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Adsorption Behaviors of Cesium and Strontium in Multicomponent System

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Abstract

Breakthrough curves for separation of cesium and strontium binary components from aqueous solutions in fixed bed by chabazite and 13X were experimentally obtained and simulated the breakthrough curves for binary component adsorption. It is shown that agreements between model predictions and experimental data are relatively good although some deviations are observed. From engineering point of view, the simple model used here can be applied to simulate adsorption breakthrough curves satisfactorily.

I. Introduction

Separation of cesium and strontium from aqueous solutions has been the main subject in radioactive waste management and controlling cooling water contamination from defective spent fuels in storage pools.[1-3] Although ion exchange resins are useful for separating cesium and strontium from aqueous solutions, it has been necessary to use inorganic exchangers for effective cesium and strontium separation by adsorption process. The applications of adsorption processes are in many cases associated with adsorption in a fixed bed. Since unsteady-state conditions happen during the adsorption process, a mathematical model is, in general, required for design of a fixed bed column. The design of a fixed bed adsorber requires information on the dynamics of the system. The experimental and theoretical works are needed to understand the adsorption and desorption mechanisms and behaviors under various operating conditions. This paper is aimed to analyze the behavior of cesium and strontium component in binary systems and to simulate the breakthrough curves for binary

component adsorption from aqueous solutions in fixed bed.

II. Theoretical

The dynamic model for adsorption of Cs and Sr in fixed beds charged with zeolites was formulated according to the general assumptions. In reality, a bed is often packed with polydispersed particles; it has been shown, however, that axial dispersion in a packed bed with polydispersed particles can be modeled as a packed bed with monodispersed particles using an effective axial dispersion coefficient. Based on the equation in the absence of better approximation,[4] the estimated value of the axial dispersion coefficient (D_L) is 1.24 x 10^{-7} m^2/s for Cs-chabazite/13X system, and 8.99 x 10^{-8} m^2/s for Sr- chabazite/13X system in the present experimental conditions.

The governing equations resulting from the assumptions stated above can be written as follows.

The solute diffusion inside a spherical adsorbent particle

$$\frac{\partial q_i}{\partial t} = D_{si}\left(\frac{\partial^2 q_i}{\partial r^2} + \frac{2}{r}\frac{\partial q_i}{\partial r}\right) \tag{1}$$

with the initial and boundary conditions:

$$q_i(r, t=0) = 0 \tag{2}$$

$$\left.\frac{\partial q_i}{\partial r}\right|_{r=0} = 0 \tag{3}$$

$$D_{si}\rho_p \left.\frac{\partial q_i}{\partial r}\right|_{r=R} = k_f\left(C_i - C_{si}\right) \tag{4}$$

A combined pore and surface diffusion model for multicomponent systems has been formulated and solved numerically for various fixed-bed operations. The fundamental

breakthrough behavior for pore diffusion, surface diffusion, and parallel diffusion cases could be compared by solving the model equations.

The solute mass balance in the liquid phase

$$-D_L\frac{\partial^2 C_i}{\partial z^2}+\frac{\partial \upsilon C_i}{\partial z}+\frac{\partial C_i}{\partial t}+\frac{1-\varepsilon_b}{\varepsilon_b}\frac{\partial q_i}{\partial t}=0 \qquad (5)$$

The corresponding initial condition is given for $0 < z < L$, where L is the length of a fixed bed.

$$c(z,t=0)=0, \qquad (6)$$

This system can not be solved analytically. The set defines a linear boundary value problem involving a pair of coupled parabolic second-order partial differential equations.

Implementation of Numerical Techniques

The partial differential equations representing the dynamics of fixed-bed systems were first reduced to a set of ordinary differential equations by the method of lines. The resulting set of the ordinary differential equations were then integrated numerically in the time domain by LSODI employing Gear's stiff method with variable order and step size. In this study, By using orthogonal collocation method on FEM, the resulting equations constitute a set of algebraic, first order ordinary differential equations. Owing to the system stiffness, its integration is made by means of a stiff solver : LSODI of the International Mathematics and Science Library (IMSL).

III. Experimental

The adsorption column was made of a glass pipe of 0.02 *m* inside diameter. The length of the column was 0.3 *m*. Pretreated zeolites of 16/30 mesh granular types were packed into the column and sustained by glass beads. The flow rate was regulated by a precision micro pump. The solution was introduced downward into the column. To prevent channeling and to enhance distribution of the solution through the column, the two layers of small glass beads were packed in the top and bottom region of the column. The chabazite and 13X zeolites were

used to constitute the fixed beds, and all the packing procedures were conducted under water to avoid the generation of bubble in the fixed bed. Liquid samples were taken periodically by a fraction collector. After the start of experiments, samples were taken at the determined time intervals.

IV. Results and Discussion

The breakthrough curves for binary adsorption of Cs and Sr on chabazite and 13X at various input concentrations were experimentally obtained. All the experimental conditions in binary adsorption system are the same as that in single ion adsorption. Fig. 1 and 2 show experimental and predicted breakthrough curves for Cs and Sr with 5 mol/m^3 of input concentration on chabazite and 13X, respectively. The predicted breakthrough curves were obtained using the proposed model, without any adjustment of model parameters. The adsorption of Cs on 13X shows an overshoot in breakthrough curve and that of Sr on chabazite shows a slight overshoot of Sr and quite different shape of breakthrough curve compared with that of Cs on 13X. The adsorption curve from the column packed with 13X has a high overshoot comparing to the case of chabazite. This result shows the surface diffusion coefficient in 13X is larger than that in chabazite, while the equilibrium amounts adsorbed on two sorbents are comparable. For a low overshoot in the case of chabazite, a possible reason could be its low adsorption capacity for Sr. In order to determine the diffusion coefficient of binary component in terms of concentration explicitly, the experimental results are compared with the combined diffusion model predictions using Extended Langmuir equation. Thus, these evaluated values stand for the effective surface and pore diffusion coefficients in binary system by the curve fitting, respectively. These values of binary component are a order lower than that of single system and increasing with concentration in the range of $1.0 \sim 5.0 \times 10^{-12}$ m^2/s for $D_{S,eff}$ and $2.0 \sim 3.5 \times 10^{-10}$ m^2/s for $D_{p,eff}$.

The adsorption affinity of Cs and Sr in systems involving a single adsorable species was to be Cs>Sr on chabazite and Sr≥Cs on 13X. The adsorption amount of each ion on two adsorbents would be obtained from the integration of breakthrough curves. Compared with the results of breakthrough curves in adsorption system of single ion on chabazite and 13X, the

adsorption amount of Sr on 13X in binary adsorption system was slightly decreased, but in case of Cs on the same adsorbent the great decrease of adsorbed amount was found. This result means that adsorption affinity of each ion on adsorbent greatly affects the shape of breakthrough curve and adsorption amount in binary adsorption system.

V. Conclusions

The ultimate goal of this work is to establish the separation of cesium and strontium from spent fuel storage pool water. Our focus was the acquisition of fundamental information and the possible model for the adsorption process. It is shown that agreements between model predictions and experimental data are relatively good although some deviations are observed. From engineering point of view, the simple model used here can be applied to simulate adsorption breakthrough curves satisfactorily.

Reference

1. B. T. Kim et al., "Adsorption of Radionuclides from aqueous solution by inorganic adsorbents", Sep. Sci. and Tech., 30(16), pp. 3165-3182 (1995)
2. H. K. Lee et al., "The Charateristic Analysis of ion exchange on inorganic ion exchangers," Proceedings of the Korean Nuclear Society Autumn meeting, Seoul, Korea, October (1993).
3. M. W. Wilding and D. W. Rhodes, ICP-1048, "Removal of cesium and strontium from fuel storage basin water," US AEC (1974).
4. E. J. Wilson and C. J. Geankoplis, Ind. Eng. Chem. Fund., 5, 9 (1966)

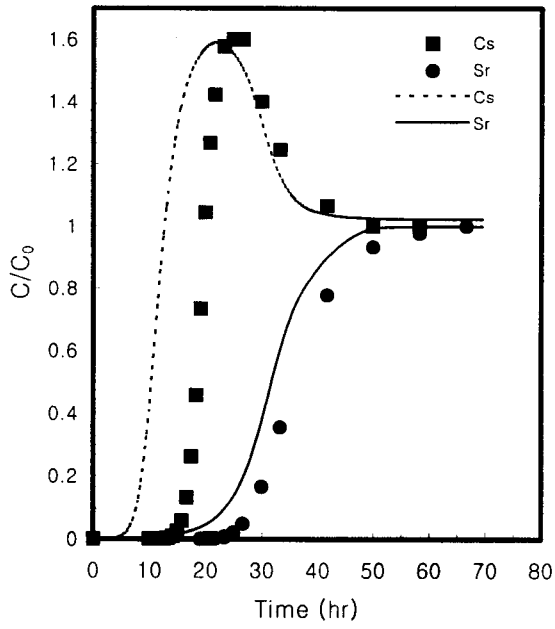

Figure 1. Breakthrough curves of binary Cs-Sr adsorption on 13X.

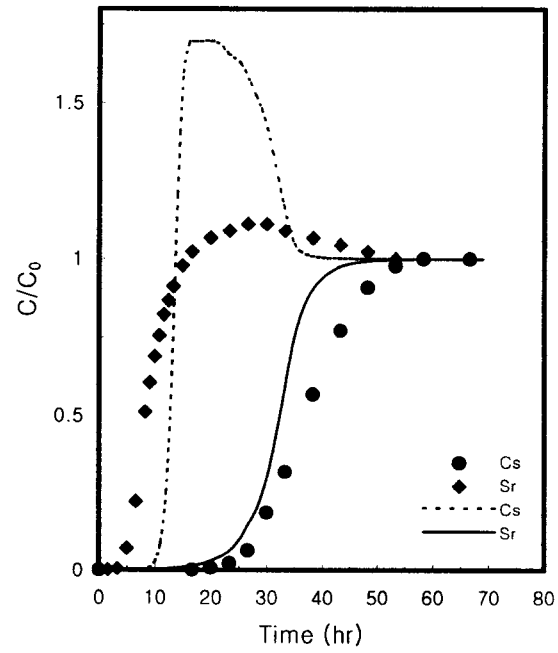

Figure 2. Breakthrough curves of binary Cs-Sr adsorption on chabazite.