Cesium Ion Exchange Kinetics with PAN-KCoFC Composite Ion Exchanger

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1. Introduction

PAN based inorganic-organic composite ion exchanger beads are recently reviewed as promising one for removal of radionuclides due to their characterizing advantages, no dissolution in liquid solution and no pressure drop problem in column operation, over the existing inorganic ion exchangers such as zeolites [1] . Also since the PAN acts as an inert binder all radionuclides are bound to inorganic materials. Therefore no radionuclides release occurs even when they are decomposed underground. In this study, ion exchange kinetics for cesium ion was performed using a PAN-KCoFC composite ion exchanger in a batch reactor together with column system.

2. Results and Discussion

2-1. Uptake curves and Modeling

The effect of stirring rate on the uptake rate of PAN-KCoFC composite ion exchanger for Cs ion showed that the stirring speed did not affect the uptake rate in case of more than 700 rpm, which means no film mass transfer resistance for more than 700 rpm. Uptake curves were obtained for multicomponent systems as well as for binary systems. Uptake curves for binary systems with the 1.47mm radius PAN-KCoFC showed that the loading of cesium is much higher than the other cations as expected in the equilibrium isotherms obtained in our previous study. The uptake behaviors for the ternary system shows much more favorable uptake for cesium over strontium ion. Separation of Cs and Sr is essential since they are importantly reused for irradiation sources rather than disposal. In the case of four component solution, uptake behaviors are similar to those for 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 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. In the batch system, 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. Orthogonal collocation method was used to convert the partial differential equations into the ordinary differential equations (ODEs). The resulting ODEs were solved by utilizing the IMSL/Math subroutine IVPAG, which is based on the Gear's stiff integration algorithm. The examples of modeling results for the multi-component systems are shown in Fig. 1
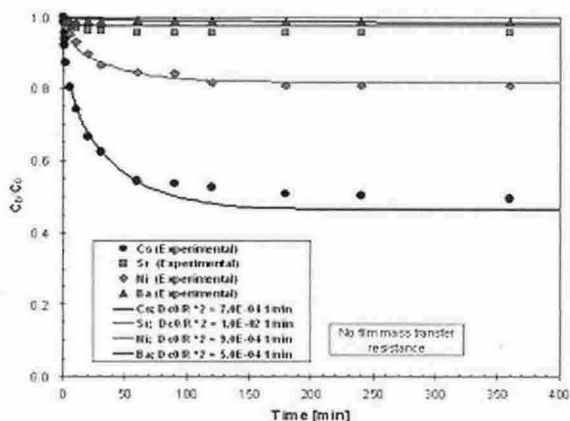

Fig.1. Uptake Curves and Modeling Results for Multi-Component Ion Exchange with PAN-KCoFC

In the case of Cs and Ni ion exchange system, a homogeneous model predicts the experimental curves quite accurately both in the binary and multi-component system. 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 [2] which used two phase homogeneous model for a silicotitanate ion exchanger, and comparable with other result [3] for zeolite particles which have obviously 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 to be so meaningful. The solid phase effective diffusivities are in the order of 10^{-5} cm^2/min for multi-component systems. 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 on 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 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.

2-2. Breakthrough Curves and Modeling

Breakthrough curves were obtained for the multi-component systems as well as for the binary systems and the results for multicomponent system are shown in Fig.2. 13.2 g of PAN-KCoFC beads in ∅ 20 x 200 L column was used for breakthrough curves and the flow rate was adjusted to 4.8mL/min, which was proven to be the best condition through the pretests.
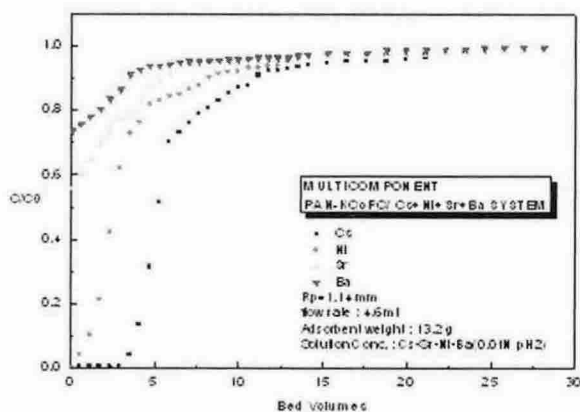

Fig.2. Breakthrough curves for Multicomponent Ion Exchange with PAN-KCoFC Bed

It shows that PAN-KCoFC bed is much more selective for cesium over the Sr, Ni and Ba ions, meaning effective separation of cesium from the other ions. The breakthrough volume of cesium ion for the bed, if we consider 95% separation, was about 4 bed volume. The breakthrough curves were modeled assuming parallel diffusion in solid phase and significant film mass transfer resistances. The numerical analysis procedures are just the same as the batch systems. Modeling result for cesium ion in multicomponent system is shown in Fig.3. It shows the model predicts the experimental data well although there are discrepancies near the plateau. Modeling for the breakthrough curves of other ions, even though they

are not shown here, could predict the experimental data. The obtained diffusion time constant for cesium ion is in the order of 10^{-2} min^{-1} and the film mass transfer time constant is about 10 min^{-1}.
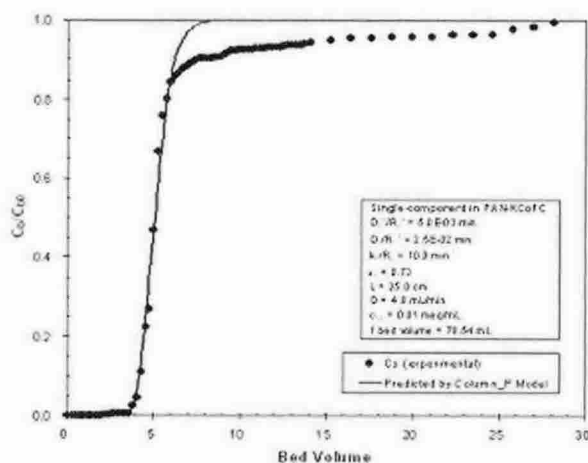

Fig. 3. Modeling Result for Cesium Ion Breakthrough Curves with PAN-KCoFC Composite Ion Exchanger bed.

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