ION EXCHANGE OF CESIUM WITH PAN-KCOFC COMPOSITE ION EXCHANGER

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ABSTRACT

PAN-KCoFC composite ion exchanger beads containing 80% KCoFC powder was prepared for selective removal of cesium. The prepared composite ion exchanger showed the dissolution stability in the acid solution of pH = 2 and radiation stability against radiation dose up to 1.89 MGy. Ion exchange equilibrium tests showed that the PAN-KCoFC was much more selective for the cesium ion over the Sr, Ba and Ni ions. Ion exchange isotherms were modeled to evaluate the equilibrium parameters such as equilibrium constants and ion exchange capacities. Ion exchange capacity for Cs in the multi-component system was found to be 0.70 meq/g. The ion uptake curves were obtained for the multi-component system as well as the binary systems. A homogeneous model, assuming no film mass transfer resistances, could predict accurately the uptake curve for both the binary and multi-component systems. Solid phase effective pore diffusivities for Cs, Ni, Sr and Ba ions were found to be in the order of 10^{-5} cm^2/min, which is the value between macro and intracrystalline diffusivities.

INTRODUCTION

Selective removal of cesium from a radioactive waste solution has long been an important issue, due to its hazardous effect on the environment [1]. Various inorganic ion exchangers have been applied to separate cesium [2~11]. Among them transition metal hexacyanoferrates such as NiFC, KNiFC and KCoFC are reportedly one of the selective ion exchanger for cesium [6, 11~12]. However, as in the most inorganic ion exchangers, it is synthesized in powder form and can cause operational problems such as a pressure drop and filtration in the column if used as it is. To solve this problem it should be pelletized or immobilized to the other supporting material. We introduced a polyacrylonitrile (PAN) for binding KCoFC powders to form a PAN-KCoFC composite bead. Many organic polymers have been suggested as binders in preparing composite beads. Especially, PAN has been reviewed as one of the most favorable binding material, due to its physico-chemical properties such as excellent beads formation, strong adhesive force with inorganic materials, good solubility in organic solvents and its chemical stability [13]. In this composite ion exchanger PAN is a simply inert binder and all the cesium ions are adsorbed on the KCoFC. For this reason, no radionuclides are released even when the PAN is decomposed. Therefore, it can be disposed off underground safely after cementation or vitrification [14]. In our previous studies [15~17], we prepared

several PAN based composite ion exchangers such as PAN-zeolite 4A, PAN-$K_2Ti_4O_9$ and PAN-NiFC, successfully. And Sebesta et al. [13] reported possible application of the various PAN based composite ion exchangers for radionuclides removal. Although PAN based composite ion exchangers have been reviewed recently as the promising ones for the removal of radionuclides, they still require more evaluation for their performances, especially the equilibrium and kinetic behaviors. For an optimal design of an ion exchange process, it is important to evaluate the dynamic behaviors of the ion exchange system. In this study we prepared a PAN-KCoFC composite ion exchanger and evaluated its ion exchange behaviors the multicomponent solution as well as the binary solution. A homogeneous model was used to predict ion exchange kinetic parameters.

Mathematical Modeling

A mathematical model was developed to simulate the diffusion kinetics for a batch ion exchange system, which is considered to be a completely mixed batch reactor where the solid particles are suspended in the liquid phase containing ionic species diffusing into the particles. We used a homogeneous diffusion model, which assumed that the particle is a homogeneous solid. The homogeneous model incorporates the mathematical descriptions of the following processes; 1) mass transfer resistance in the liquid film surrounding the ion exchanger particle, 2) local equilibrium adjacent to the exterior surface of the ion exchanger, and 3) diffusion resistance within the particle. The cb is the cation concentration in the bulk fluid, cs is the cation concentration in the liquid phase at the particle surface, and q is the cation concentration in the solid phase. At the particle surface, c_s is in equilibrium with q. It is assumed that the system is isothermal and the liquid phase concentration is uniform throughout the reactor except for the liquid film. The ion exchange rate is assumed to be much faster than the diffusion rate. Therefore, the ion exchange rate does not affect the kinetics of the system. The diffusion in the solid particle is assumed to follow Fick's law.

The unsteady-state diffusion in a solid sphere can be described by the following partial differential equation:

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

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

$$D_c = D_c^0 \frac{d\ln c}{d\ln q} = D_c^0 H(q) \tag{Eq.2}$$

where D_c^0 is the corrected diffusivity, independent of concentration. Substituting Eq. (2) into Eq. (1) gives

$$\frac{\partial q}{\partial t} = D_c^0\left[H(q)\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2 \frac{\partial q}{\partial r}\right) + \frac{\partial H(q)}{\partial r}\frac{\partial q}{\partial r}\right] \tag{Eq.3}$$

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:

$$q = \frac{ac_s}{1+bc_s} \qquad \text{at } r = r_c \qquad \text{(Eq.4)}$$

Thus, the Darken's law in Eq. (2) is given by the following equation.

$$H(q) = \frac{a}{a-bq} \qquad \text{(Eq.5)}$$

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

$$\frac{\partial \bar{q}}{\partial t} = \frac{3}{r_c^3} \int_0^{r_c} \frac{\partial q}{\partial t} r^2 dr = \frac{3k_f}{\rho r_c}(c_b - c_s) \quad \text{at } r = r_c \qquad \text{(Eq.6)}$$

where $\bar{q}$ is the average concentration in the solid phase and k_f is the mass transfer coefficient in the liquid film. Eq. (6) can be modified by substituting Eq. (1) into the integral in Eq. (6).

$$\left[H(q)\frac{\partial q}{\partial r} \right]_{r=r_c} = \frac{k_f}{\rho D_c^0}(c_b - c_s) \qquad \text{at } r = r_c \qquad \text{(Eq.7)}$$

Thus,

$$c_s = c_b - \frac{\rho r_c}{Bi}\left[H(q)\frac{\partial q}{\partial r} \right]_{r=r_c} \qquad \text{at } r = r_c \qquad \text{(Eq.8)}$$

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

$$Bi = \frac{k_f/r_c}{D_c^0/r_c^2} \qquad \text{(Eq.9)}$$

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. (8) is replaced by the equation:

$$c_b = c_s \qquad \text{at } r = r_c \qquad \text{(Eq.10)}$$

Under this condition, q at r_c is in equilibrium with c_b. The overall mass balance leads to:

$$\varepsilon \frac{\partial c_b}{\partial t} + (1-\varepsilon)\rho \frac{\partial \bar{q}}{\partial t} = 0 \qquad \text{(Eq.11)}$$

where ε is the void fraction in the batch reactor and ρ is the particle density. Substituting Eq. (6) into Eq. (11) and then combining it with Eq. (7) gives

$$\frac{\partial c_b}{\partial t} = -\frac{3(1-\varepsilon)k_f}{\varepsilon r_c}(c_b - c_s) = -\frac{3(1-\varepsilon)\rho D_c^0}{\varepsilon r_c}\left[H(q)\frac{\partial q}{\partial r}\right]_{r=r_c} \tag{Eq.12}$$

Finally, the initial conditions are:

$$c_b = c_0, \quad c_s = q = 0 \qquad \text{at } t = 0. \tag{Eq.13}$$

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

$$C_b = \frac{c_b}{c_0}, \; C_s = \frac{c_s}{c_0}, \; Q = \frac{q}{q_0}, \; \lambda = \frac{r}{r_c} \tag{Eq.14}$$

where q_0 is in equilibrium with c_0. The symmetry of the problem at $\lambda = 0$ suggests the transformation of the independent variable [Rice and Do, 1995], $\eta = \lambda^2$. With these new variables, Eqs. (3), (4), (5), (8), (11), and (12) become

$$\frac{\partial Q}{\partial t} = \frac{D_c^0}{r_c^2}\left[H(Q)\left(4\eta\frac{\partial^2 Q}{\partial \eta^2} + 6\frac{\partial Q}{\partial \eta}\right) + 4\eta\frac{\partial H(Q)}{\partial \eta}\frac{\partial Q}{\partial \eta}\right] \tag{Eq.15}$$

$$Q = \frac{ac_0 C_s}{q_0(1+bc_0 C_s)} \qquad \text{at } \eta = 1 \tag{Eq.16}$$

$$H(Q) = \frac{a}{a - bq_0 Q} = 1 + bc_0 C_s \tag{Eq.17}$$

$$C_s = C_b - \frac{2\rho q_0}{c_0 Bi}\left[H(Q)\frac{\partial Q}{\partial \eta}\right]_{\eta=1} \qquad \text{at } \eta = 1 \tag{Eq.18}$$

In case of the insignificant film mass transfer resistance, this must be replaced by the following equation:

$$C_s = C_b \qquad \text{at } \eta = 1 \tag{Eq.19}$$

$$\frac{\partial C_b}{\partial t} = -\frac{3(1-\varepsilon)k_f}{\varepsilon r_c}(C_b - C_s) = -\frac{6(1-\varepsilon)\rho q_0 D_c^0}{\varepsilon c_0 r_c^2}\left[H(Q)\frac{\partial Q}{\partial \eta}\right]_{\eta=1} \tag{Eq.20}$$

$$C_b = 1, \; C_s = Q = 0 \qquad \text{at } t = 0 \tag{Eq.21}$$

Eqs. (15) to (21) constitute a set of the partial differential equations (PDEs) which 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 [18]. This set of the ODEs was solved by utilizing the IMSL/Math subroutine IVPAG, which is based on the Gear's stiff integration algorithm. The average absolute deviation percent of determination (AAD%) was calculated using a equation defined as

$$AAD\% = \frac{1}{n}\sum_{i=1}^{n}\frac{\left|C_{b,i}^{calc} - C_{b,i}^{\exp}\right|}{C_{b,i}^{\exp}} \times 100 \qquad\qquad (Eq.22)$$

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

Experimental

To prepare PAN-KCoFC composite ion exchanger beads in which the content of KCoFC powder is 80 percent, the given amount of KCoFC powder was dispersed in DMSO (dimethylsulfuroxide) solvent and then mixed with PAN (polyacrylonitrile) polymer to make homogeneous composite dope. Then the composite beads were prepared using the dual nozzle technic described in our previous studies [15~16]. The gelled composite beads were washed with ultra pure water and then dried in freeze dryer for 3 days at 1.33 x 10-1 Pa. Pore size distribution and porosity of the prepared composite beads were measured by mercury porosimeter (Micrometrics, AutoPore III). The pore structure and the distribution of KCoFC powder in the composite bead were observed by scanning electron microscope (JEOL Co., JSM 5200).

The chemical stability of the composite beads was tested in the nitric acid solution of pH = 2. The dried composite beads were contacted with the nitric acid solution for period up to 5 days, and the weight loss and distribution coefficient were measured for stability assessment. The radiation stability of PAN-KCoFC was evaluated in radiation dose range up to 1.89 MGy. The preconditioned PAN-KCoFC samples were transferred into polyethylene test tubes. The total volume of the beads and solution mixture was adjusted to 20 mL by adding the nitric acid solution of pH = 2. After irradiation, the stability of the composite beads was assessed by weight loss, morphology change and distribution coefficient changes.

Ion exchange tests for Cs+, Sr2+, Ba2+ and Ni2+ ions were carried out to determine the ion exchange equilibrium isotherms and adsorption kinetics in the binary and multi-component systems. Ion exchange equilibrium isotherms were determined in the batch tests at constant pH value pH = 2, and solution volume to exchanger mass ration V/m = 100 mLg-1. The concentration of sorbing metals varied from 0.0002 N up to 0.2 N in these experiments. Ion exchange kinetic tests were performed in a batch reactor. In each experiment, 1 g of PAN-KCoFC was added to the reactor which contained 100 mL of the solutions. Impeller speeds were varied between 500 and 1,000 rpm. The samples were decanted using 0.2 µm syringe filter and analysed by AAS (PERKIN-ELMER, Model 1100B).

Results and Discussion

In preparing spherical composite beads, the viscosity of composite dope is reportedly important for their sphericity [15]. For preparing PAN-KCoFC composite bead, the most favourable viscosity of the composite dope for spherical bead formation were found to be ranged from 440 cP up to 450 cP. The prepared PAN-KCoFC composite beads are represented in Fig. 1 together with the cross sections and inner pore structures observed by SEM. It shows that the spindle-shaped channels and inner pores of the composite bead were well developed. The KCoFC powders, which are active materials, are found to be dispersed throughout the binding matrix. The pore size distribution and porosity of the composite beads were measured using mercury porosimeter and the results are summarized in Table 1. The porosity of more than 70 % is considered much higher than existing inorganic particles such as zeolites.
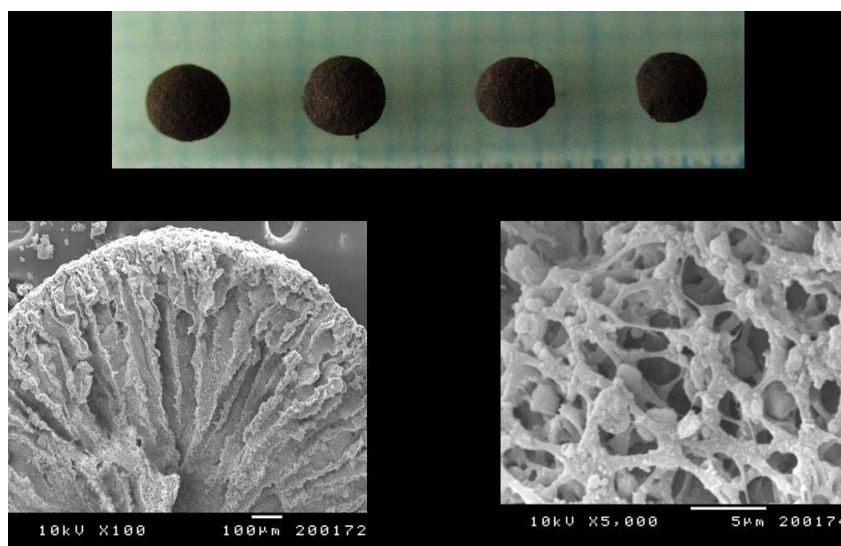

Fig. 1. Photos showing the PAN-KCoFC beads and internal pore structures.

**Table I. Summary of the porosimeter data for PAN-KCoFC beads.**

Average Pore Diameter (μm)	Bulk Density (g/mL)	Apparent Density (g/mL)	Porosity (%)
0.078	0.502	2.064	75.690

The chemical and radiation stability tests of PAN-KCoFC composite ion exchanger showed that the PAN- KCoFC composite ion exchanger was stable in acid solution of pH = 2 and after the irradiation up to 1.89 MGy, by observing no weight loss and no changes ion exchange performances. Ion exchange equilibrium data were fitted to Langmuir isotherm (Eq. 4) in order to determine maximum sorption capacity a/b (meq/g) and respective equilibrium constants for the ions.

Figure 2 is the result of fitting for the cesium ion exchange with the KCoFC powder and PAN-KCoFC composite ion exchanger, respectively. The maximum sorption capacities calculated by modelling the Langmuir equation for KCoFC and PAN-KCoFC composite ion exchanger were 1.303 meq/g and 1.070 meq/g, respectively. The value for PAN-KCoFC makes almost 80% of sorption capacities determined for the pure KCoFC powder, which indicates that sorption sites are not seriously hindered by PAN binding matrix. The ion exchange equilibrium data for the multi-component system as well as the binary systems at pH = 2 were obtained.
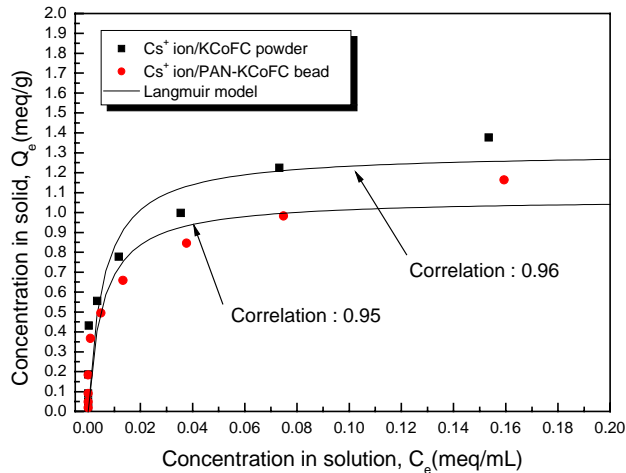
Fig. 2. Comparison of the cesium ion exchange isotherms with KCoFC and PAN-KCoFC.
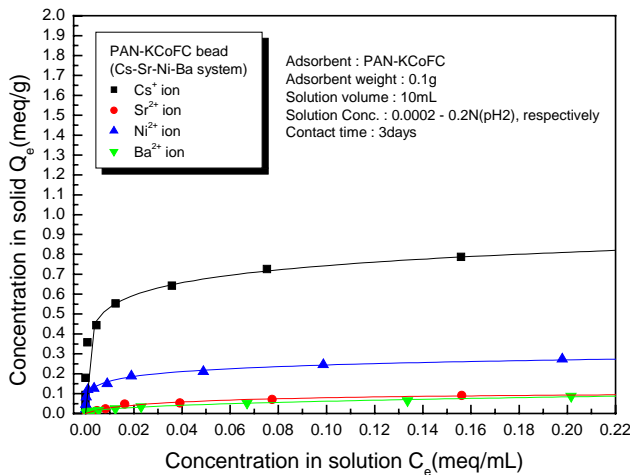
Fig. 3. Multi-component ion exchange isotherms and modelling examples.

The modeling results for the multi-component system are represented in Fig. 3 and Table 2. It shows that the PAN-KCoFC is much selective for cesium ion over the other ions such as strontium, barium and nickel ions. The maximum loading capacity of the PAN-KCoFC for Cs ion is o.7 meq/g at the solution pH = 2

Table II. Langmuir parameters for multi-component ion exchange with PAN-KCoFC.

| Ions \ Parameters	Cs	Sr	Ni	Ba
a/b (meq/g)	0.70	0.10	0.24	0.09
b (-)	761.59	38.24	396.41	23.74
R^2	0.99	0.98	0.99	0.98

The effect of stirring rate on the uptake rate of PAN-KCoFC composite ion exchanger for Cs ion was investigated and the result showed that the stirring speed did not affect the uptake rate in case of more than 700 rpm. Therefore, most experiments were carried out at 700 rpm and film mass transfer resistance was not considered in modeling the uptake curve. The uptake rates for the different sizes of PAN-KCoFC particles in the range between 1.47mm and 2.10 mm were shown to be not very different. Considering that the PAN-KCoFC beads are mainly composed of macropores with average sizes of 0.078 μm and the nonporous structure of KCoFC, it possibly means that the mass transfer resistance in the macropores for the given particle size range is not significant. The uptake tests for the binary systems with the 1.47mm radius PAN-KCoFC particles showed that the loading of the cesium was much higher than the other cations such as the strontium, nickel and barium ions, as expected from the equilibrium isotherms obtained in our previous study [11]. In the case of four component solution, the uptake behaviors as in Fig. 4 are similar to those for the binary system, except that the loadings for Cs and Ni are lower and the favorability for Cs is higher than in the binary system. The lower loadings for the specific ions in the multi-component system are obviously due to the competition among the coexisting cations.

A homogeneous model was used to model the kinetic data and to evaluate the solid phase effective diffusivities. Here, the film mass transfer coefficient is assumed to be negligible since the uptake rates are not function of the stirring speed. The effective diffusivity is considered to be dependent on the solute concentration in solid phase and the model is incorporated into to Darken's Law as in Eq.(2). The examples of modeling results for the multi-component systems are shown in Fig. 4.

In the case of Cs and Ni ion exchange curves, a homogeneous model predicts the experimental curves fairly accurately. It might indicate that the PAN-KCoFC beads have homogeneous pore structures, even though the PAN-KCoFC beads are composed of the two phases of KCoFC powder and PAN binder. This result is consistent with the reference [19] which used two phase homogeneous model for a silicotitanate ion exchanger, and comparable with other results for zeolite particles [20], which obviously have heterogeneous macro and micro pore structures.

While, in the case of Ba and Sr ions, the model does not predict the uptake curve so accurately, possibly due to the very low uptake behaviors and inaccurate evaluation of the equilibrium parameters. Considering that the PAN-KCoFC is mainly designed for selective separation of Cs ion, a little deviation is not considered meaningful. The solid phase effective diffusivities obtained for multi-component systems are shown to be in the order of 10-5 cm2/min. The effective diffusivities for PAN-KCoFC system are rather new so that they can not be compared with the other results directly. However, if we look into the fact that the macropore diffusivities for clay-binder zeolite particles are reportedly in the order of 10^{-4} cm^2/min and intracrystalline diffusivities are normally less than 10^{-8} cm^2/min, those for PAN-KCoFC particles are considered to be ranged between macro and intracrystalline diffusivities. The deviation of the obtained diffusivities range from 0.18 to 3.58 %. Considering that the macropore resistances for the PAN-KCoFC system are not significant and the KCoFC powder is almost nonporous, the main mass-transfer resistances are possibly due to the diffusion through the very thin layer which is formed on the surface of the beads by the PAN binder, and this fact requires further investigation.
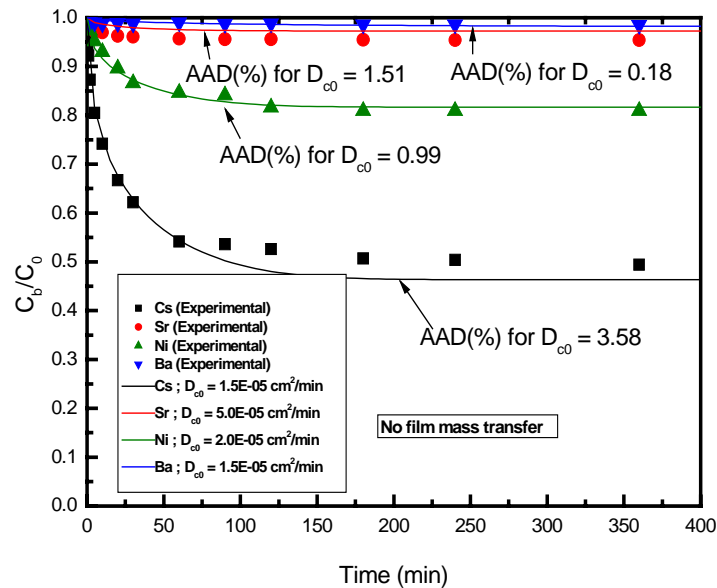
Fig. 4. Modeling examples for multi-component ion exchange system with PAN-KCoFC.

CONCLUSION

PAN-KCoFC composite ion exchanger was prepared to separate the cesium ions in acid solution. The prepared composite beads were stable in acid solution of pH = 2 and radiation dose up to 1.89 MGy. The ion exchange tests showed that PAN-KCoFC was selective for the cesium ion over the strontium, nickel and barium ions. Ion exchange capacities for Cs^+ ions in multi-component solution at pH = 2, estimated by Langmuir equation, were 0.70 meq/g. The uptake curves of a PAN-KCoFC composite ion exchanger were obtained for the multi-component solution as well as the binary solution.

The particle radii variation in the range between 1.47mm and 2.10 mm did not affect the uptake rate seriously, which means there was little macropore resistance. A homogeneous model, assuming no film mass transfer resistances, could predict accurately the uptake curves for both the binary and multi-component systems. Solid phase effective pore diffusivities for Cs, Ni, Sr and Ba ions were found to be in the order of 10^{-5} cm^2/min for multi-component system.

ACKNOWLEDGMENT

REFERENCES

1. Enarsson, A., Landgren, a., Liljenzin, J. O., Skalberg, M., Spjuth, L., Gudowski, W. and Wallenius, J., "Partitioning and Transmutation (P&T) 1997," SKB annual Report, TR-98-14 (1998).

2. Anthony, R. G., Philip, C. V. and Dosch, R. G., "Selective Adsorption and Ion Exchange of Metal Cations and Anions with Silico-Titanates and Layered Titanates," Waste Management, 13, 503 (1993).

3. Sinha, P. K., Panicker, P. K., Amalraj, R. V. and Krishnasamy, V., "Treatment of Radioactive Liquid Waste Containing Cesium by Indigenously Available Synthetic Zeolites: A Comparative Study", Waste Management, 15(2), 149 (1995).

4. Sinha, P. K., Lal, K. B., Panicker, P. K., Amalraj, R. V. and Krishnasamy, V., "Application of commercial zeolite-13X in the Treatment of Simulated and Actual Radioactive Effluent Containing Caesium," Indian Journal of Chemistry, 33A, 924 (1994).

5. Ernest, M. V., Jr., Pibler, J. P., Whitley, R. D. and Wang, N.-H. L., "Development of a Carousel Ion Exchange Process for Removal of Cesium-137 from Alkaline Nuclear Waste," Ind. Eng. Chem. Res., 36, 2775 (1997).

6. Mimura, H., Lehto, J. and Harjula, R., "Ion Exchange of Cesium on Potassium Nickel Hexacyanoferrate(II)s," J. of   Nuclear Science and Technology, 34(5), 484 (1997a).

7. Mimura, H., Letho J. and Harjula, R., "Chemical and Thermal Stability of Potassium Nickel Hexacyanoferrate(II)s," J. of Nuclear Science and Technology, 34(6) 582 (1997b).

8. Tarasevich, Yu. I., Kardasheva, M. V. and Polyakov, V. E., "Selectivity of Ion Exchange on Clinoptilolite," Colloid Journal, 59(6), 754 (1997).

9. Mardan, A., Rumana, A., Mehmood, A., Raza, S. M. and Ghaffar, A., "Preparation of Silica Cobalt Hexacyanoferrate Composite Ion Exchanger and Its Uptake Behavior for Cesium," Separation and Purification Technology, 16, 147 (1999).

10. Marageh, M. G., Husain, S. W. and Khanchi, A. R., "Selective Sorption of Radioactive Cesium and Strontium on Stannic Molybdophosphate Ion Exchanger," Applied Radiation and Isotopes, 50, 459 (1999).

11. Moon, J. K., Kim, Lee, E. H. and Kim, H. T., "Ion Exchange of Cs Ion in Acid Solution with Potassium Cobalt Hexacyanoferrate," Korean J. Chem. Eng. , 21(5), 1026 (2004).

12. Rao, S. V. S., Lal, K. B., Narasimhan, S. V. and Ahmed, J., "Copper ferrocyanide-Polyurethane foam as Composite Ion Exchanger for Removal of Radio Cesium," J. of Radioanalytical and Nuclear Chemistry, 240(1), 269 (19990.

13. Sebesta F. and John J.: An Overview of the Development, Testing, and Application of Composite Absorbers, LA-12875-MS, 1995.

14. John, J., Sebesta, F. and Motl, A., "Composite Absorbers Consisting of Inorganic Ion-Exchangers and Polyacrylonitrile Binding Matrix: Leaching of 137Cs from Cemented NiFC-PAN Absorber," Radiochimica Acta, 78, 131 (1997).

15. Moon, J. K., Kim, K. W., Jung, C. H., Lee, E. H., Shul, Y.G., " Preparation of Organic-Inorganic Composite Beads for Removal of Radionuclides and Heavy Metal Ions," J. Radioanalytical and Nuclear Chemistry, 246(2), 299 (2000).

16. Moon, J. K., Kim, Jung, C. H., Lee, E. H., Kim, H. T. and Shul, Y.G., "Preparation of PAN-zeolite 4A Composite Ion Exchanger and its Uptake Behavior for Sr and Cs Ions in Acid Solution," Korean J. Chem. Eng. , 19(5), 838 (2002).

17. Kim, H. T., Lee, C. H., Shul, Y. G., Moon, J. K. and Lee, E. H., " Evaluation of PAN-TiO2 Composite Adsorbent for Removal of Pb(II) Ion in Aqueous Solution," Separation Science and Technology, 38(3), 695 (2003).

18. Villadsen, J. and Michelsen, M. L., "Solution of Differential Equation Models by Polynomial Approximation," Prentice-Hall, Englewood Cliff, NJ (1978).

19. Gu, D., Nguyen, L., Philip, C. V., Huckman, M. E., Anthony, R. G., Miller, J. E. and Trudell, D. E., "Ion Exchange Kinetics in Complex Electrolyte Solutions Using Hydrous Crystalline Silicotitanate," Ind. Eng. Chem. Res., 36, 5377 (1997).

20. 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).