Adsorption of rhenium and rhodium in nitric acid solution by Amberlite XAD-4 impregnated with Aliquat 336

Jei-Kwon Moon†, Yoon-Ju Han, Chong-Hun Jung, Eil-Hee Lee and Byung-Chul Lee*

Korea Atomic Energy Research Institute, P.O. BOX 105 Yuseong, Daejeon 305-600, Korea
*Department of Chemical Engineering, Hannam University, Ojung, Daeduk, Daejeon 306-791, Korea

Abstract–An Extractant Impregnated Resin (EIR) was prepared by impregnation of Aliquat 336 into Amberlite XAD-4 for tentative separation of rhenium from rhodium in nitric acid solution. An optimum loading ratio of the XAD-4 resin for Aliquat 336 was found to be about 0.4 (g Aliquat 336/g resin). The prepared EIR showed high preference for rhenium over rhodium and adsorption isotherms for rhenium were described well by Langmuir equation in both the single and multi-component systems. Maximum adsorption capacities obtained by modeling the isotherms of rhenium were 2.01 and 1.97 meq/g for the single and the multi-component systems, respectively. On the other hand, only little adsorption of rhodium ions was observed. The homogeneous model fitted the kinetic data quite well and the obtained effective diffusivities of rhenium and rhodium ions were on the order of 10^{-7} and 10^{-6} cm^2 min^{-1}, respectively.

Key words: Adsorption, Impregnated Resin, Technetium, Rhenium, Aliquat 336, Rhodium, Spent Fuel

INTRODUCTION

Removal of technetium has long been important issue around the world, due to its radio toxicity [Asakura et al., 2004; Wei et al., 2003; Taylor and May, 2001; Uchida and Tagami, 1997; Panesko, 1967]. Tc-99 has a long half-life of 2.13×10^5 yr and reportedly exists with an amount of 0.77 kg per 1 ton of SNF. Normally, conventional extraction methods have been applied for bulk separation of technetium. However, because of its high radio toxicity even at very low concentration, new materials and various methods have been developed to improve removal efficiency. Adsorptive separation is one of those selective methods being developed to obtain high selectivity. New trends of this type are to combine characteristic advantages of ion exchange and extraction, thereby to expedite the development of EIR [Yang et al., 2005; Saha et al., 2004; Bartosova et al., 2003; Kabay et al., 2003; Fontas et al., 1999; Beauvais and Alexandratos, 1998; Rovira et al., 1998; Cortina and Warshawsky, 1997; Jerabek et al., 1996; Alonso and Pantelides, 1995]. The concept of EIR is based on the incorporation of an extractant into a porous resin by physical impregnation [Cortina and Warshawsky, 1997; Kaby et al., 2003]. The EIR process combines the advantages of both solvent extraction and 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 adsorption [Cortina and Warshawsky, 1997]. 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 porosity, uniform pore size distribution and high surface area as well as chemically homogeneous nonionic structures [Kaby

et al., 2003]. Various extractants have been incorporated with XAD resins and applied to metal recovery and separation in the nuclear industry [Cortina and Warshawsky, 1997] as well as in hydrometallurgy [Saha et al., 2004]. Among them, Aliquat 336 has been reviewed as selective for TcO_4^- [Strauss, 1994] as well as Cr(VI) [Saha et al., 2004].

In this study, an EIR was prepared by impregnation of Aliquat 336 onto XAD-4 and tentatively applied to the separation of ReO_4^- which is a chemical analogue of TcO_4^- from rhodium in nitric acid solution. The impregnation conditions and adsorption performances of the prepared EIR were evaluated.

EXPERIMENTAL

1. Preparation of Adsorbent

The adsorbent was prepared by impregnating a Trioctylmethylammonium chloride (Aliquat 336, Aldrich) into an Amberlite XAD-4 resin. Amberlite XAD-4 is a highly cross-linked acrylic resin with surface area of 725 m^2/g and pore volume of 0.98 mL/g. The particle size is 20-40 mesh with mean pore size of 4 nm. First, the Amberlite XAD-4 was washed with pure water to remove any impurities and dried in an oven for 24 hours at 40 °C. Then, the resin was impregnated with Aliquat 336 dissolved in 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 the solvent was filtered, the impregnated resins were rewashed with pure water, and then dried 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 impregnation.

2. Adsorption Equilibrium Test

The effect of impregnation ratio of EIR on the adsorption performance was investigated. One gram of each EIR with different extractant loading ratios was added to 100 ppm rhenium solution. Since rhenium is a chemical analogue of technetium, the information on

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

the adsorption behaviors for rhenium makes it possible to understand adsorption characteristics of technetium indirectly, thereby avoiding the use of a radioactive element at high concentration. The solutions were placed in a shaking water bath at 25 °C for 24 hours. Then, the residual rhenium concentrations were determined by atomic absorption spectroscopy (AAS) for distribution coefficient evaluation with a GBC Model 906 spectrometer.

Adsorption equilibrium isotherms of EIR were obtained for the single and multi-component solutions of rhenium and rhodium in 0.5 M nitric acid solution. $Rh(NO_3)_3$ (Aldrich) was used for rhodium sources, and Re_2O_3 (Aldrich) after dissolving in 0.5 M nitric acid, was used for the source of rhenium. The initial concentration of each ion was fixed at 100 ppm and the weights of EIR were varied in the range between 0.002-0.3 g. The equilibrium tests were performed at 25 °C in triplicate and averaged to obtain one isotherm point.

3. Kinetic Test

First, kinetic studies were performed in a batch reactor for single and mixed solutions of rhenium and rhodium at 100 ppm in 0.5 M nitric acid, respectively. 1 g of EIR was added to the 100 mL of preconditioned testing solutions at 25 °C. The solutions were stirred and the impeller speeds were varied in the range between 500 and 1,000 rpm to evaluate film mass-transfer resistance of the system.

RESULTS AND DISCUSSION

1. Preparation of EIR

To determine the efficiency of the impregnation process, the degree of Aliquat 336 loading into the resin was evaluated with the variation of impregnation ratio (g Aliquat 336/g resin) and the result is shown in Fig. 1.

The loading weight increases constantly without a plateau as the impregnation ratio increases up to 2.0 even though the loading efficiency decreases with the impregnation ratio. No observation of equilibrium plateau is quite unlikely. Similar situation was reported by Saha et al. [2004] in their study for impregnation of Aliquat 336 into XAD-7 for removal of Cr(VI). They mentioned that a plateau was observed at an impregnation ratio above 2.5 g Aliquat 336/g polymer. Higher loading ratio is generally desirable for the higher adsorption capacity. However, considering the possible leaching of
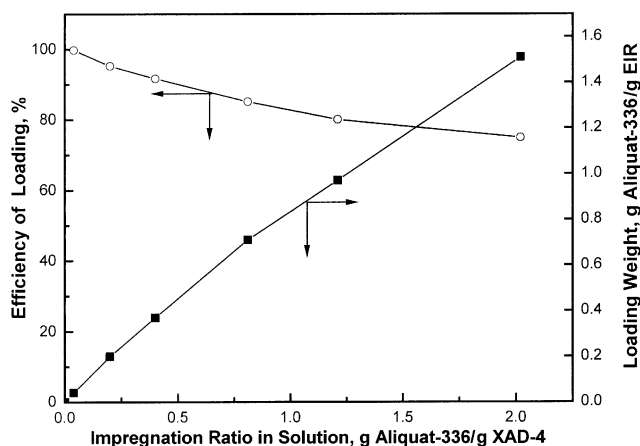

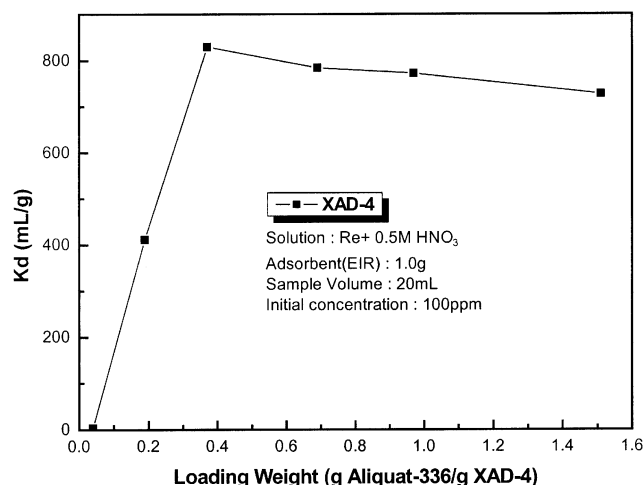Fig. 1. Loading efficiency and weight with impregnation ratio.

Fig. 2. Distribution coefficients of EIR with different loading weight.

Aliquat 336 from EIR at higher concentration, impregnation ratios above 2.0 were not investigated in this experiment. Adsorption performance tests for the EIR with different loading ratios were carried out to evaluate the effect of loading ratios on the adsorption performances of EIR for rhenium.

Fig. 2 shows the distribution coefficients of EIRs with different loading ratios for adsorption of rhenium. The distribution coefficient, K_d (mL/g), was calculated by the following equation:

$$K_d = \frac{c_s}{c_L} \tag{1}$$

where, c_s=equilibrium concentration in solid phase (meq/g)
　　　　c_L=equilibrium concentration in liquid phase (meq/mL)

The distribution coefficient is the maximum value at a loading ratio of about 0.4 (g Aliquat 336/g XAD-4) and then decreases gradually with the loading ratio increase. It is quite different from the general expectation that adsorption performances will increase proportionally to the loading ratio. It is possibly due to the leaching of extractant from EIR at higher loading. Therefore, in case of EIR, optimum loading of an extractant which insures stability in the resin should be importantly considered. In this study, therefore, EIR with loading ratio of about 0.4 g Aliquat 336/g XAD-4 was used for adsorption equilibrium and kinetic performance tests.

2. Adsorption Equilibrium

Adsorption isotherms of an EIR for the rhenium and rhodium were obtained to evaluate the adsorption capacity and the equilibrium constant. Experimental data were modeled by Langmuir equation given by

$$q = \frac{q_s bc}{1 + bc} \tag{2}$$

where q (meq/g), q_s (meq/g), and c (meq/mL) are the equilibrium and saturation concentrations of metals in solid and liquid phases, respectively. The isotherms and modeling examples are shown in Figs. 3 and 4. They show that the model fits the data well with high regression values in the case of rhenium. The EIR shows much higher preference for rhenium over the rhodium ion. The maximum loading capacities of the EIR for rhenium are 2.01 and 1.97 meq/g for
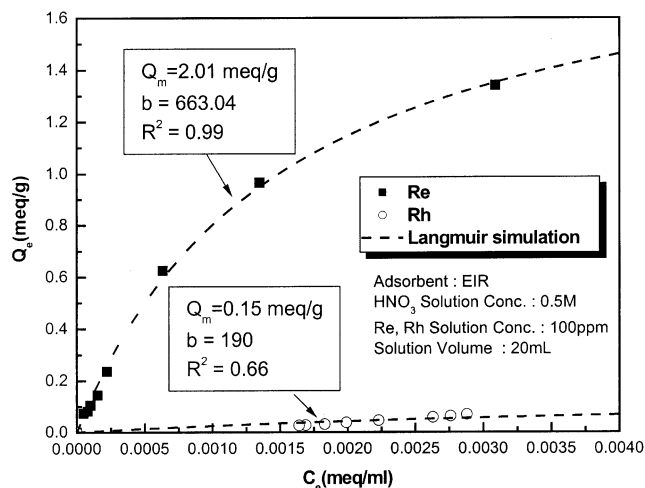
Fig. 3. Adsorption isotherms of EIR for rhenium and rhodium ions and Langmuir modeling in single component system.
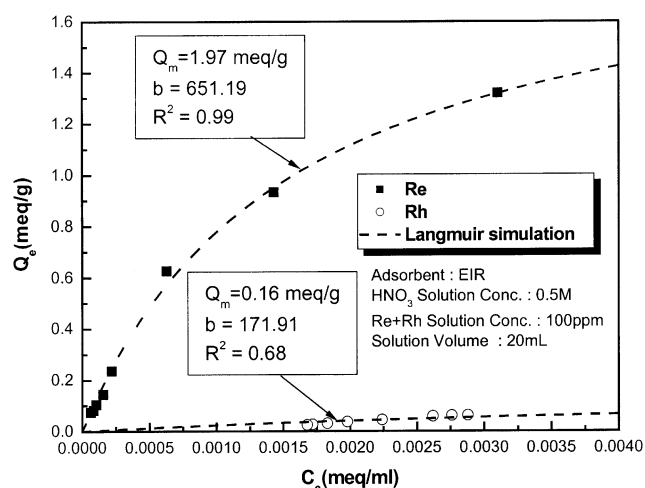

Fig. 4. Adsorption isotherms of EIR for rhenium and rhodium ions and Langmuir modeling in two component system.
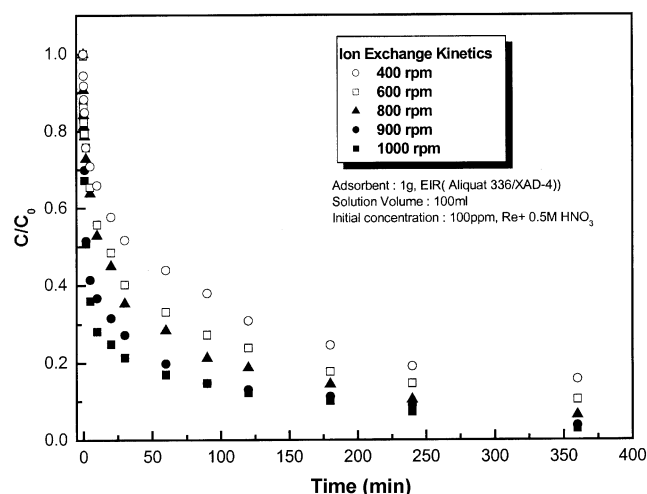

Fig. 5. Effect of impeller speed on the uptake rates of rhenium ion with EIR.

Fig. 6. Uptake rates of rhenium and rhodium ions with EIR for the single component system.

single and two component systems, respectively. On the other hand, only a little adsorption of rhodium ions was observed and furthermore, due to the unfavorable adsorption characteristics, the equilibrium data shows poor fitting with the Langmuir model. The difference in adsorption preference of Aliquat 336 for rhenium and rhodium ions is possibly attributed to the difference in chemical species of each ion in nitric acid solution. The chemical formula of Aliquat 336 is $CH_3N[(CH_2)_7CH_3]_3Cl$ and contains a chloride ion in its structure. This chloride ion is exchanged with rhenium or rhodium ion. Hence rhenium ion in nitric acid is mainly in the form of ReO_4^-, it could be easily exchanged with Cl^- ion in Aliquat 336. However, most favorable species of rhodium in 0.5 M nitric acid, although the exact species are unknown due to its complex coordination chemistry, are in the form of completely or incompletely nitrated oligomers [Belyaev et al., 2002; Varentsova and Varentosov, 2003]. Those oligomers with high positive charges and peculiar hydration shell prevent effective extraction by any types of extracting agents.

3. Kinetic Behavior

Experimental studies of the adsorption kinetics were performed

in a batch reactor, which is known for easy control of the film mass-transfer resistance by stirrer speed. The effect of the stirrer speed on the uptake rate is shown in Fig. 5. Impeller speeds varied in the range between 400 and 1,000 rpm. Since impeller speeds of more than 1000 have no impact for the uptake rates, the experiments were performed at 1,000 rpm. Fig. 6 shows the uptake curves for the single component systems of rhenium and rhodium. The loading of rhenium is much higher than the rhodium as expected from the equilibrium isotherms. The uptake behaviors for the mixed solution are shown in Fig. 7. It shows that the EIR has much more favorable uptake for rhenium over rhodium as in a single component system, even though the loadings are slightly lower than in a single component system. The lower loadings in a multi-component system are obviously due to the competition among the coexisting ions.

The metal adsorption onto EIR can be considered as a heterogeneous reaction between solid and solution. The reaction steps are generally defined by three steps: mass-transfer through the liquid film, diffusion through the particle pores, and finally a chemical
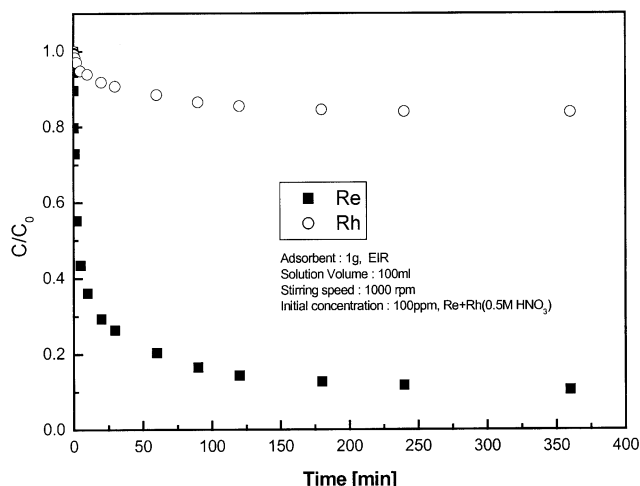
Fig. 7. Uptake rates of rhenium and rhodium ions with EIR for the two component system.

reaction with the functional groups. Among them, in most cases, the chemical reaction is generally considered to be very fast and the film mass-transfer resistance can be eliminated by vigorous agitation. Therefore, it could be speculated that the rate limiting step is the pore diffusion. To evaluate the uptake rate of the rhenium and rhodium, effective diffusivities for sorption into EIRs have been calculated by modeling the experimental data with a homogeneous diffusion model [Moon et al., 2005; Kim et al., 2003]. This model assumes that the particle is a homogeneous solid, and the diffusion occurs through the liquid filled pores with local equilibrium between the solid and the pore liquids. It is also assumed that the concentration of adsorbates is uniform throughout the batch reactor and the adsorbents are spherical particles with an identical radius. The system is also operated under isothermal conditions. By assuming that the diffusion follows Fick's law, the differential mass balance in the adsorbent gives:

$$\frac{\partial q}{\partial t} = \frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2 D_c \frac{\partial q}{\partial r}\right) \tag{3}$$

where D_c is the solid phase diffusivity for an ion. If D_c is concentration-dependent, it can be represented by Darken's law:

$$D_c = D_c^0 \frac{d\ln c}{d\ln q} = D_c^0 H(q) \tag{4}$$

where D_c^0 is the corrected diffusivity, independent of concentration. Substituting Eq. (4) into Eq. (3) gives

$$\frac{\partial q}{\partial t} = D_c^0\left[H(q)\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial q}{\partial r}\right) + \frac{\partial H(q)}{\partial r}\frac{\partial q}{\partial r}\right] \tag{5}$$

At the particle surface, $r = r_c$, equilibrium exists between the liquid phase concentration (c_s) and the solid phase concentration (q), expressed by the following equilibrium isotherm equation:

$$q = f(c_s) \qquad \text{at } r = r_c \tag{6}$$

For the Langmuir isotherm, Eq. (6) becomes

$$q = \frac{ac_s}{1 + bc_s} \qquad \text{at } r = r_c \tag{7}$$

Thus, Darken's law in Eq. (4) is given by the following equation"

$$H(q) = \frac{a}{a - bq} \tag{8}$$

A material balance at the particle surface leads to the boundary condition:

$$\frac{\partial \overline{q}}{\partial t} = \frac{3}{r_c^3}\int_0^{r_c}\frac{\partial q}{\partial t}r^2 dr = \frac{3k_f}{\rho r_c}(c_b - c_s) \qquad \text{at } r = r_c \tag{8}$$

where $\overline{q}$ is the average concentration in the solid phase and k_f is the mass transfer coefficient in the liquid film. Eq. (8) can be modified by substituting Eq. (3) into the integral in Eq. (8).

$$\left[H(q)\frac{\partial q}{\partial r}\right]_{r=r_c} = \frac{k_f}{\rho D_c^0}(c_b - c_s) \qquad \text{at } r = r_c \tag{10}$$

Thus,

$$c_s = c_b - \frac{\rho r_c}{Bi}\left[H(q)\frac{\partial q}{\partial r}\right]_{r=r_c} \qquad \text{at } r = r_c \tag{11}$$

where Bi is the non-dimensional Biot number, defined as:

$$Bi = \frac{k_f/r_c}{D_c^0/r_c^2} \tag{12}$$

The Biot number measures the relative resistance from the liquid film surrounding the particle to the internal diffusion resistance. For most systems, the internal resistance is more important than the film resistance. If the film mass transfer resistance is insignificant, Eq. (10) is replaced by the equation:

$$c_b = c_s \qquad \text{at } r = r_c \tag{13}$$

Under this condition, q at r_c is in equilibrium with c_b.

The overall mass balance leads to:

$$\varepsilon\frac{\partial c_b}{\partial t} + (1 - \varepsilon)\rho\frac{\partial \overline{q}}{\partial t} = 0 \tag{14}$$

where ε is the void fraction in the batch reactor and ρ is the particle density.

Substituting Eq. (9) into Eq. (14) and then combining it with Eq. (10) gives

$$\frac{\partial c_b}{\partial t} = -\frac{3(1-\varepsilon)k_f}{\varepsilon r_c}(c_b - c_s) = -\frac{3(1-\varepsilon)\rho D_c^0}{\varepsilon r_c}\left[H(q)\frac{\partial q}{\partial r}\right]_{r=r_c} \tag{15}$$

Finally, the initial conditions are:

$$c_b = c_0, \ c_s = q = 0 \qquad \text{at } t = 0. \tag{16}$$

The above equations can be rewritten in dimensionless form by introducing the following dimensionless variables:

$$C_b = \frac{c_b}{c_0}, \quad C_s = \frac{c_s}{c_0}, \quad Q = \frac{q}{q_0}, \quad \lambda = \frac{r}{r_c} \tag{17}$$

where q_0 is in equilibrium with c_0.

A set of the dimensionless form of the partial differential equations (PDEs) are reported in the previous work [Moon et al., 2005]. These equations should be solved by a numerical method. In this work, we converted the PDEs into ordinary differential equations (ODEs) by using the orthogonal collocation method [Villadsen and Michelsen, 1978]. Then the set of the ODEs was solved by utiliz-

ing the IMSL/Math subroutine IVPAG, which is based on Gear's stiff integration algorithm.

The average absolute deviation percent of determination (AAD%) was calculated by using a equation defined as

$$AAD\% = \frac{1}{n}\sum_{i=1}^{n}\frac{|C_{b,i}^{calc} - C_{b,i}^{exp}|}{C_{b,i}^{exp}} \times 100 \qquad (18)$$

where,

$C_{b,i}^{calc}$: dimensionless bulk phase concentration calculated by the model

$C_{b,i}^{exp}$: experimental value of dimensionless bulk phase concentration

n   : number of data points

The kinetic data of EIR were modeled by using the homogeneous model described above to determine the effective diffusivities. The variables evaluated to determine the impact on effective diffusivity included the concentration dependence of diffusivities as in Eq. (4). Fig. 8 is the modeling results for the uptake data of rhenium and rhodium ions in the single component system. It shows that the homo-
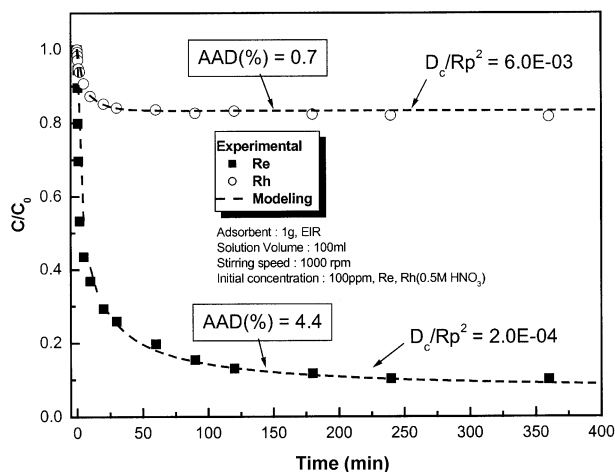
geneous model fits the kinetic data quite well and then the obtained diffusion time constant, D_c/R_p^2, is 2.0×10^{-4} min^{-1} for rhenium and 6.0×10^{-3} min^{-1} for rhodium. Considering that the particle radius is 0.027 cm, the effective diffusivities of rhenium and rhodium ions are 1.5×10^{-7} and 4.4×10^{-6} cm^2 min^{-1}, respectively.

The example of modeling results for the two component system is shown in Fig. 9, showing quite accurate prediction of the uptake curves for both components. The diffusion time constants of rhenium and rhodium ions are 1.7×10^{-4} and 1.0×10^{-3} min^{-1}, respectively. Then the effective diffusivities of rhenium and rhodium ions are 1.2×10^{-7} and 7.3×10^{-7} cm^2 min^{-1}, respectively. The effective diffusivities for adsorption of rhenium and rhodium with a XAD-4 impregnated with Aliquat 336 system are new so that they cannot be compared with the other results directly. The average absolute deviation percent of determination (AAD%) range is from 0.3 to 4.4%, well within the limits of accuracy for diffusivities reported in the literature. Typical deviations for intarparticle diffusivities are reportedly ±3-8% [Robinson et al., 1994].

CONCLUSIONS

An EIR was prepared by impregnation of Aliquat 336 into Amberlite XAD-4 for tentative separation of rhenium from rhodium in nitric acid solution. Loading of Aliquat 336 increased with the impregnation ratio in solution (g Aliquat 336/g resin) up to 2.0 without plateau. However, adsorption tests for the EIR with different loading ratios showed that the distribution coefficient was maximum at the loading ratio of about 0.4 (g Aliquat 336/g XAD-4), due to the leaching of extractant from EIR at higher loading of Aliquat 336. The prepared EIR showed high preference for rhenium over rhodium and adsorption isotherms for rhenium were described well by Langmuir equation in both the single and two component systems. Maximum adsorption capacities obtained by Langmuir modeling of isotherms for rhenium were 2.01 and 1.97 meq/g for the single and the two component systems, respectively. On the other hand, only a little adsorption of rhodium ions was observed. The kinetic data of EIR were modeled by using a homogeneous model to determine the effective diffusivities. The homogeneous model fitted the kinetic data quite well and the effective diffusivities of rhenium and rhodium ions are in the order of 10^{-7} and 10^{-6} cm^2 min^{-1}, respectively. The average absolute deviation percent of determination (AAD%) range is from 0.3 to 4.4%, well within the limits of accuracy for diffusivities reported in the literature.

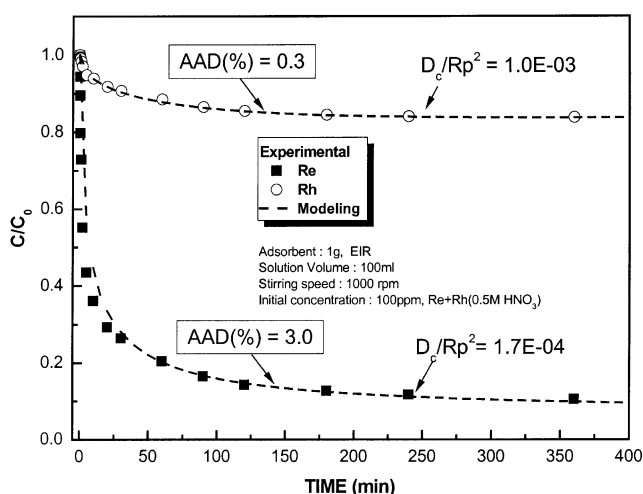**Fig. 8. Modeling of the uptake rates of rhenium and rhodium ions with EIR for the single component system.**

Fig. 9. Modeling of the uptake rates of rhenium and rhodium ions with EIR for the two component system.

REFERENCES

Alonso, A. I. and Pantelides, C. C., "Modeling and simulation of impregnated membrane processes for recovery of Cr(VI) with Aliquat 336," *J. of Membrane Science*, **110**, 151 (1996).

Asakura, T., Hotoku, S., Ban, Y., Kim, S. Y., Mineo, H. and Morita, Y., *Research on PARC for future reprocessing*, ATLANTE 2004, Nimes, 012-04 (2004).

Beauvais, R. B. and Alexandratos, S. P., "Polymer-supported reagents for the selective complexatio of metal ions: an overview," *Reactive & Polymers*, **36**, 113 (1998).

Belyaev, A. V., Renard, E. V., Khraanenko, S. P., Emel'yanov, V. A. and Fedotov, M. A., "State of radiorhodium in high-level liquid waste from regeneration of spent nuclear fuel," *Radiochemistry*, **44**(6), 546 (2002).

Cortina, J. L. and Warshawsky, A., "Developments in solid-liquid extraction by solvent-impregnated resins," *Ion Exchange and Solvent Extraction*, **13**, 195 (1997).

Fontas, C., Salvado, V. and Hidalgo, M., "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 (1999).

Jerabek, K., Hankova, L., Strikovsky, A. G and Warshawsky, "Solvent impregnated resin: relation between impregnation process and polymer support morphology I. di-(2-ethylhexyl)dithiophosphoric acid," *Reactive & Functional Polymer*, **28**, 201 (1996).

Kim, H. T., Lee, C. H., Shul, Y. G, Moon, J. K. and Lee, E. H., "Evaluation of PAN-TiO$_2$ composite adsorbent for removal of Pb(II) ion in aqueous solution," *Separation Science and Technology*, **38**(3), 695 (2003).

Moon, J.-K., Lee, E.-H., Han, Y.-J., Lee, B.-C. and Kim, H.-T., "Multicomponent ion exchange kinetics with PAN-KCoFC ion exchanger," *Korean J. Chem. Eng.*, **22**, 127 (2005).

Panesko, J. V., *Recovery of rhodium, palladium and technetium on strongly basic anion exchange resin*, ARH-1279 (1969).

Robinson, S. M., Arnold, W. D. and Byers, C. H., "Mass-transfer mechanisms for zeolite ion exchange in wastewater treatment," *AIChE J.*,

40(12), 2045 (1994).

Rovira, M., Cortina, J. L., Arnaldos and Sastre, A. M., "Recovery and separation of platinum group metals using impregnated resins containing Alamine 336," *Solvent Extraction and Ion Exchange*, **16**(5), 1279 (1998).

Saha, B., Gill, R. J., Bailey, D. G, Kabay, N. and Arda, M., "Sorption of Cr(VI) from aqueous solution by amberlite XAD-7 resin impregnated with Aliquat 336," *Reactive & Functional Polymers*, **60**, 223 (2004).

Taylor, R. J. and May, I., "Advances in actinide and technetium kinetics for applications in process flowsheet modeling," *Separation Science and Technology*, **36**(5&6), 1225 (2001).

Uchida, S. and Tagami, K., "Separation and concentration of technetium using a Tc-selective extraction chromatographic resin," *J. of Radioanalytical and Nuclear Chemistry*, **221**(1-2), 35 (1997).

Varentosov, V. K. and Varentosova, V. I., "Electrodeposition of rhodium on cathodes of carbon-fiber material from Rh(III) complexes in nitric acid solutions," *Russian J. of Electrochemistry*, **39**(6), 703 (2003).

Villadsen, J. and Michelsen, M. L., *Solution of differential equation models by polynomial approximation*, Prentice-Hall, Englewood Cliff, NJ (1978).

Wei, Y., Arai, T., Kumagai, M. and Bruggeman, A., *Development of the ERIX process for reprocessing spent FBR-MOX fuel*, Global 2003, New Orleans, LA, 479 (2003).

Yang, W. W., Luo, G. S. and Gong, X. C., "Extraction and separation of metal ions by a column packed with polystyrene microcapsules containing Aliquat 336," *Separation and Purification Technology*, **43**, 175 (2005).