

Recovery of Noble Metals and Technetium from Nuclear Waste

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ABSTRACT

An adsorptive separation of Pd, Rh and Tc was tested by using simulated chemical solutions. $\text{Pd}(\text{NO}_3)_2$ and $\text{Rh}(\text{NO}_3)_3$ were used for the noble metal sources, and Re_2O_3 after dissolving it in 0.5M nitric acid was used for the technetium substitute, respectively. A felt type ACF (activated carbon fiber) after being pretreated with 1M NaOH, and an EIR (extractant impregnated resin) which was prepared by impregnating Aliquat 336 onto Amberlite XAD-4 resin were evaluated on their adsorption equilibrium and kinetic performances. As the results, the ACF showed a high selectivity for the palladium ions over the rhodium and rhenium ions. On the other hand, the EIR was shown to be effective for separation of rhenium from the palladium-free two component system of rhenium and rhodium. Column tests were also performed to confirm the separation efficiency of palladium and rhenium using a jacketed glass column ($\varnothing 11 \times L 150$). The ACF bed showed the complete separation of palladium from rhenium and rhodium. The breakthrough volume, when 1% of breakthrough is considered, was about 140 BV for palladium, while only a small amount of an adsorption of rhenium and rhodium were found in the column. Then the EIR column was applied to separate rhenium from rhodium and showed successful separation performance with about 122 BV of breakthrough volume. The palladium and rhenium with high purity were recovered effectively by eluting the beds with nitric acid.

INTRODUCTION

Recovery of the platinum group metals such as palladium, rhodium and ruthenium, and a transition element such as technetium in SNF (Spent Nuclear Fuel) have been reviewed as important issues, due to their economic values of noble metals and also radio toxicity of technetium. One ton of SNF with 33,000MWd/MTU (megawatt days per metric ton of uranium) contains 1.24 kg of Pd, 0.47 kg of Rh and 2.27 kg of Ru, respectively. The platinum group metals are normally generated together with transition metal such as Tc-99 which exists at an amount of 0.77 kg per 1 ton of SNF. Since Tc-99 is a reportedly toxic nuclide with a long half-life of 2.13×10^5 yr. Some research results have been reported with relation to the separation of noble metals and Tc-99 from nuclear waste. Lee et al. [1] reported a possibility for selective

precipitation of palladium from a simulated fission product solution using an ascorbic acid. Some works on the separation of palladium by extraction have been reported [2]. Also some research results have been reported in relation to the selective separation of palladium from acidic waste solutions by ion exchange or adsorption process. El-Said et al. [3] carried out a basic study on the separation of palladium from simulated intermediate radioactive waste/chloroacetic acid/nitrate medium by using IRA-410 and IRA-900 anion exchangers. Hubicki and Leszczynska [4] studied a sorption of Pd(II) micro-quantities from chloride and chloride-nitrate systems by using strongly basic anion exchangers. Although some possibilities for selective separation of palladium from different model solutions have been reported, until now there are not enough research results on the selective recovery of palladium from various waste solutions.

In relation to the separation of technetium, normally conventional extraction method has been applied for bulk separation. However, because of its high radio toxicity even when the concentration is very low, new materials and various methods have been developed to improve removal efficiency. Adsorptive separation is one of those selective methods being developed to obtain a high selectivity. New trends of this type are to combine characteristic advantages of ion exchange and extraction, thereby expediting the development of an EIR (Extractant Impregnated Resin) [5-9]. The EIR process combines the advantage of both a solvent extraction and a chromatographic separation based on adsorption. Furthermore it is easy to prepare an EIR and possible to chose various extractants depending on the specific requirements. The impregnation of a reagent on the hydrophobic internal surface of macroporous nonionic resins is reportedly due to the mechanism of an adsorption [6]. The resins as supporting materials in EIRs are macroporous organic polymers with good mechanical and chemical stabilities. Among them, Amberlite XAD resins are reviewed as promising ones due to their good physical properties such as their porosity, uniform pore size distribution and high surface area as well as their chemically homogeneous nonionic structures. Various extractants have been incorporated with XAD resins and applied to metal recovery and separation in the nuclear industry as well as in hydrometallurgy [8]. Among them, Aliquat 336 has been reviewed as selective for TcO_4^- [10].

In this study, an adsorptive separation of platinum group metals and technetium was tentatively performed by using an ACF and an EIR.

EXPERIMENTAL

A pitch-based ACF felt (Osaka Gas Co., FN-200PS-15) was modified with NaOH solution to improve the adsorption performances. 5g of ACF was immersed into 1L of a 1M NaOH solution for 24 hours. After being filtered, it was washed with pure water and dried at 110 °C for 24 hours. An EIR was prepared by impregnating a trioctylmethylammonium chloride (Aliquat 336, Aldrich) into an Amberlite XAD-4 resin. First, the Amberlite XAD-4 was washed with pure water to remove any impurities and dried in the oven for 24 hours at 40 °C. Then, the resin was impregnated with Aliquat 336 dissolved in an ethanol solution. The impregnation ratios were varied in the range between 0.1 and 2.0 (g Aliquat 336/g resin). The samples were stirred at 100 rpm in a constant temperature water bath for 24 hours. After filtering the solvent, the impregnated resins were rewashed with pure water, and then left to dry for 24 hours at 40 °C. The degree of impregnation of Aliquat 336 was evaluated by measuring the weight changes of

the adsorbents before and after an impregnation. The prepared EIR with the different loading ratios were evaluated for their performances by measuring the distribution coefficients for rhenium ion.

Adsorption equilibrium tests were performed for the single and multi-component solutions containing palladium, rhodium and rhenium, a chemical analogue of technetium, in an isothermal condition of 25 °C. Pd(NO₃)₂ and Rh(NO₃)₃ were used for the palladium and rhodium sources, respectively. Re₂O₃ was used for the rhenium source after being dissolved in 0.5M nitric acid. Each ion concentration was fixed at 100 ppm and the weights of the adsorbents were varied in the range between 0.002 and 0.3 g to obtain equilibrium isotherms. The equilibrium tests were performed in triplicate and averaged to obtain one isotherm point.

Breakthrough curves were also obtained for the single and mixed solutions using a jacketed glass column (Ø11 x L 150, Bed Volume =14.25 mL) which was packed with 2.35 g of ACF or 82.4 g of EIR. Flow rates were varied in the range between 2.0 ~ 9.4 cm min⁻¹. The samples were collected with a fractional collector and the solution concentrations were measured by using an AAS (GBC Co, Model 906).

RESULTS AND DISCUSSION

Adsorbent Preparation and Adsorption Equilibria

The ACF was preconditioned with 1M NaOH solution for 24hrs to give the OH⁻ form on the surface of the ACF, which would behave as an active site for adsorption. The EIRs with the different loading ratios were prepared by impregnation of Aliquat 336 by varying the concentrations of the impregnating solutions. The EIRs with different loading ratios were evaluated by measuring the distribution coefficients for rhenium. Distribution coefficient, K_d (mL g⁻¹), was calculated by following equation,

$$K_d = \frac{c_s}{c_L} \quad (\text{Eq. 1})$$

where, c_s = equilibrium concentration in solid phase (meq g⁻¹)

c_L = equilibrium concentration in liquid phase (meq mL⁻¹)

The distribution coefficient was a maximum value at the loading ratio of about 0.4 (g Aliquat 336/ g XAD-4) and then decreased gradually with a loading ratio increase. It is quite different from the general expectation that the adsorption performances will increase proportionally with the loading ratio. It is possibly due to the leaching of extractant from EIR at higher loading. In this study, therefore, EIR with a loading ratio of about 0.4 g Aliquat 336/g XAD-4 was used for the adsorption equilibrium and kinetic performance tests.

Single and multi-component adsorption isotherms of an ACF and an EIR for the palladium, rhodium and rhenium were obtained to evaluate the adsorption capacity and the equilibrium constant. Experimental data were modeled by the Langmuir equation given by

$$q = \frac{q_s bc}{1 + bc} \quad (\text{Eq. 2})$$

where q (meq g^{-1}), q_s (meq g^{-1}) and c (meq mL^{-1}) are the equilibrium and the saturation concentrations of the metals in the solid and liquid phases, respectively. Fig. 1 is the isotherms for the multi-component system with ACF which shows a much higher selectivity for palladium over the rhodium and rhenium ions. The isotherm for palladium is shown to be modeled quite well with a Langmuir equation. The loading capacity obtained by the Langmuir model for palladium is 1.25 meq g^{-1} for the three component system. The adsorption isotherms for the single component system, although the detailed figure is not represented here, showed the same trends as those for the multi-component system. On the other hand, only a small amount and an unfavorable type of an adsorption was found for the rhenium and rhodium ions. This result implies that the ACF can separate palladium selectively from a mixed solution.

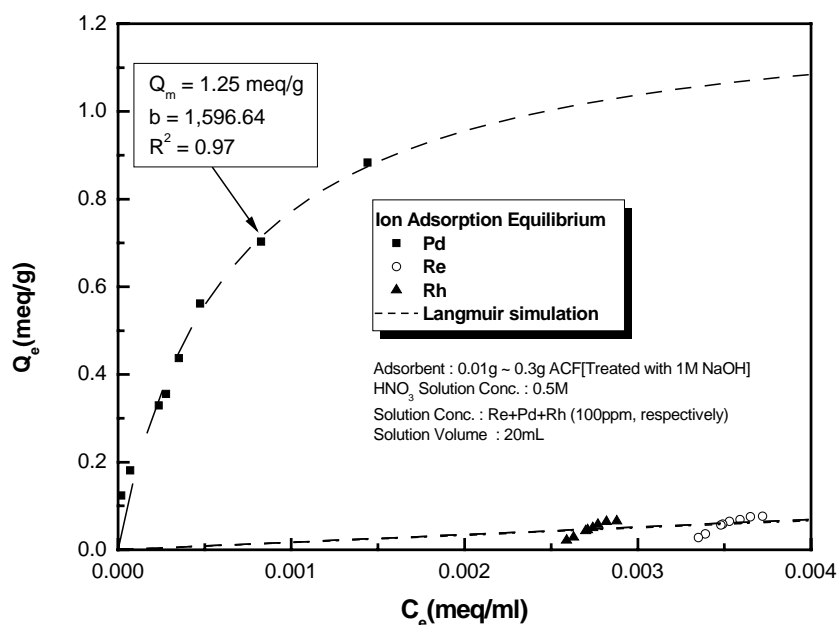


Fig. 1. Adsorption isotherms for multi-component system with an ACF

Single and multi-component (two and three component) adsorption isotherms with the EIR were obtained. In the single and three component systems, which are not represented here, the isotherms were modeled with the Langmuir equation. The Langmuir parameter, b for each ion, which represents the degree of favorable adsorption, was 1,980 for palladium, 332 for rhenium and 84 for rhodium. This means that the EIR has more preference for palladium over rhenium and rhodium. However, it also showed a more or less favorable adsorption for rhenium. Furthermore the maximum loading capacity for rhenium was higher than that of palladium. This implies that it is not very effective to separate palladium or rhenium from the mixed solution using the EIR. However, since the EIR showed much higher selectivity for rhenium over rhodium, if the palladium is separated in advance from the mixed solution with the ACF, it

would be applicable for a separation of rhenium and rhodium from a palladium-free solution. The adsorption isotherms for the palladium-free two component system with the EIR were obtained to confirm the performance of the EIR and the results are represented in Fig. 2. As expected in the three component system, the EIR shows a far greater preference for rhenium over rhodium. The maximum capacities of the EIR for rhenium and rhodium are 1.97 meq g^{-1} and 0.16 meq g^{-1} , respectively. Normally rhenium ion is reportedly in the form of ReO_4^- in a nitric acid solution. This ion is easily exchanged with Cl^- which is a functional group in the EIR. However, in the case of rhodium, the main ionic forms in the nitric acid are reportedly oligomers with positive charges even though the exact forms are unknown due to its complex chemistry in a nitric acid solution. This kind of large molecular size rhodium is unlikely to adsorb onto the EIR.

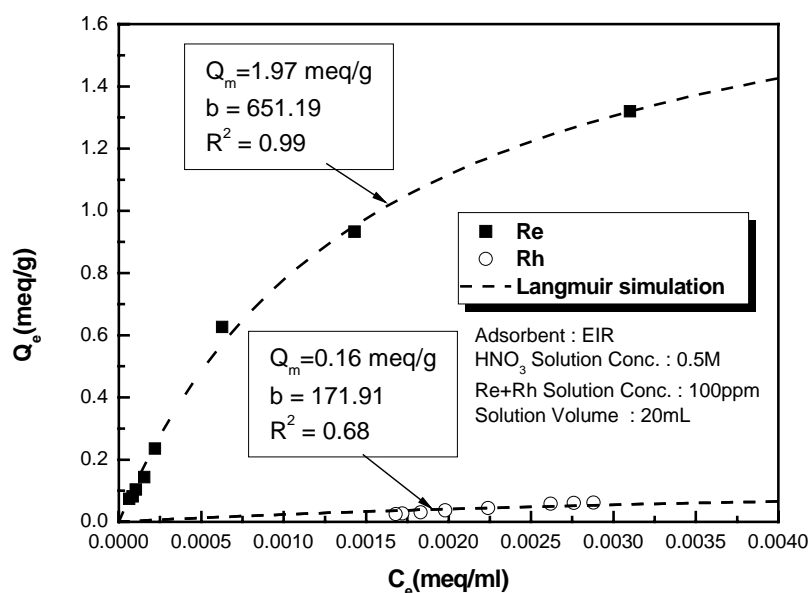


Fig. 2. Adsorption isotherms for the two component system with an EIR

Breakthrough Behaviors

The optimum flow rate was determined by using 100 ppm of palladium and rhenium solutions for the ACF and EIR columns, respectively. In both columns, the optimum flow rate for the best breakthrough was found to be 6.2 mL min^{-1} (6.5 cm min^{-1}). Fig. 3 is the breakthrough behaviour of the mixed solution of palladium, rhodium and rhenium for the ACF bed which was packed with 2.35g of preconditioned ACF. As expected in the equilibrium tests, the ACF bed adsorbs almost all the palladium and very small fractions of the rhenium and rhodium, which implies a successful separation of palladium from the mixture. When the breakthrough point is 0.7% of the initial palladium concentration, then the throughput is almost 140 BV. Within this breakthrough volume, almost palladium-free rhodium and rhenium is possible. This solution is then processed with the EIR column for a separation of rhenium and rhodium in the next step. For desorbing palladium from the loaded ACF bed, NH_4Cl , HCl and HNO_3 were tested as the candidates for a

desorbing solution. The tests were performed in a batch reactor and the concentrations of the tested solutions were varied in the range between 0.5 M and 5 M. Among them, 5 M HNO₃ solutions showed the best desorbing performance. It is natural that the desorbing performance is proportional to the solution concentration. However, considering the chemical economy, the concentration of more than 5 M was not tested. Therefore, the loaded column was eluted with 5 M HNO₃ solution for palladium recovery. The flow rate of eluting solution was adjusted to the same flow rate as in the adsorption step. In this way, about 98% of the adsorbed palladium was recovered by using 2.4L of a 5 M HNO₃ solution. While the rhenium and rhodium, since they are adsorbed on the bed in a small amount, are eluted at negligible amounts. Therefore palladium (palladium nitrate) with a purity of more than 99% could be recovered. The purity is found to be decreased with the recovery of palladium. Therefore if the recovery is reduced to 50 %, the purity of the palladium was shown to be increased to 99.9%.

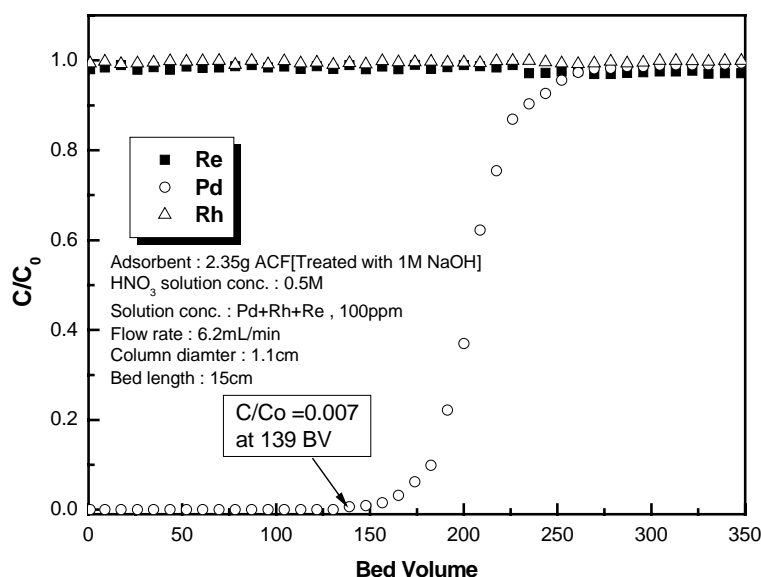


Fig. 3. Breakthrough curves for the three component system with an ACF

Fig. 4 is the breakthrough curves for the two-component system of rhenium and rhodium with an EIR. The bed shows 122 BV of a breakthrough volume for rhenium when the breakthrough point is 0.008. More or less different from ACF bed, it adsorbs rhodium although the amount is much less than that of rhenium. However, the adsorbed rhodium, if it is recovered together with the rhenium, can be an impurity. For this reason, a fractional desorption is considered. Since the higher concentration of a desorbing solution can bring about a simultaneous desorption of both components, the concentration of the desorbing solution was lowered to 0.5 M in the first cycle and then increased to 1 M in the second cycle. This is based on the concept that the rhenium is more sensitive for the concentration of desorbing solution. In the first desorption step, about 65 % of rhenium was desorbed from the bed and 33 % in the second step with 1 M HNO₃. The purity and recovery of the rhenium are summarized in Table I. As in the table, the total recovery

for rhenium is about 98 % and the purity is 97.5%. However, if the recovery is reduced to 95 %, the purity becomes more than 99 %. These results, although they are the results for a chemical analogue of Tc, show the possibility for a recovery of radioactive technetium from a nuclear stream. On the other hand, rhodium, due to its complex chemical forms in a nitric acid solution, would require other methods.

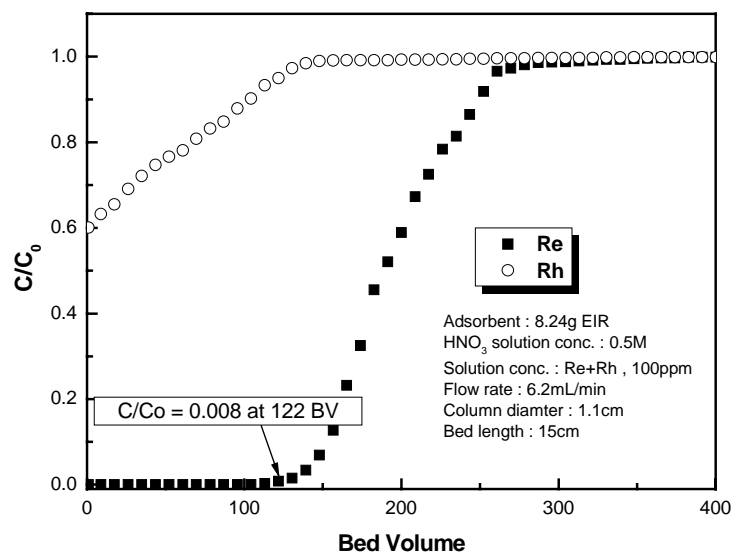


Fig. 4. Breakthrough curves for the two component system with an EIR

Table I. Relation Between Recovery and Purity of Rhenium for the Desorption Steps

1 st step (desorption with 0.5 M nitric acid)		2 nd step (desorption with 1 M nitric acid)		Total	
Recovery (%)	Purity (%)	Recovery (%)	Purity (%)	Recovery (%)	Purity (%)
64.5	99.4	33.0	95.2	97.5	98
62.3	99.9	30.1	98.9	94.6	99.2
60.9	99.9	27.0	99.9	91.5	99.5
51.3	99.9	17.9	100.0	89.3	99.9

CONCLUSION

An adsorptive separation of palladium, rhodium and technetium was performed by using simulated chemical solutions. $\text{Pd}(\text{NO}_3)_2$ and $\text{Rh}(\text{NO}_3)_3$ were used for the noble metal sources, and Re_2O_3 after dissolving it in 0.5M nitric acid was used for the technetium substitute, respectively. The adsorption equilibria and kinetic performances were studied by using a felt type ACF (activated carbon fiber) and an EIR (extractant impregnated resin) which was prepared

by impregnating Aliquat 336 onto Amberlite XAD-4 resin. As the results, the ACF showed high selectivity for the palladium ions over the rhodium and rhenium ions. On the other hand, the EIR showed adsorption preferences for the palladium together with rhenium. Although the EIR showed no specific preference between rhenium and palladium, however, when it is applied to the palladium-free two component system of rhenium and rhodium, it showed a high selectivity for rhenium over rhodium. In order to confirm the separation efficiency of palladium and rhenium, column tests were also performed by using a jacketed glass column. The ACF bed showed a complete separation of the palladium from rhenium and rhodium. The breakthrough volume, when 1% of a breakthrough is considered, was about 140 BV for palladium, while only a small amount of an adsorption of rhenium and rhodium were found in the column. Then the EIR bed was applied to separate the rhenium from the rhodium and it showed a successful separation with about 122 BV of breakthrough volume. The loaded beds were eluted effectively with nitric acid, and palladium and rhenium with a high purity could be recovered. In the case of rhodium, however, an adsorptive separation was not effective and thus it requires other methods.

REFERENCES

1. Lee, S.H., Jung, C.H., Shon, J.S. and Chung, H.S.(2000). Separation of Palladium from a Simulated Radioactive Liquid Waste by Precipitation Using Ascorbic Acid. *Separation Science and Technology* 35(3): 411-420.
2. Dutta, K.K. and Roy, U.S. (2003). Extraction Chromatographic Studies of Palladium (II) with Aliquat-336. *CHEM. ENVIRON. RES.* 12(1&2): 113-119.
3. El-Said, N., Mekhail, A., Khalifa, S.M. and Aly, H.F. (1996). Selective Separation of Palladium from Simulated Intermediate Radioactive Waste Nutrate by IRA-410 and IRA-900 Anion Exchangers. *J. of Radioanalytical and Nuclear Chemistry* 208(1): 243-255.
4. Hubicki, Z. and Leszczynska, M. (2005). Studies of sorption of Pd(II) microquantities on strongly basic polyacrylate anion exchangers. *Desalination* 175: 289-295.
5. Yang, W. W., Luo, G. S. and Gong, X.C. (2005). Extraction and Separation of Metal Ions by a Column Packed with Polystyrene Microcapsules Containing Aliquat 336. *Separation and Purification Technology*. 43: 175.
6. Cortina, J. L. and Warshawsky, A. (1997). Developments in Solid-Liquid Extraction by Solvent-Impregnated Resins. *Ion Exchange and Solvent Extraction* 13: 195-293.
7. Fontas, C., Salvado, V. and Hidalgo, M. (1999). Solvent Extraction of Pt(IV) by Aliquat 336 and its Application to Solid Supported Liquid Membrane System. *Solvent Extraction and Ion Exchange* 17(1): 149-162.
8. Saha, B., Gill, R. J., Bailey, D. G., Kabay, N. and Arda, M. (2004). Adsorption of Cr(VI) from Aqueous Solution by Amberlite XAD-7 Resin Impregnated with Aliquat 336. *Reactive & Functional Polymers* 60: 223-244.
9. Alonso, A. I. and Pantelides, C. C. (1996). Modeling and Simulation of Impregnated Membrane Processes for Recovery of Cr(VI) with Aliquat 336. *J. of Membrane Science* 110: 151-167.

WM'06 Conference, February 26–March 2, 2006, Tucson, AZ

Not Reviewed by WMSymposia, Inc.

10. Strauss, S. H. (1994). Separation of Technetium from Nuclear Waste Stream Simulants. Final Report Contract 669HH0013-9Z, September.