Preparation of PAN-zeolite 4A Composite Ion Exchanger and its Uptake Behavior for Sr and Cs Ions in Acid Solution

Jei-Kwon Moon†, Chong-Hun Jung, Eil-Hee Lee, Hyung-Tae Kim* and Yong-Gun Shul*

Korea Atomic Energy Research Institute, Yuseong P.O. Box 105, Daejeon 305-600, Korea
*Department of Chemical Engineering, Yonsei University, Seoul 120-749, Korea

Abstract−A PAN-4A composite ion exchanger containing about 80% 4A powder was prepared to remove strontium and cesium ions from acidic solution. The SEM image of the fracture of composite bead showed that zeolite 4A powder was dispersed homogenously and the pores were well formed. The mean pore size of composite bead was 0.14 μm and its porosity was about 74%, which is much higher in comparison with the existing inorganic adsorbent beads. The acid and radiation stability tests showed that PAN-4A was stable against acid solution higher than pH 2 and radiation dose less than 1.89×10^8 rad, respectively. Ion exchange tests showed that the PAN-4A was selective for Sr ion. The distribution coefficients of PAN-4A for Sr and Cs ions at pH 2 were 2×10^4 mL/g and 280 mL/g, respectively. The ion exchange capacities (q_s) of PAN-4A for Sr and Cs ions at pH 2, which are modeled by Dubinin-Polanyi equation, were 3.92 meq/g and 2.47 meq/g, respectively.

Key words: Composite Ion Exchanger, Ion Exchange, Radionuclide, PAN, Zeolite 4A

INTRODUCTION

Of the fission products present in the nuclear stream, cesium-137 and strontium-90 are reportedly the most predominant, hazardous and difficult to handle and store safely.

To remove Cs and Sr ions selectively, inorganic ion exchangers have been widely used [Mimura et al., 1995, 1997; Marageh et al., 1999; Moon et al., 2000a]. In particular, synthetic and natural zeolites have been applied effectively to radwaste treatment as well as to heavy metal removal, due to their selectivity for specific cations, thermal and radiation stabilities [Liang and Hsu, 1993; Lopez et al., 1995; Mimura et al., 1995; Perona et al., 1995; Robinson et al., 1994; Sinha et al., 1995; Moon and Lee, 1990; Lee and Moon, 2001]. However, in spite of the characterizing advantage of zeolites, their microcrystalline or powdered forms, if used as they are, cause a pressure drop problem in column operation. For this reason, inorganic ion exchangers have to be pelletized by using suitable binder. The required properties of such a binding material are the sufficient aggregation force, chemical stability, no adverse effect on the ion exchange properties of the inorganic ion exchanger, no ion exchange properties of their own, and high permeability for aqueous solutions of the targeted ions. For zeolites, clay minerals have been generally used as binder for pelletization, and applied quite successfully for gaseous separation processes. However, dissolution of binders when used in aqueous solution would be the impediment for extensive application to column operation.

These reasons have recently expedited study on the preparation of organic binder based composite ion exchangers for industrial applications [Mardan et al., 1999; Mariamichel and Kishnamoorthy, 1997; Hwang et al., 1998; John et al., 1997; Sebesta et al., 1995a,

b; Moon et al., 2000b; Rao et al., 1999; Pandit and Chudasama, 1998; Simanova, 1999]. Many organic polymers have been proposed as a binder in preparing composite ion exchangers. Among them, PAN (polyacrylonitrile) is reportedly one of the most favorable binding materials for any inorganic materials, due to its physicochemical properties such as excellent pelletizing property, strong adhesive force with inorganic materials, good solubility for organic solvents and chemical stability [Sebesta et al., 1995a; Xue et al., 1997].

Several researchers have studied PAN-based composite adsorbents. Sebesta et al. [1995b] conducted chemical and radiation stability tests for PAN and AMP-PAN beads, and proved that they had no limitation by chemical and radiation decomposition. John et al. [1997] conducted dynamic leaching tests of Cs-137 from cesium loaded cemented NiFC (nickelferrocyanate)-PAN composite ion exchanger. They proved that the leachability was much lower than that from simply cemented samples. In a previous study [Moon et al., 2000b], we also successfully prepared $K_2Ti_4O_9$-PAN and $Ni_2Fe(CN)_6$-PAN composite adsorbents. In spite of some successful results on the preparation of PAN based composite adsorbents, there are not enough data on the preparation characteristics depending on the kind of inorganic active materials, and only few on the equilibrium and kinetic performances.

Therefore this study was focused on the preparation of spherical PAN-4A composite ion exchanger, and then the evaluation of its ion exchange behaviors for Sr and Cs ions.

EXPERIMENTAL

1. Preparation of PAN-4A Composite Ion Exchanger Bead

First, given amounts of 4A powder were homogeneously dispersed at 50 °C for 2 hours by using DMSO (dimethylsulfuroxide) solvent in one liter three-neck flask furnished with mechanical stir-

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

rer, then mixed with PAN (polyacrylonitrile) powder and a few drops of TWEEN-80 surfactant at 50 °C for another 3 hours to make homogeneous composite dope. The viscosity of PAN-4A composite dope was measured by viscometer (BROOKFIELD. INC., Model DV-II). The composite dope, as described in a previous study [Moon et al., 2000b], was passed through inside the dual nozzle by metering pump, while the compressed air in the range of 0-6 psig was ejected through the outside annulus of the dual nozzle to adjust the sphericity and the size of the composite beads. The ejected composite beads were then dropped in distilled water, which was used as a gelation agent. Finally, the spherical composite beads were washed by using de-mineralized water and dried in freeze dryer for 7 days at 10^{-3} torr.

A scanning electron microscope (JEO. Co., JSM 5200) was used to observe the pore structure and the distribution of 4A powders in the bead. Pore size distribution and porosity of the composite bead were measured by using mercury porosimeter (Micromeritics, Auto-PoreIII). Its morphology was observed by digital camera (OLYM-PUS Co., Model 2500).

2. Chemical and Radiation Stabilities

Chemical stability of the composite bead was performed in the nitric acid solution of pH 2. The dried sample was immersed into nitric acid solution for 5 days. The resulting weight loss and the distribution coefficient variation were determined for stability assessment.

Radiation stability of PAN-4A was determined in radiation dose range of 1.00×10^3-1.89×10^8 rad. Given amounts of preconditioned PAN-4A samples were transferred into polyethylene test tubes. Total volume of the beads and solution mixture was adjusted to 20 mL by adding nitric acid solution of pH 2. After irradiation, the weight loss, changes in morphology and ion exchange property were measured to confirm the radiation effect.

3. Ion Exchange Tests

Distribution coefficients and ion exchange equilibrium isotherms of PAN-4A beads were determined for strontium and cesium ion solutions in a batch reactor. In determining distribution coefficients, strontium and cesium ion concentrations were fixed at 0.01 N, respectively, while solution pHs were varied in the range 2-6. Next, 0.5 g of PAN-4A composite beads was contacted with 10 mL/g of 0.01 N $Sr(NO_3)_2$ and $CsNO_3$ solutions, respectively for 24 hours. Distribution coefficient, K_d in mL/g, was calculated by using 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]

Ion exchange isotherms of PAN-4A beads were obtained for strontium and cesium ion solutions in batch reactor where the dosage, pH were held constant at 10 mL/0.1 g and 2, respectively, and the solution concentrations were varied between 0.0002-0.2 N. The composite ion exchangers were contacted with the exchange solutions for 72 hours at 25 °C and the tests were performed in triplicate to obtain each isotherm points. Then the equilibrated solutions were decanted by using 0.2 μm syringe filter and analyzed by AA (Perkin-Elmer, Model 1100B) for cations.

RESULTS AND DISCUSSION

1. Preparation of PAN-4A Composite Ion Exchanger Beads

In the previous study on the preparation of composite ion exchanger beads [Moon et al., 2000b], it was confirmed that sphericity of composite bead was greatly affected by viscosity of the composite dope, even though the optimum viscosity ranges would be somewhat different from the kinds and contents of the inorganic materials.

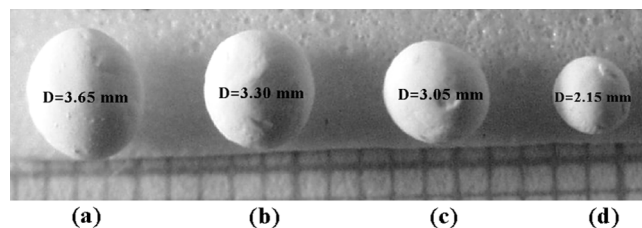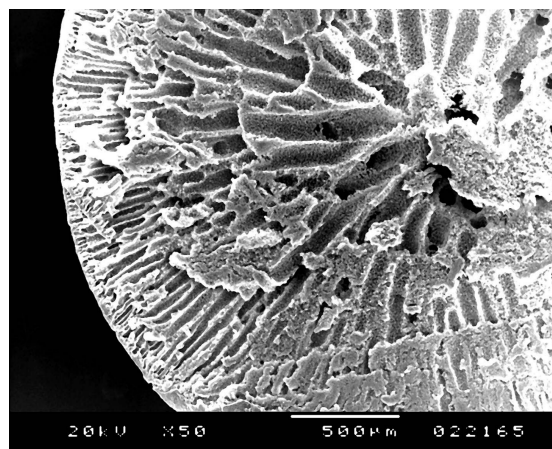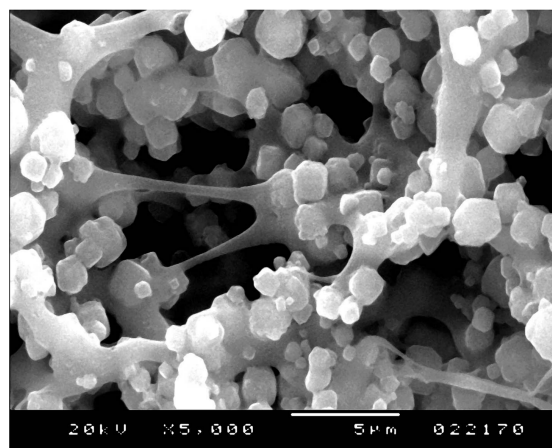In this experiment for preparing a composite ion exchanger con-

(a)   **(b)**   **(c)**   **(d)**

Fig. 1. Photograph of the PAN-4A composite ion exchanger beads showing the size variation with the air pressure flowing outside of the dual nozzle.
(a) atmosphere, (b) 2 psig, (c) 4 psig, (d) 6 psig

(a)

(b)

Fig. 2. SEM image of the fracture (a) and the inside pore (b) of the PAN-4A bead.

taining about 80 percent 4A powder, the optimum viscosities for spherical beads were found to be in the range 830-860 cP. Composite bead sizes are normally controlled by nozzle size variation. However, even though the nozzle size is fixed, the bead sizes were found to be controlled more or less by air pressure flowing outside channel of the dual nozzle. The effect of air pressure on the bead size, for fixed nozzle size, was tested and the resulting morphology of the beads was represented in Fig. 1. It showed that the bead sizes were varied in the range of 3.65-2.15 mm for air pressure variations between atmospheric pressure and 6 psig. Fig. 2, which is the SEM image for the cross section of the composite bead, shows homogeneous distribution of 4A powder and well developed pores inside the composite bead.

The pore size distribution and average pore size of the composite bead were analyzed by using a mercury porosimeter. The results were represented in Fig. 3 and summarized in Table 1. The average pore size of the bead was 0.14 μm and the porosity was about 74 percent, which is an outright high value, considering that the porosities of the other inorganic adsorbent beads such as zeolites are normally less than 50 percent. Such a high porosity would be one of the characterizing features of organic binder based composite beads, which might improve remarkably the kinetics.

2. Chemical and Radiation Stability of the PAN-4A Composite Ion Exchanger

The structural stability of the PAN-4A composite ion exchanger against acid solution was proven by observing no weight loss for 5 day contact with the nitric acid solution of pH 2. Also, the results of ion exchange performance tests confirmed that the composite ion exchanger did not deteriorate by contacting with the acid solutions of pH 2 for 5 days as shown in Fig. 4.
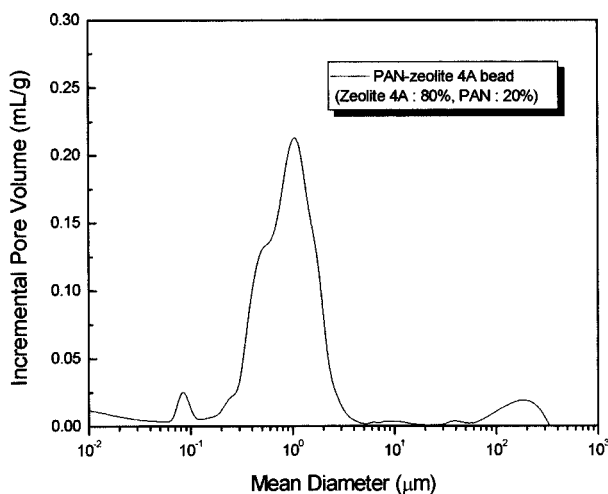

Fig. 3. Pore size distribution of the PAN-4A composite ion exchanger bead.

Table 1. Porosimeter analysis data for PAN-4A composite ion exchanger bead

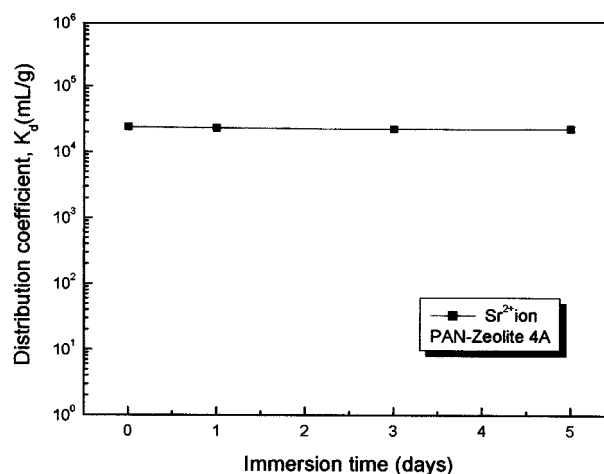| Average pore diameter, μm	0.14
Bulk density, g/mL	0.48
Apparent density, g/mL	1.82
Porosity, %	73.67

Fig. 4. Distribution coefficients of PAN-4A composite ion exchanger beads for Sr ion before and after immersion into acid solutions of pH 2.

Evaluation of radiation stability of PAN-4A beads was carried out by measuring weight loss and variation in ion exchange property together with observing morphology change for the radiation dose ranging from 1.00×10^3 to 1.89×10^8 rad. A view of the irradiated samples is shown in Fig. 5, which shows no external changes of the bead shape. The radiation effect on the weight loss was neg-
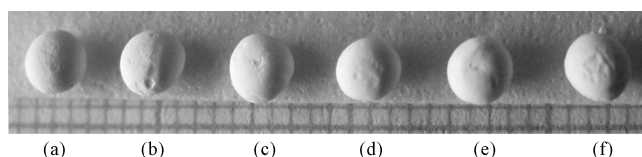

Fig. 5. Morphology of PAN-Zeolite 4A composite bead after irradiatioin.
(a) before irradiation, (b) 10^3 Rad, (c) 10^4 Rad, (d) 10^5 Rad, (e) 10^6 Rad, (f) 1.89×10^8 Rad
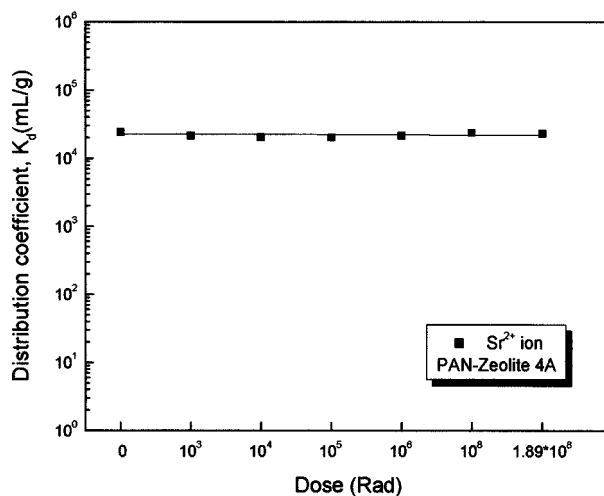

Fig. 6. Comparison of distribution coefficients of PAN-4A composite ion exchangers for Sr ion before and after irradiation.
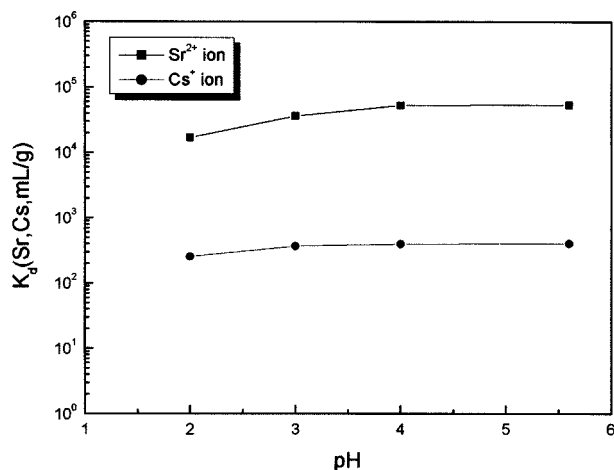
Fig. 7. Effect of pH on the distribution coefficients of PAN-4A composite ion exchanger for Sr and Cs ions.
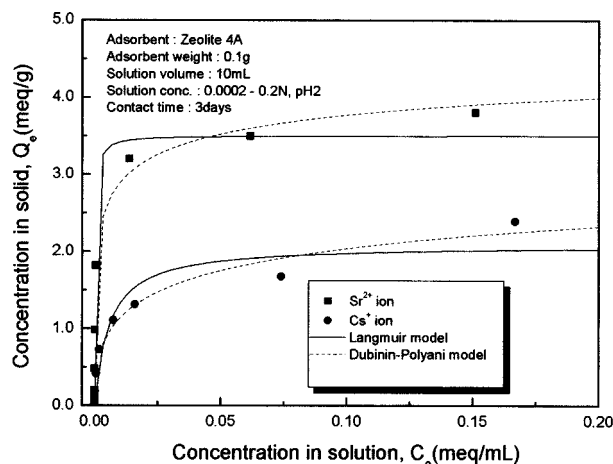

Fig. 8. Equilibrium isotherms modeled by Langmuir and Dubinin-Polanyi equation for Sr and Cs ion exchange with 4A powder.
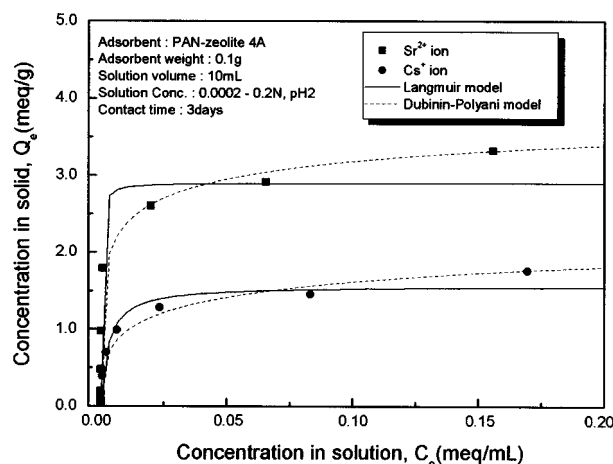

Fig. 9. Equilibrium isotherms modeled by Langmuir and Dubinin-Polanyi equation for Sr and Cs ion exchange with PAN-4A composite ion exchanger bead.

ligible and ion exchange property changes were not observed up to 1.89×10^8 rad irradiation as shown in Fig. 6.

3. Ion Exchange Behavior for Cs and Sr Ions

3-1. Distribution Coefficients

Fig. 7 shows the distribution coefficients depending on the solution pH for Sr and Cs ions. Both distribution coefficients of Sr ($K_{d,sr}$) and Cs ($K_{d,cs}$) are shown to be increased proportional to solution pH. However $K_{d,sr}$ (~2×10^4 at pH 2) is much higher than $K_{d,cs}$ (~200), which gives the separation coefficient, α (=$K_{d,sr}/K_{d,cs}$) of about 100. This result indicates that PAN-4A is much more selective for Sr ion than Cs and H ions.

3-2. Equilibrium Isotherms

Ion exchange isotherms for 4A/Cs-Sr and PAN-4A/Cs-Sr systems were obtained to evaluate the equilibrium parameters such as ion exchange capacity and equilibrium constant for kinetic calculations. The experimental data of zeolite 4A powder and PAN-4A composite ion exchanger for single component were obtained and modeled by Langmuir and Dubinin Polanyi equations [Moon et al., 2000a] given by

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

$$q = q_s \exp[-kR^2T^2\{\ln(c_s/c)\}^2] \tag{3}$$

where q (meq/g), q_s (meq/g), c (meq/mL) and c_s are the equilibrium and saturation concentrations in solid and liquid phases, respectively, and b, k are coefficients fitted to the experimental data. Values for c_s, the solubility of the salts, were obtained from the literature [Broul et al., 1981] and 11.4 meq/mL for $CsNO_3$ and 15.7 for $Sr(NO_3)_2$, respectively.

The experimental data and modeling results were represented in Figs. 8-9. The results indicate that the Dubinin-Polanyi model fit the data more correctly, although both models fit the data. The modeling results are summarized in Table 2. The ion exchange capacities of the PAN-4A composite ion exchanger obtained for strontium and cesium ions using Dubinin-Polanyi model were 3.92 meq/g and 2.47 meq/g, respectively. These values are almost 80% of those for 4A powder as in Table 2, which are obviously due to the dif-

Table 2. Equilibrium parameters for Sr and Cs ions with 4A powder and PAN-4A composite bead modeled by Dubinin-Polanyi equation

Coefficient (unit)	4A powder		PAN-4A composite bead	
	Sr	Cs	Sr	Cs
q_s (meq/g)	4.56	3.30	3.92	2.47
k	3.07×10^{-8}	6.15×10^{-8}	3.39×10^{-8}	5.39×10^{-8}
R^2	0.98	0.98	0.97	0.98

ference in inorganic contents between them. It also indicates, taking into account the 80% inorganic contents in the composite ion exchanger, that the PAN binder provides smooth pathway for ion transfer without blocking the adsorption sites.

CONCLUSION

PAN-4A composite ion exchanger bead containing about 80%

4A powder was prepared to evaluate ion exchange behavior for strontium and cesium ions in acid solution. The optimum viscosity for the spherical bead formation was found to be around 830-860 cP. The porosity of composite bead was about 74 percent, which is much higher comparing with the clay binder based zeolite pellets. The acid and radiation stability tests showed that PAN-4A was stable against acid solutions higher than pH 2 and radiation dose less than 1.89×10^8 rad, respectively.

Ion exchange tests showed that the PAN-4A was selective for Sr ion. The distribution coefficients of PAN-4A for Sr and Cs ions at pH 2 were 2×10^4 mL/g and 280 mL/g, respectively. The ion exchange capacities (q_s) of PAN-4A for Sr and Cs ions at pH 2, which are modeled by Dubinin-Polanyi equation, were 3.92 meq/g and 2.47 meq/g, respectively.

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REFERENCES

Broul, M., Nyvlt, J. and Sohnel, O., "Physical Sciences Data 6, Solubility in Inorganic Two-Component Systems," Elsevier Scientific Publishing Company, Amsterdam-Oxford-New York (1981).

Hwang, D. K., Jung, K. T., Shul, Y. G., Lee, W. S., Moon, J. K. and Oh, W. Z., "A Study on the Preparation of Partially Activated PAN Composite Fiber Containing Zeolite Particles," HWAHAK KONGHAK, 36, 627 (1998).

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

Lee, D. H. and Moon, H., "Adsorption Equilibrium of Heavy Metals on Natural Zeolites," Korean J. Chem. Eng., 18, 247 (2001).

Liang, T. and Hsu, C., "Sorption of Cesium and Strontium on Natural Mordenite," Radiochimica Acta, 61, 105 (1993).

Lopez, H., Olguin, M. T., Bosch, P. and Bulbulian, S., "Co-60 Sorption in Zeolite 4A and Effect of Radiation," J. Radioanl. Nucl. Chem., Letters, 200(1), 19 (1995).

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).

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).

Mariamichel, A. and Kishnamoorthy, S., "Synthesis and Characterization of New Composite Ion Exchangers," J. of Scientific & Industrial Research, 56, 680 (1997).

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

Mimura, H., Kobayashi, T. and Akiba, K., "Chromatographic Separation of Strontium and Cesium with Mixed Zeolite Column," J. of Nuclear Science and Technology, 32(1), 60 (1995).

Moon, J. K., Kim, H. T., Shul, Y. G., Lee, E. H. and Yoo, J. H., "Ion Exchange Behavior for Mixed Solution of Sr and Cs Ions with Potassium Titanate," HWAHAK KONGHAK, 38, 847 (2000a).

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

Moon, J. K. and Lee, H., "A Study on Ion Exchange Mechanisms of Zeolite NaA Crystallites," Korean J. Chem. Eng., 7, 61 (1990).

Pandit, B. and Chudasama, U., "A New Inorgano-organo Ion Exchanger; Chromotropic Acid Anchored onto Zirconium Molybdate," Colloids and Surfaces A: Physicochemical Engineering Aspects, 132, 145 (1998).

Perona, J. J., Coroneos, A. C., Kent, T. E. and Richardson, S. A., "A Simple Model for Strontium Breakthrough on Zeolite Columns," Separation Science and Technology, 30(7-9), 1259 (1995).

Rao, S. V. S., Lal, K. B., Narasimhan, S. V. and Amhed, J., "Copper Ferrocyanide-Polyurethane Foam as a Composite Ion Exchanger for Removal of Radioactive Cesium," J. of Radioanalytical and Nuclear Chemistry, 240(1), 269 (1999).

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).

Sebesta, F. and John, J., "An Overview of the Development, Testing, and Application of Composite Absorbers," LA-12875-MS (1995a).

Sebesta, F., John, J., Motl, A. and Watson, J., "Development of PAN-Based Adsorbers for Treating Waste Problems at U.S. DOE Facilities," In: SLATE, S.FEIZOLLAHI, F.-CREER, J., eds.: ICEM, '95 Proc. the Fifth International, Conference on Radioactive Waste Management and Environmental Remediation, Berlin, ASME, New York, 361 (1995b).

Simanova, S. A., Belyaev, K. A. N., Knyazkov, O. V. and Konovalov, L. V., "Complexation of Platinum in Sorption of Tetrachloroplatinate(II) Ion by Fibrous Sorbent Based on Polyacrylonitrile Modified with Thiosemicarbazide," Russian J. of Applied Chemistry, 72(8), 1344 (1999).

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

Xue, T. J., McKinney, A. and Wilkie, C. A., "The Thermal Degradation of Polyacrylonitrile," Polymer Degradation and Stability, 58, 193 (1997).