Dynamic Fixedbed Adsorption of Radionuclides from Aqueous Solutions by Inorganic Adsorbents

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Abstract

Radionuclides such as Cs and Sr were removed from dilute aqueous solutions by means of inorganic adsorbents, 13X and chabazite. The physical adsorption obeyed the DA equation and non-equilibrium dynamic adsorption model, which describes surface diffusion mechanism with the DA equation, simulated the adsorption behavior of cesium and strontium on zeolite in fixed bed adsorbers. The dynamic model simulated the adsorption behavior of cesium and strontium.

1. Introduction

The informations for the equilibrium isotherm and mass transfer in zeolite adsorbents have been studied the removal of radionuclides from aqueous solutions in controlling cooling water contamination from defective spent fuels in storage pools[1-5]. However, it is still not easy to describe the performance of adsorption process quantitatively. Quantitative analysis of adsorption in general requires accurate information on adsorption equilibrium and mass transport of adsorbates. The selection of a proper sorbent for a given separation is a complex problem. For the proper design of such processes knowledge for the breakthrough characteristics of the column is required. A mathematical model is needed to obtain design and optimal operating conditions. The development of an adsorption model requires information on adsorption equilibria in addition to interparticle and intraparticle transport phenomena. The success of modelling in general depends on how to incorporate the adsorption equilibrium relationship and the transport mechanism with mass balance equations[6].

This study addresses a simple method for prediction the equations for simulating fixed-bed performances by using Dubinin-Astahkov(DA) equation[7]. This simplification makes it possible to use a nonequilibrium dynamic model, which was developed for single component adsorptions. The major emphasis of this study is placed on the acquisition of valuable information on adsorption operation in order to analyze and to simulate the adsorption of zeolite filter in storage canisters for controlling cooling water contamination from defected spent fuels.

2. Dynamic Adsorption in a Fixed Bed Adsorber

Among the various isotherm equations for single-species adsorptions, the DA equation was selected for the radionuclides-zeolites system in order to develop the dynamic model. The DA equation is expressed as follow[8] :

$$q = q_m \exp\left\{-\left(\frac{kT}{E} \ln \frac{c_s}{c}\right)^n\right\} \tag{1}$$

It is possible to link this equation into a fixedbed adsorption model, which allows a formal description of its basis and its parameters.

The following unsteady state mass balance equation can be written for the external bulk phase:

$$-D_L \frac{\partial^2 c}{\partial z^2} + v \frac{\partial c}{\partial z} + \frac{\partial c}{\partial t} + \frac{\rho_b}{\varepsilon} \frac{\partial \overline{q}}{\partial t} = 0 \tag{2}$$

with the following initial and boundary condition :

$$c(z,0) = \overline{q}(z,0) = 0 \tag{3}$$

$$D_L \frac{\partial c}{\partial z} \Big|_{z=0} = -v \, (c \mid_{z=0-} - c \mid_{z=0+}) \tag{4}$$

$$D_L \frac{\partial c}{\partial z} \Big|_{z=L} = 0 \tag{5}$$

The average accumulation of adsorbate in the solid phase, can be calculated in terms of the adsorbate flux at the surface of the adsorbent particle.

$$\frac{\partial \overline{q}}{\partial t} = D_S A \frac{\partial q}{\partial r} \Big|_{r=R_p} \tag{6}$$

3. Experimental

The inorganic adsorbents used in this study were 13X and chabazite (AW-500) supplied by

Aldrich Co. For the column experiment, the pellets of adsorbents were crushed and sieved to give the fraction of a 16~30 mesh particle size. All adsorbent particles were used after washing with the deionized water and drying at 110℃. Stock solutions of each ion were made up by dissolving the reagent-grade CsCl and SrCl$_2$ supplied by Sigma Chemical Co. into the distilled water. The concentration range of each ion was 5~10 M. The concentrations of ions were measured by an atomic absorption spectroscopy.

The column experiments were carried out in a typical fixedbed system. The solution was supplied with a micro metering pump. Glass beads were used to prevent the channeling effects of the feed solutions. Distillated water was supplied into the column at the constant flow rate as the solution for about 5 hr prior to the start of experiments in order to fill the zeolite bed with water and to prevent sudden disturbance of the experimental system at the beginning of experiments. Pretreated zeolites were packed in the column and confined by fine stainless steel screens. A water bath was installed and the column was also jacketed, and water was circulated through this jacket to maintain the temperature of the adsorber and to maintain the column at constant temperature, 30℃. Liquid samples were taken from small sampling tube periodically by fraction collector every 10 min. The properties of operating system are listed in Table 1.

Table 1. Experimental Conditions for Fixedbed Adsorptions in This Study

Variables	Experimental conditions
-Bed length	0.047m
-Bed diameter	0.02m
-Flow rate	2 ml/min
-Voidage	0.49
-Packing density	690 g/cc
-Bed Temperature	30℃
-Concentration of solution	0.01 ~ 0.005M

4. Results and Discussion

Since intraparticle diffusion is usually the rate-controlling step in general adsorption processes, the determination of diffusion coefficients is an essential step. The values of Ds are approximately 3.5×10^{11} m^2/s for Cs-13X system, 3.2×10^{12} m^2/s for Sr-13X system, 5.1×10^{12} m^2/s for Cs-Chabazite system, and 1.0×10^{11} m^2/s for Sr-Chabazite system from the

previous paper[1].

When a fluid flows through a packed bed there is a tendency for axial mixing to occur. Any such mixing is undesirable because it reduces the efficiency of separation. Therefore, the minimization of axial dispersion is a major design objective, particularly when the separation factor is small. In this model the effects of all mechanisms which contribute to axial mixing are lumped together into a single effective axial dispersion coefficient. For adsorption systems with highly favorable isotherms, Wakao's correlation can be used[9].

In Wakao's equation, the molecular diffusivity, Dm, is estimated to be 2.09×10^{-9} m^2/s for cesium ion and 4.03×10^{-10} m^2/s for strontium ion from Nernst-Einstein relation[10-11]. The axial dispersion coefficient is estimated to be 1.34×10^{-7} m^2/s for Cs-Chabazite and 13X systems, 1.0×10^{-7} m^2/s for Sr-Chabazite and 13X systems.

For liquids in the low Reynold's number region ($0.0015 < Re < 55$), the film coefficient correlation of Wilson and Geankoplis[12] can be used. The film mass-transfer coefficient estimated from that equation are listed in the Table 2. Based on the estimated values of the axial dispersion coefficients and the diffusion coefficients obtained from the correlations, some adjustment of the film mass transfer coefficinents was made in order to fit between the experimental results and those of simulations as shown in Table 2.

Table 2. Comparison of parameters used in simulation with those obtained from correlations.

Parameters Systems	K_f		D_s		D_L	
	Correlation	Simualtion	Correlation	Simulation	Correlation	Simulation
Cs-Chabazite	1.14×10^{-6}	3.5×10^{-6}	5.1×10^{-12}	5.1×10^{-12}	1.34×10^{-7}	1.34×10^{-7}
Cs-13X	1.12×10^{-5}	1.0×10^{-5}	3.5×10^{-11}	3.5×10^{-11}	1.34×10^{-7}	1.34×10^{-7}
Sr-Chabazite	3.80×10^{-6}	3.5×10^{-6}	1.0×10^{-11}	1.0×10^{-11}	1.0×10^{-7}	1.0×10^{-7}
Sr-13X	3.72×10^{-6}	4.0×10^{-6}	3.2×10^{-12}	3.2×10^{-12}	1.0×10^{-7}	1.0×10^{-7}

The observed and predicted breakthrough curves in various adsorption systems are shown in Figs. 1~2. From the results, it has been confirmed that the dynamic model is useful in simulating the adsorption behavior.

5. Conclusions

From simulation of the dynamic model using the DA equation developed for a single

component system, it was confirmed that the intraparticle transport was a rate-controlling step and the surface diffusion mechanism was dominant. It shows that the model used here can be applied in simulating the adsorption of zeolite filter in a defected spent fuel storage canister for controlling the cooling water contamination.

Additional studies to examine the adsorption behavior of radionuclides on zeolites in themulti-component adsorption system are recommended.
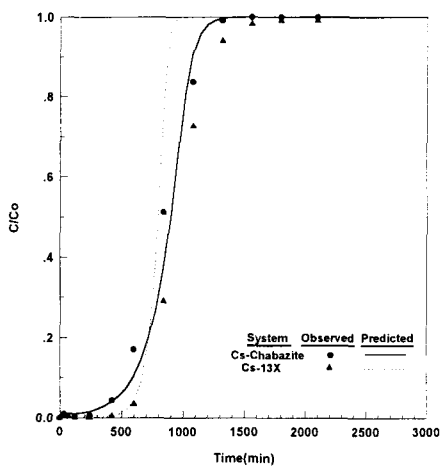

Fig. 1. Predicted and observed breakthrough curves of Cs ion adsorption on the Chabazite and 13X at 0.01M of feed concentration.
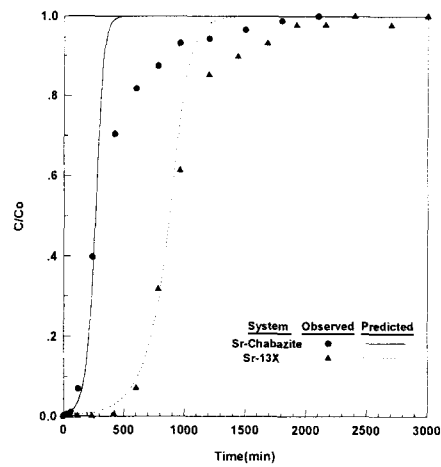
Fig. 2. Predicted and observed breakthrough curves of Sr ion adsorption on the Chabazite and 13X at 0.01 M of feed concentration.

Nomenclature

A	:	surface area of sorbent particles, m^2
C	:	concentration in the liquid phase, mol/m^3
Cs	:	saturated concentration in the liquid phase, mol/m^3
Ds	:	effective surface diffusion coefficient, m^2/sec
E	:	characteristic adsorption energy, J/mol
kf	:	film mass transfer coefficient, m/sec
k	:	Boltzman constant, $J/moloK$
n	:	exponent in Eq. (1)
q	:	amount adsorbed, mol/kg
qm	:	amount adsorbed for monolayer formation, mol/kg

Rp   : mean radius of particle, m
r   : radial distance, m
T   : temperature, $^{\circ}K$
t   : time, s or min
v   : volume of solution, m^3
ε : void fraction

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