 (1984).

Kondo, Y. and Kuboto, M., "Precipitation Behavior of Platinum Group Metals from Simulated High Level Liquid Waste in Sequential Denitration Process," *J. Nucl. Sci. Technol*., **29**(2), 140 (1992).

Lee, S. H., Kim, K. R. and Chung, H. S., "Precipitation Characteristics of Palladium from Simulated Radioactive Liquid Waste by Ascorbic Acid," *Korean J. Chem. Eng.*, **16**, 166 (1999).

Marina, I. J., Jarvis, I., Totland, M. M. and Jarvis, K. E., "Assessment of Dowex 1×8 Based Anion Exchange Procedures for the Separation and Determination of Ruthenium, Rhodium, Palladium, Iridium, Platinum and Gold in Geological Samples by ICP," *Analyst*, **122**, 19 (January 1997).

Naito, K., Natsui, T. and Tanaka, Y., "Recovery of Noble Metals from Insoluble Residue of Spent Fuel," *J. Nucl. Sci. Technol*., **23**(6), 540 (1986).

Navratil, J. D., "Ion Exchange Technology in Spent Fuel Reprocessing," *J. Nucl. Sci. Technol*., **26**(8), 735 (1989).

Rizvi, G. H., Mothur, J. N., Murall, M. S. and Iyer, R. H., "Recovery of Fission Product Palladium from Acidic High Level Waste Solution," *Sep. Sci. Technol*., **31**(13), 1805 (1996).

Smith, F. J. and Mcduffie, H. F., "Recovery of Nonradioactive Palladium and Rhodium from Radioactive Waste," *Sep. Sci. Technol*., **16**(9), 1071(1981).

Wei, Y. Z., Kumagi, M. and Takashima, "Adsorption and Elution Behavior of Platinum Group Metals in Nitric Acid Medium," Proceeding of IEX '96, 174, Royal Society of Chemistry (July, 1996).