Mass-Transfer Mechanisms for Zeolite Ion Exchange in Wastewater Treatment

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In spite of the increasing commercial use of zeolites for binary and multicomponent ion exchange, understanding of the basic mass-transfer processes associated with multicomponent zeolite systems is quite limited. This study evaluates Na-Ca-Mg-Cs-Sr ion exchange from an aqueous solution using a chabazite zeolite. Mass-transfer coefficients are determined from experimental batch-reactor data for binary and multicomponent systems. The experimental data indicate that diffusion through the microporous zeolite crystals is the primary diffusional resistance. Macropore diffusion also significantly contributes to the mass-transfer resistance. Various mass-transfer models are compared with the experimental data to determine values for intraparticle diffusivities. Effective diffusivities obtained accurately predict experimental data using a variety of models. Only the model accounting for micropore and macropore diffusion occurring in series accurately predict multicomponent data using diffusivities from the binary system. Liquid and surface diffusion both contribute to macropore diffusion. Surface and micropore diffusivities are concentration-dependent for the system of interest.

Introduction

Fixed-bed separation processes are utilized widely in chemical and petrochemical industries and are becoming increasingly attractive in environmental control engineering. For an optimal design of an industrial sorption or ion-exchange process where disposal of secondary waste is expensive, it is important to have accurate modeling and simulation of the dynamic behavior of fixed-bed systems to optimize column design and operation. Considerable effort was made in the 1980s in modeling multicomponent liquid separations. The mathematics required to model adsorption and ion exchange are essentially the same if the ion-exchange process is not rate limiting. Several models have now been developed to predict results for a variety of adsorption and ion-exchange systems (Wankat, 1986; Weber and Smith, 1987; Gierke, 1991). Unfortunately, a general solution for multicomponent ion exchange or adsorption, which includes hydrodynamic dispersion, mass-transfer effects, interference effects, and nonlinear complex isotherms, is still not available (Yu and Wang, 1989).

The mathematical models developed to date have used different degrees of complexity to describe multicomponent ion-exchange processes. Basically, they can be classified into the following three major categories: staged equilibrium models, interference theory, and rate equation models. The rate equation models are the most realistic and will be discussed in this report. These consist of mass balances on each species in the bulk fluid and particle phases. They generally consider external (fluid) mass transfer, intraparticle diffusion, and equilibrium equations. Due to the complexity and nonlinearity of the models, analytical solutions are impossible. Numerical solutions of stiff partial differential equations are usually required.

The ion-exchange/adsorption processes for zeolite molecular sieves can be even more complicated than for organic ion-exchange resins. The zeolite sorbent consists of small crystals, of sizes ranging approximately from 1 to 10 μm, which are pelletized with a small amount of binder. Thus, two distinct types of pore structures exist for zeolites: micropores in the crystals and macropores in the binder. The kinetics in these heterogeneous particles are governed by three distinct diffusional resistances (shown conceptually in Figure 1): film diffusion from the bulk liquid to the pellet surface, diffusion through the macropores of the pellet, and diffusion within the

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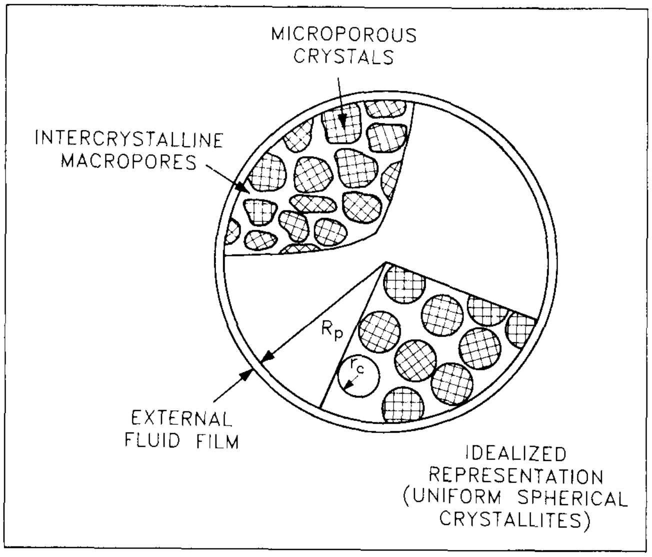

Figure 1. Composite pellet showing the three principal resistances to mass transfer (Ruthven, 1984).

micropores of the zeolite crystals. The relative importance of the resistances depends on the materials involved and on the specific operating conditions (Ruthven and Loughlin, 1972). Zeolite ion exchange can also be complicated by ion-sieve, steric, and electrostatic forces within the zeolite pores (Barrer and Klinowski, 1972; Franklin et al., 1986).

Zeolites have been studied since the 1950s for separations in gases and liquids. Several versions of the rate equation model have been used to evaluate the available zeolite data to obtain values for diffusion coefficients. These include the homogeneous, heterogeneous, pore, surface, and combined diffusion models.

The homogeneous diffusion model (Rosen, 1952; Prazniak and Byers, 1987; Garg and Ruthven, 1974; Liapis and Crosser, 1982; Ruthven and Doetsch, 1979; Hsu and Hayes, 1981; Weber and Smith, 1987; Dominguez et al., 1991) assumes that the particle is a homogeneous solid through which diffusion can be modeled by a solid-phase diffusivity. The heterogeneous diffusion model assumes that diffusion in the particle occurs by macropore diffusion through the voids of the porous binder and micropore diffusion in the zeolite crystals. The micropore diffusion mechanism is assumed to be solid diffusion only because molecular species in zeolite crystals should never be free from force fields associated with the pore walls. For liquid systems, macropore diffusion can be due to molecular diffusion and/or surface diffusion. The frequently used pore diffusion, surface diffusion, and combined diffusion models are special cases of the heterogeneous diffusion model. They assume that intraparticle mass-transfer resistance is due to macropore diffusion only.

Models for the heterogeneous diffusion model have been developed that assume macropore and micropore diffusion occur in series (Weber and Smith, 1987; Smith and Weber, 1988; Sun and Meunier, 1991; Kapoor and Yang, 1988) or in parallel (Komiyama and Smith, 1974; Nagel et al., 1987). Several researchers (Do and Rice, 1986; Akulov and Ustinov, 1981; Liaw et al., 1979; Doong and Yang, 1987; Cen and Yang, 1986; Kapoor and Yang, 1988) have simplified the mathematics for adsorption processes by assuming that the intraparticle concentration profiles have parabolic shapes.

Multicomponent models are usually extended from those applied to binary systems, and the competitive effects are most often accounted for through the multicomponent equilibrium equation. Such work has been done using the film-homogeneous diffusion (Crittenden and Weber, 1978; Fritz et al., 1981; Merk et al., 1980; Thacker et al., 1981, 1983; Takeuchi and Suzuki, 1983; Mathews and Su, 1983; Larson and Tien, 1984; Liang and Weber, 1985; Carter and Husain, 1974); film-pore diffusion (Liapis and Rippin, 1977, 1978; Fritz et al., 1981; Merk et al., 1980; Liapis and Litchfield, 1981; Larson and Tien, 1984; Crittenden et al., 1986); and film-heterogeneous diffusion models with macropore and micropore diffusion (Fritz et al., 1981; Merk et al., 1980; Weber and Smith, 1987; Smith and Weber, 1988; Sun and Meunier, 1991; Kapoor and Yang, 1988; Nagel et al., 1987). Differences between the kinetic behavior in binary and multicomponent systems have also been interpreted as being due to solute interactions during diffusion (Mathews, 1975; Liang and Weber, 1985; Marutovsky and Bulow, 1987; Fritz et al., 1981; Merk et al., 1980; Moon and Lee, 1986; Barba et al., 1983; Liapis and Litchfield, 1981). In most cases, binary diffusivities could not be used to directly predict multicomponent data.

The picture presented in the literature for diffusion in zeolites is confusing, conflicting, and/or inconsistent with theory. For example, diffusivities obtained from the pore diffusion model accurately predict experimental uptake data (Liapis and Rippin, 1977; Fritz et al., 1981; Teo and Ruthven, 1986). However, the values were often higher than molecular diffusivities, a finding which is physically impossible (Fritz, 1978; Furusawa and Smith, 1973, 1974; Spahn and Schlunder, 1975; Raghavan and Ruthven, 1984; Carter and Husain, 1974; Nagel et al., 1987).

More fundamental studies are needed to aid in the development of models for zeolite ion-exchange systems. This article summarizes the results of an investigation directed at modeling multicomponent ion exchange in chabazite zeolites for application in treating slightly contaminated groundwater. The prime objective of this study is to identify diffusion mechanisms and determine their relative importance for multicomponent diffusion in chabazite. The impact of multicomponent solute interactions is also investigated.

The work described here is concerned with the use of batch reactor experiments to characterize binary and multicomponent ion exchange. Batch studies are convenient for experimental determination of diffusion coefficients, and they simplify the mathematical model because the film mass-transfer resistance is insignificant at high impeller speeds. Several rigorous mathematical models are presented which utilize different mechanisms for diffusion within the particle. Intraparticle diffusivities of the components are estimated by matching the predictions of the model to the results of the batch experiments.

Mathematical Model

Ion exchange is considered for a finite batch reactor with liquid containing a number of dissolved ionic components diffusing into particles which are suspended in the liquid by agitation so that the liquid has free access to them. The liquid concentration is assumed to be uniform throughout the reactor. The zeolite is modeled as an assembly of spherical macroporous particles comprised of small spherical microporous particles of uniform size.

All the mathematical models assume that the ion-exchange rate is much faster than the rate of diffusion. Therefore, the reaction rate does not significantly affect the kinetics of the system. The system is isothermal. Local equilibrium is assumed to exist between the liquid and solid at the particle surface and at the pore surfaces in the macropores.

Both homogeneous and heterogeneous mass-transfer models are evaluated in this study. Heterogeneous models are developed for intraparticle diffusion (macropore and micropore diffusion) occurring in parallel and series. The concentration dependence of diffusivities is also examined.

Homogeneous diffusion model

The homogeneous diffusion model assumes that the particle is a homogeneous solid through which diffusion of each individual species can be modeled by a single solid-phase diffusivity. Diffusion in the zeolite crystal is assumed to follow Fick's law. The differential mass balance for each species i in the crystal gives:

$$\frac{\partial Q_i}{\partial t}=\frac{1}{r_c^2\bar{r}^2}\frac{\partial}{\partial \bar{r}}\left(\bar{r}^2 D_{ci}\frac{\partial Q_i}{\partial \bar{r}}\right). \tag{1}$$

The overall mass balance leads to:

$$\frac{\partial C_{di}}{\partial t}=\frac{-3\rho(1-\epsilon)q_{0i}}{\epsilon c_{0i}}\frac{\partial}{\partial t}\int_0^1 Q_i\bar{r}^2 d\bar{r}. \tag{2}$$

One boundary condition is set because of the symmetry of the system:

$$\frac{\partial Q_i}{\partial \bar{r}}=0 \quad \text{at} \quad \bar{r}=0. \tag{3}$$

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

$$\frac{\partial}{\partial t}\int_0^1 Q_i\bar{r}^2 d\bar{r}=\frac{k_{fi}c_{0i}}{\rho r_c q_{0i}}(C_{di}-C_{si}). \tag{4}$$

The initial conditions are:

$$C_{di}=1, \quad C_{si}=Q_i=0 \quad \text{at} \quad t=0. \tag{5}$$

Also, C_{si} is in equilibrium with the solid at the particle surface (Q_i at $\bar{r}=1$), and q_{0i} is in equilibrium with c_{0i}. If film mass transfer is insignificant, C_{si} becomes equal to C_{di}.

Heterogeneous diffusion model

This model is the same as the homogeneous model except the rate of diffusion in the solid phase is assumed to be governed by both micropore and macropore diffusion. Micropore diffusion occurs in the zeolite crystals, and macropore diffusion occurs in the pores of the binder. The micropore diffusivity is assumed to be the same as the solid-phase diffusivity obtained in the homogeneous diffusion model for Ionsiv IE-90. The first model is developed assuming these processes occur in parallel. A second model is developed assuming they occur in series.

Parallel micropore and macropore diffusion

The differential mass balance in the solid phase gives:

$$\xi_i\frac{\partial C_{pi}}{\partial t}+\frac{\partial Q_i}{\partial t}=\frac{1}{R_p^2\bar{R}^2}\frac{\partial}{\partial \bar{R}}\left[\bar{R}^2\left(D_{ci}\frac{\partial Q_i}{\partial \bar{R}}+\xi_i D_{pi}\frac{\partial C_{pi}}{\partial \bar{R}}\right)\right] \tag{6}$$

where

$$\xi_i=\frac{\epsilon_p c_{0i}}{(1-\epsilon_p)\rho q_{0i}}. \tag{7}$$

The overall mass balance leads to

$$\frac{\partial C_{di}}{\partial t}=-(1-\epsilon_p)D_{gi}\frac{\partial}{\partial t}\int_0^1 (Q_i+\xi_i C_{pi})\bar{R}^2 d\bar{R}. \tag{8}$$

The boundary condition at $\bar{R}=0$ is:

$$\frac{\partial C_{pi}}{\partial \bar{R}}=\frac{\partial Q_i}{\partial \bar{R}}=0 \tag{9}$$

because of symmetry. The material balance at the particle surface leads to

$$\frac{\partial}{\partial t}\int_0^1 (Q_i+\xi_i C_{pi})\bar{R}^2 d\bar{R}=\frac{k_{gi}}{D_{gi}(1-\epsilon_p)}(C_{di}-C_{si}) \quad \text{at} \quad \bar{R}=1. \tag{10}$$

The initial conditions are:

$$C_{di}=1, \quad C_{si}=C_{pi}=Q_i=0 \quad \text{at} \quad t=0. \tag{11}$$

The liquid concentrations, C_{si} and C_{pi}, are in equilibrium with the solid at the particle surface and the surfaces of the pores, respectively. Also, q_{0i} is in equilibrium with c_{0i}. If film mass transfer is insignificant, C_{si} becomes equal to C_{di}. Under these conditions, Eq. 10 reduces to

$$\frac{\partial}{\partial t}\int_0^1\left(\frac{Q_i}{\xi_i}+C_{pi}\right)\bar{R}^2 d\bar{R}=-\frac{\epsilon}{3\epsilon_p(1-\epsilon)}\frac{\partial C_{di}}{\partial t} \tag{12}$$

where Q_i at $\bar{R}=1$ is in equilibrium with C_{di}.

Series micropore and macropore diffusion

Mass balances performed on each solute in the liquid phase lead to the following relationship:

$$\frac{\partial C_{di}}{\partial t}+\frac{\rho(1-\epsilon)q_{0i}}{\epsilon c_{0i}}\frac{\partial \bar{\bar{Q}}_i}{\partial t}=0 \tag{13}$$

where

$$\frac{\partial \bar{\bar{Q}}_i}{\partial t} = 3(1-\epsilon_p)\int_0^1 \bar{R}^2 \frac{\partial \bar{Q}_i}{\partial t} d\bar{R} + \frac{3\epsilon_p c_{0i}}{\rho q_{0i}} \int_0^1 \bar{R}^2 \frac{\partial C_{pi}}{\partial t} d\bar{R}. \quad (14)$$

The equations that represent mass transfer within the solid are:

$$\frac{\partial \bar{\bar{Q}}_i}{\partial t} = \frac{3c_{0i}k_{fi}}{\rho R_p q_{0i}} (C_{di} - C_{pi}) \quad (15)$$

and

$$\frac{1}{R_p^2 \bar{R}^2} \frac{\partial}{\partial \bar{R}} \left(\bar{R}^2 D_{pi} \frac{\partial C_{pi}}{\partial \bar{R}} \right) = \frac{\partial C_{pi}}{\partial t} + \frac{\rho(1-\epsilon_p) q_{0i}}{\epsilon_p c_{0i}} \frac{\partial \bar{Q}_i}{\partial t} \quad (16)$$

where

$$\frac{\partial \bar{Q}_i}{\partial t} = 3 \int_0^1 \frac{\partial Q_i}{\partial t} \bar{r}^2 d\bar{r} \quad (17)$$

and

$$\frac{\partial Q_i}{\partial t} = \frac{1}{r_c^2 \bar{r}^2} \frac{\partial}{\partial \bar{r}} \left(\bar{r}^2 D_{ci} \frac{\partial Q_i}{\partial \bar{r}} \right). \quad (18)$$

Because of symmetry:

$$\frac{\partial C_{pi}}{\partial \bar{R}} = \frac{\partial \bar{Q}_i}{\partial \bar{R}} = \frac{\partial Q_i}{\partial \bar{r}} = 0 \quad \text{at} \quad \bar{R}=0, \quad \bar{r}=0. \quad (19)$$

The initial conditions are:

$$C_{di} = 1, \quad C_{pi} = Q_i = 0 \quad \text{at} \quad t = 0. \quad (20)$$

If film mass transfer is insignificant, Eq. 15 is replaced with $C_{di} = C_{pi}$ at $\bar{R} = 1$.

Parabolic profile model

The assumption that macropore and micropore diffusion occurs in series results in coupled partial differential equations involving time and spatial variables. Researchers (Do and Rice, 1986; Akulov and Ustinov, 1981; Liaw et al., 1979; Doong and Yang, 1987; Cen and Yang, 1986; Kapoor and Yang, 1988) often simplify the mathematics by assuming that the concentration profiles in the zeolite crystals have parabolic shapes. This type of profile has been shown to be valid for binary adsorption, but may not be valid for multicomponent ion exchange where ion competition occurs. If the zeolite crystal has a parabolic profile:

$$q_i = a_{0i} + a_{2i} r^2 \quad \text{where} \quad a_{2i} = \frac{5}{2r_c^2} (q_i|_{r_c} - \bar{q}_i) \quad (21)$$

and a_{0i} is a constant. Substitution of Eq. 21 into Eqs. 17 and 18 results in

$$\frac{\partial \bar{Q}_i}{\partial t} = \frac{15 D_{ci}}{r_c^2} (Q_i|_{\bar{r}=1} - \bar{Q}_i). \quad (22)$$

Macropore diffusivity equations

The macropore diffusivity given in the above equations is an effective diffusivity which accounts for up to four transport mechanisms (Ruthven, 1984): molecular diffusion, Knudsen diffusion, Poiseuille flow, and surface diffusion. For liquid systems, diffusion due to molecular and/or surface diffusion might be expected. If the transport within the macropores occurs only by molecular diffusion, the pore diffusivity is given by:

$$D_{pi} = \frac{D_{li}}{\tau} \quad (23)$$

where the tortuosity factor, τ, is introduced to allow for the fact that the diffusion path through zeolite pores is greater than that of straight round tubes. Values of τ usually range from 2 to 6 for zeolites (Ruthven, 1984). Values less than 2 indicate that surface diffusion of intracrystalline diffusion is contributing to mass transfer. If surface diffusion significantly contributes to macropore diffusion, molecular and surface diffusion will occur in parallel. The effective macropore diffusivity will then be:

$$D_{pi} = \frac{D_{li}}{\tau} + D_{si}. \quad (24)$$

The surface diffusivity is generally found to be concentration-dependent (Ruthven, 1984) and is assumed to follow Darken's equation.

Concentration-dependent micropore and surface diffusivity equations

If the micropore or surface diffusivity is concentration-dependent, it follows Darken's law:

$$D_i = D_{0i} \frac{d \ln C_{si}}{d \ln Q_i} \quad (25)$$

where D_{0i} is independent of concentration. Equilibrium equations are needed to define the relationship between C_{si} and Q_i in Darken's equation. The Langmuir isotherm was used to represent the equilibrium relationship for binary systems:

$$q_i = \frac{q_{si} b_i c_i}{1 + b_i c_i} = \frac{a_i c_i}{1 + b_i c_i}. \quad (26)$$

The Dubinin-Polyani potential theory, a theory for single-component gas adsorption, was modified by Bering et al. (1963) to apply to binary mixtures. A modified version of this equation (Robinson et al., 1991) for multicomponent liquid systems was used:

$$q_i = \exp\{ b_{0i} + b_{1i} \cdot \ln(c_i) + b_{2i} \cdot [\ln(c_i)]^2 \}. \quad (27)$$

When the Langmuir isotherm equation is substituted into Darken's equation, one obtains:

$$D_i = \frac{D_{0i}}{\left(1 - \frac{b_i Q_i q_{0i}}{a_i}\right)}. \tag{28}$$

For the modified Dubinin-Polyani isotherm:

$$D_i = \frac{D_{0i}}{\sqrt{b_{1i}^2 - 4b_{2i}[b_{0i} - \ln(Q_i q_{0i})]}} \tag{29}$$

is obtained.

Numerical methods

The mass balances for each of the preceding mathematical models result in a series of parabolic partial differential equations. Orthogonal collocation is used to convert the partial differential equations into ordinary partial differential equations. Orthogonal collocation subroutines have been published by Villadsen and Michelsen (1978), Finlayson (1980), and Carnahan (1969). The resulting set of ordinary differential equations is solved using the August 13, 1981 version of Livermore Solver for Ordinary Differential Equations (LSODE). LSODE is a public-domain software package which is based on the Gear's stiff integration algorithm (Hindmarsh, 1980). The absolute and relative tolerances of LSODE are set at 10^{-5}. The double-precision program is written in Fortran IV language and run on a VAX computer system.

Experimental

The finite batch reactor studies were performed using binary and multicomponent solutions containing Cs, Sr, Ca, and/or Mg contacted with Ionsiv IE-90 and IE-96, chabazite zeolites which were initially in the sodium form. Ionsiv IE-90 particles are zeolite crystals, while Ionsiv IE-96 particles are zeolite crystals which have been pelletized with a clay binder. The Ionsiv IE-90 zeolite crystals were 24-μm irregularly shaped particles. The Ionsiv IE-96 pellets were typically 30- to 35-mesh (590- to 500-μm) irregularly shaped particles, but particles with diameters as small as 48 μm were tested. The physical properties of both zeolites were measured by the Martin Marietta Energy Systems Analytical Chemistry Division.

Simulated wastewater solutions were prepared by dissolving 2×10^{-3} $\underline{N}$ $SrCl_2 \cdot 6H_2O$, 1×10^{-3} $\underline{N}$ CsCl, 2×10^{-3} $\underline{N}$ $CaCl_2$, and/or 8×10^{-3} $\underline{N}$ $MgCl_2 \cdot 6H_2O$ in distilled water. The solutions containing strontium and cesium were also spiked with ^{85}Sr and ^{137}Cs tracers, respectively. The temperature of the solutions was held constant at 24 to 25°C in all tests.

The batch reactor is a Carberry-type reactor (Ruthven, 1984) that was constructed at Oak Ridge National Laboratory. It consists of a 5.2-cm-dia. baffled vessel with a 2.6-cm-wide, 1.2-cm high glass impeller. The four 0.5-cm-wide, 0.5-cm-deep baffles are located at 90° angles. The system was operated with 80 mL of solution and 0.05 g of zeolite. Both Ionsiv IE-90 and IE-96 were tested. A 100-mesh stainless steel envelope that was 3.2 cm wide and 2.5 cm high is attached to the impeller. The one-particle-thick bed of zeolite is placed inside the envelope so that liquid could adequately flow around the particles. Impeller speeds varied between 500 and 1,000 RPM. Since impeller speeds did not impact the uptake rates, most experiments were performed at 750 RPM, and film mass transfer was determined to be insignificant.

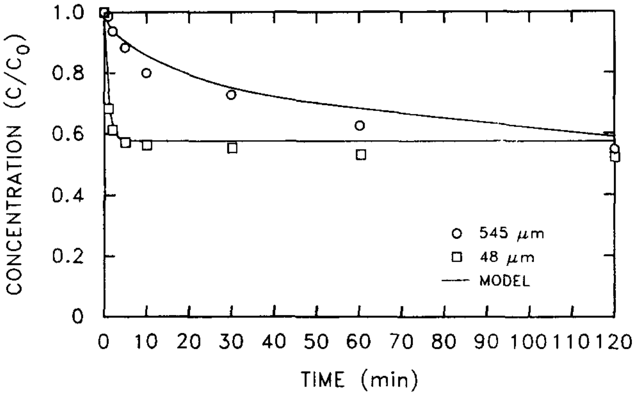

Figure 2. Effect of particle size on uptake rates for $CaCl_2$ with Ionsiv IE-96.

Calcium, sodium, and magnesium concentrations in the aqueous solutions were measured by an atomic adsorption spectrometer. Cesium and strontium concentrations in the aqueous solutions were measured by gamma counting of ^{137}Cs and ^{85}Sr tracers using a NaI detector for single isotopes and a Ge detector for multiple isotopes. The concentration of cations in the zeolite was calculated from mass balances using the initial and final solution concentrations.

Experimental data from the batch reactor are shown in Figures 2 and 3. Figure 2 shows the calcium uptake curves for different particle sizes of Ionsiv IE-96. The uptake rate for the 48-μm-dia. particles was significantly faster than for the 545-μm-dia. particles. Since the uptake curves were a function of particle size, macropore diffusion significantly contributes to the mass-transfer resistance for Ionsiv IE-96 chabazite pellets. Figure 3 shows uptake curves with IE-90 and IE-96 for both the binary and multicomponent systems. Uptake rates for the 24-μm Ionsiv IE-90 particles are significantly faster than for the 545-μm IE-96 particles. The loading for each cation is lower in the multicomponent systems than in the binary systems. The selectivity for the cations is Cs > Sr > Ca > Mg > Na.

Results and Discussion

Intraparticle diffusivities were estimated by matching the predictions of the various models to the results of the batch reactor data shown in Figure 3. Uptake data for Ionsiv IE-90 were modeled to determine solid-phase diffusivity values. Experiments with Ionsiv IE-96 were made to model uptake curves from pelletized particles where both macropore and micropore diffusion occur. The solid-phase diffusivities obtained from the IE-90 crystals were used for the micropore diffusivity values in this model. The experimental IE-96 data were matched with model results to determine the macropore diffusivity values. The calculated values for the diffusivities are given in Tables 1-3. The results are discussed in the following sections.

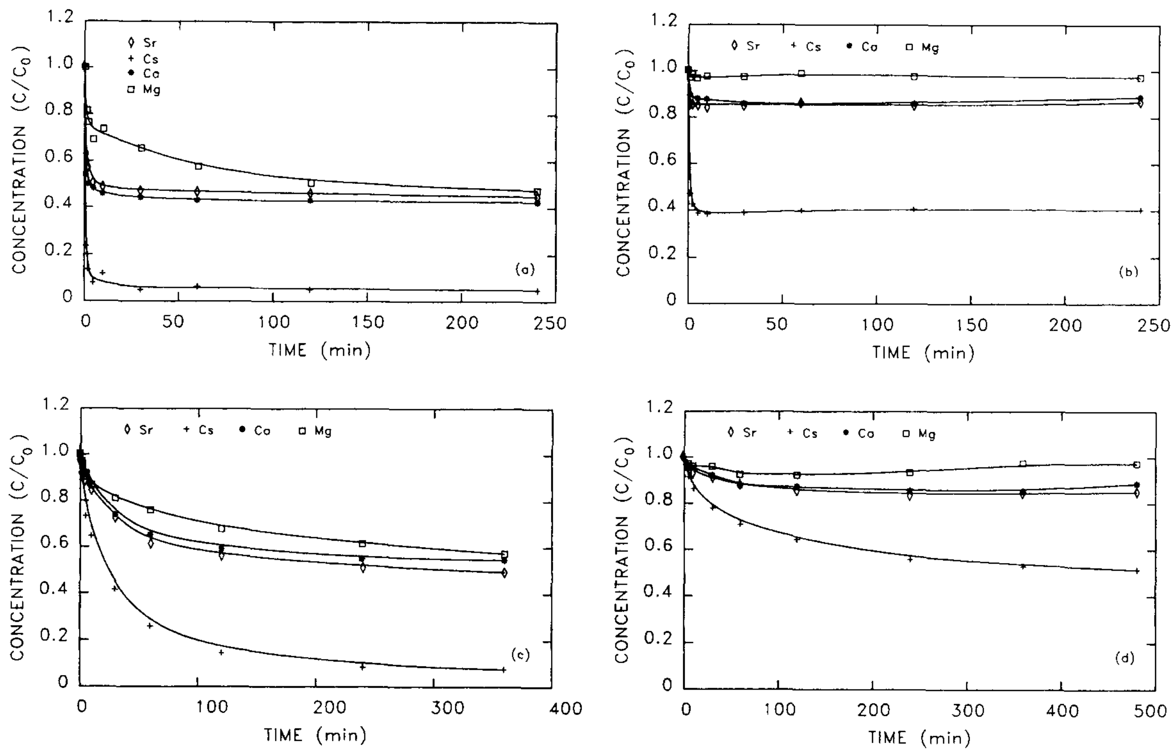

Figure 3. Experimental uptake data.

(a) IE-90 binary systems; (b) IE-90 multicomponent systems; (c) IE-96 binary systems; (d) IE-96 multicomponent systems.

Homogeneous diffusion model results for Ionsiv IE-90 zeolite crystals

The data for Ionsiv IE-90 zeolite crystals were modeled using the homogeneous diffusion model to determine the solid-phase diffusivities. Solid-phase diffusivities were obtained for both binary and multicomponent systems. The resulting diffusivities are listed in Table 1. The effective diffusivities obtained when D_c was assumed not to be a function of concentration ranged between 10^{-9} and 10^{-11} cm^2/s for binary systems. These effective solid-phase diffusivities accurately predicted the experimental data as shown in Figure 4a. The effective solid-phase diffusivities generated from modeling binary data did not accurately predict multicomponent uptake curves for Ionsiv IE-90, as shown in Figure 4b. However, effective solid-phase diffusivities could be found which accurately modeled the multicomponent data (also shown in Figure 4b). The effective solid-phase diffusivities for multicomponent Ionsiv IE-90 ranged between 10^{-9} and 10^{-10} cm^2/s.

When Darken's equation (Eqs. 28–29) was incorporated into

Table 1. Solid-Phase Diffusivities for Ionsiv IE-90 Based on the Homogeneous Diffusion Model

	Binary System		Multicomponent System	
	$D_{c,\mathrm{eff}}$* (cm^2/s)	D_{c0}** (cm^2/s)	$D_{c,\mathrm{eff}}$ (cm^2/s)	D_{c0} (cm^2/s)
Sr	1.5E-9	6.4E-10	1.5E-9	6.4E-10
Cs	9.5E-9	4.5E-10	3.0E-9	4.5E-10
Ca	3.0E-9	9.0E-10	3.0E-10	9.0E-10
Mg	6.0E-11	1.8E-10	5.0E-10	1.8E-10

*Effective diffusivity assuming diffusion is not a function of solute concentration in the solid phase.

**Corrected diffusivity assuming diffusion is a function of solute concentration in the solid phase.

Table 2. Effective Solid-Phase Diffusivities for Ionsiv IE-96 Based on the Homogeneous Diffusion Model

	$D_{c,\mathrm{eff}}$* (cm^2/s)	D_{c0}** (cm^2/s)
Sr	1.5E-8	6.4E-9
Cs	8.0E-9	4.0E-9
Ca	9.0E-9	4.0E-9
Mg	6.0E-9	3.0E-9

**Effective diffusivity assuming that diffusion is not a function of solute concentration in the solid phase.

**Corrected diffusivity assuming diffusion is a function of solute concentration in the solid phase.

Table 3. Macropore Diffusivities* for Ionsiv IE-90 Based on the Heterogeneous Diffusion Model

	Binary System		Multicomponent System	
	$D_{p,\mathrm{eff}}$** (cm^2/s)	D_{s0}† (cm^2/s)	$D_{p,\mathrm{eff}}$ (cm^2/s)	D_{s0} (cm^2/s)
Sr	2.8E-4	6.0E-9	5.0E-5	6.0E-9
Cs	9.0E-4	4.0E-9	1.5E-4	4.0E-9
Ca	2.0E-4	3.0E-9	6.0E-5	3.0E-9
Mg	1.4E-4	3.5E-9	1.0E-3	3.5E-9

*Obtained from the series heterogeneous diffusion model assuming the micropore diffusivities are equal to the solid-phase diffusivities listed in Table 1.

**Assumes that a single effective diffusion coefficient describes macropore diffusion.

†Corrected surface diffusivity assuming liquid and surface diffusion contribute to macropore diffusion.

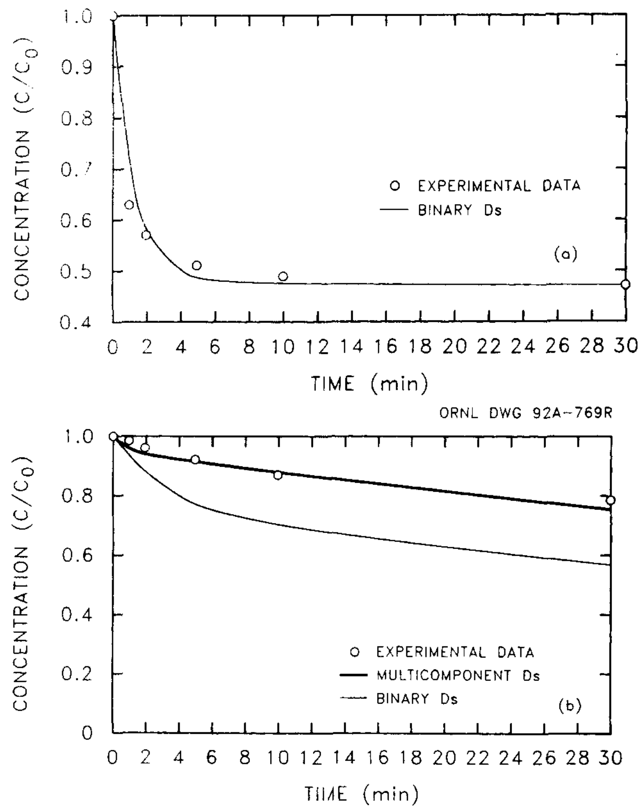

Figure 4. Homogeneous diffusion model of strontium uptake curves for Ionsiv IE-90.

(a) Sr-Na system; (b) Sr-Cs-Ca-Mg-Na system. Diffusivity values ($D_{c,eff}$) are given in Table 1.

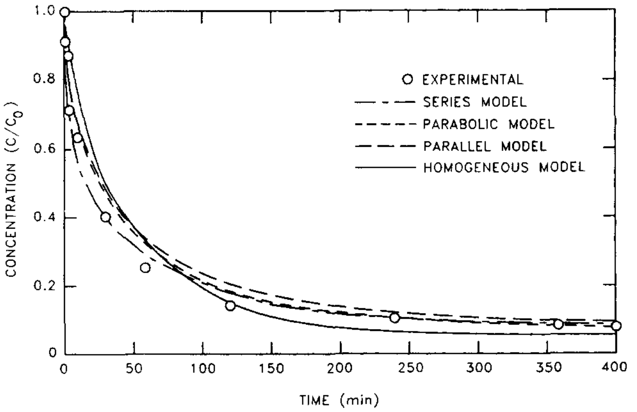

Figure 5. Models of Cs-Na uptake curves for Ionsiv IE-96.

Effective solid-phase diffusivity values for the homogeneous diffusion model are given in Table 2. Micropore and macropore diffusivity values for the series, parabolic, and parallel diffusion models are given in Tables 1 and 3, respectively.

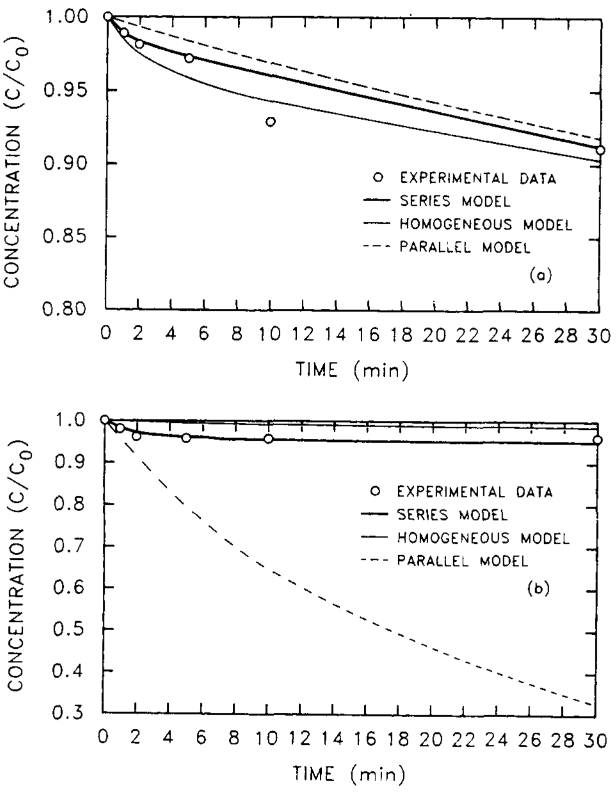

Figure 6. Models of Sr-Cs-Ca-Mg-Na uptake curves for Ionsiv IE-96.

(a) Strontium and (b) magnesium. Effective solid-phase diffusivity values for the homogeneous diffusion model are given in Table 2. Micropore and macropore diffusivity values for the series, parabolic, and parallel diffusion models are given in Tables 1 and 3, respectively.

the model to account for the concentration dependence of solid-phase diffusion, corrected diffusivities were obtained which accurately modeled both the binary and multicomponent data. These D_{c0} values, listed in Table 1, were between 2×10^{-10} and 9×10^{-10} cm^2/s, which is approximately an order of magnitude different than the effective diffusivities obtained from the constant-diffusivity model. These models result in curves very similar to the binary and multicomponent model curves shown in Figures 4a and 4b, respectively.

Homogeneous diffusion model results for Ionsiv IE-96 zeolite particles

The homogeneous model was evaluated for application to the Ionsiv IE-96 particles since this model had been previously reported to accurately predict ion exchange in zeolite particles as well as zeolite crystals (Rosen, 1952; Prazniak and Byers, 1987; Garg and Ruthven, 1974; Liapis and Crosser, 1982; Ruthven and Doetsch, 1979; Hsu and Hayes, 1981; Weber and Smith, 1987; Dominguez et al., 1991). The values for the micropore diffusivities obtained for the Ionsiv IE-90 zeolite crystals (Table 1) were used in the homogeneous diffusion model for Ionsiv IE-96 system. This model significantly underestimated the uptake rate, indicating that macropore diffusion was significant. However, values for effective solid-phase diffusivities were found which resulted in accurate predictions of the uptake data using Ionsiv IE-96 for both the binary and multicomponent systems, as shown in Figures 5 and 6. Effective diffusivities were found that would predict the experimental data using the homogeneous diffusion model, but the results did not fit the data as well as those from Ionsiv IE-90 systems.

Different sets of diffusivity values were obtained from the homogeneous model, which accurately predicted the data when the solid-phase diffusivities was assumed to be concentration-dependent and unaffected by solution concentration. These values are listed in Table 2. Effective diffusivities obtained when the diffusion was assumed to be concentration-independent were approximately twice as high as those obtained for corrected diffusivities that accounted for concentration effects. Both were an order of magnitude higher than the corresponding micropore diffusivities obtained for Ionsiv IE-90.

The data in Figure 2 indicate that both micropore and macropore diffusion must be accounted for in Ionsiv IE-96 systems since the mass transfer is a function of particle size (Ruthven, 1984). Although effective solid-phase diffusivities were found which accurately predicted the experimental data, this model is not considered to be physically correct since both micropore and macropore diffusivities actually occur in the heterogeneous zeolite particles. More elaborate models were pursued.

Heterogeneous diffusion model results

Various heterogeneous diffusion models (series, parallel, and parabolic) were successfully used to predict the uptake curves for the binary Ionsiv IE-96 systems. The solid-phase diffusivities, listed in Table 1, obtained from the Ionsiv IE-90 crystal data were used as the micropore diffusivities in the heterogeneous models for Ionsiv IE-96 particles. Experimental data for Ionsiv IE-96 were matched with the model results to predict the effective macropore diffusivities listed in Table 3. Examples of the resulting curves are shown in Figure 5. The results were basically the same when macropore and micropore diffusion were assumed to occur in parallel or in series. The assumption that the concentration profile in the zeolite crystal had a parabolic profile also gave an accurate prediction. All three models predicted the uptake profiles for Ionsiv IE-96 particles of different sizes (Figure 2). These findings are consistent with literature findings (Ma and Ho, 1974; Neretnieks, 1976).

Similar attempts were made to model the multicomponent data for Ionsiv IE-96. Typical results are shown in Figure 6. The effective macropore diffusivities obtained from binary and multicomponent Ionsiv IE-96 were different, but all values were on the order of 10^{-4} cm^2/s.

The values for the effective macropore diffusivities listed in Table 3 and liquid diffusivities obtained from the literature were used in Eq. 23 to calculate tortuosity factors for the chabazite zeolite. The Nernst-Haskell equation (Reid et al., 1987) was used to calculate molecular diffusivities of 1.2×10^{-5} cm^2/s for strontium, 1.9×10^{-5} cm^2/s for cesium, 1.3×10^{-5} cm^2/s for calcium, and 1.3×10^{-5} cm^2/s for magnesium. This resulted in tortuosity factors well below 0.1. The tortuosity is essentially a geometric factor which accounts for a longer diffusion path through randomly oriented pores than through a straight cylindrical pore. By definition, the tortuosity must be greater than one. If values less than one are obtained, this indicates that both surface and molecular diffusion contribute to pore diffusion (Ruthven, 1984).

When Eq. 24 is used to describe the effective macropore diffusivity in the series heterogeneous diffusion model, the model represents surface and molecular diffusion occurring in parallel in the macropores, followed by micropore diffusion occurring in series. The liquid diffusivities obtained from the literature and a tortuosity factor of 2 were used to model the Ionsiv IE-96 data. Values of the surface diffusivity, D_s, were varied until the model results fit the experimental data. The resulting values were on the order of 10^{-9} cm^2/s, one order of magnitude higher than the corrected micropore diffusivities. The surface diffusivity values were the same for both binary and multicomponent systems, as shown in Table 3.

The various heterogeneous diffusion models gave significantly different results for multicomponent Ionsiv IE-96 systems. The concentration profile in the zeolite crystals were not parabolic for the components which were displaced during multicomponent exchange. Therefore, the parabolic model did not converge under these circumstances and could not be used for multicomponent Ionsiv IE-96 systems. The parallel heterogeneous diffusion model predicted the data for strongly held components rather well. However, it did not accurately predict the data for weakly held components. Typical examples are the strontium and magnesium uptake curves shown in Figure 6. The series heterogeneous diffusion model accurately predicted the uptake curves for all components (see Figure 6).

These results indicate that effective diffusivities which vary by orders of magnitude can be used in the various mathematical models to predict ion exchange in chabazite zeolite. Differences in the kinetic mechanisms and the multicomponent interactions were adequately accounted for by the effective diffusivity values. These errors are relatively small for components diffusing in one direction, that is, binary systems and strongly held multicomponent cations. In these cases, single values of the effective diffusivities are adequate to allow modeling of the uptake curves. However, the resulting effective diffusivities can be physically unrealistic and do not allow prediction of multicomponent interactions.

Single values of effective diffusivities are not adequate to account for incorrect kinetic modeling and multicomponent interactions for weakly held cations in the multicomponent systems. In these highly nonideal cases, only the true mass-transfer mechanisms, macropore and micropore diffusion occurring in series, actually predict experimental data. Both surface and molecular diffusion contribute to macropore diffusion. Concentration-dependent micropore and surface diffusivities must be used. If the diffusion mechanisms are coupled with nonlinear equilibrium equations, they adequately predict multicomponent interactions. The introduction of cross-term diffusional coefficients to account for solute interactions was not necessary for the systems tested in this study.

Conclusions

Experimental kinetic data were taken in a batch reactor using zeolite crystals and zeolite particles (crystals plus binder) to determine the mass-transfer mechanisms which significantly affect multicomponent ion exchange in chabazite zeolites. The micropore diffusivities on the order of 10^{-10} cm^2/s were the most significant mass-transfer resistance. The effective macropore diffusivity, typically 10^{-4} cm^2/s, also significantly contributed to mass-transfer resistance in the zeolite particles. Film mass transfer dif not significantly contribute to the mass-transfer resistance.

The values obtained for the effective macropore diffusivities were two orders of magnitude higher than expected from liquid diffusivities. Mathematical modeling determined that liquid diffusion plus surface diffusion significantly contributed to macropore diffusion. Models indicated that surface diffusivities were on the order of 10^{-9} cm^2/s.

This study showed that several simplified mathematical models can be used to predict the experimental uptake data (both binary and multicomponent systems). These include assuming that diffusivities in the solid are independent of concentration, macropore and micropore diffusion occur in parallel or in series, the concentration profile inside the zeolite crystal is parabolic, and solutes diffuse independently. Effective diffusivities were obtained that would predict experimental data for most of these models. However, binary diffusivities could not be used to predict multicomponent diffusivities in these cases, and many of the resulting values were physically impossible. The results were similar to those obtained in several literature references that employed simple models to predict zeolite and carbon adsorption data.

Only the most rigorous model predicted multicomponent batch-reactor data using physically realistic diffusivities obtained from binary batch-reactor data. This model incorporated parallel molecular diffusion and surface diffusion occurring in series with micropore diffusion in the zeolite crystal. The surface and micropore diffusivities were concentration-dependent and followed Darken's equation. Solute interactions were accounted for in multicomponent equilibrium equations and concentration dependency of the solid diffusivities.

The findings in this study increase the understanding of why the results of zeolite studies reported in the literature are so confusing. Most researchers have looked at a few models to predict a limited amount of experimental data. These researchers tend to assume that a given model represents the mass-transfer mechanism if effective diffusivities can be found to predict experimental data. Most researchers who have modeled dual intraparticle mass transfer simultaneously varied both the macropore and micropore diffusivities to determine values that predict experimental data. They have not verified their models with both binary and multicomponent data using various sizes of crystals and pellets. This study shows that such limited testing of zeolite systems can result in erroneous conclusions about the mass-transfer mechanisms.

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Notation

a_i = constant for cation i in Langmuir isotherm in Eq. 26
a_{2i} = constant in Eq. 21
b_i = constant for cation i in Langmuir isotherm in Eq. 26
b_{0i} = constant for cation i in Dubinin-Polyani isotherm in Eq. 27
b_{1i} = constant for cation i in Dubinin-Polyani isotherm in Eq. 27
b_{2i} = constant for cation i in Dubinin-Polyani isotherm in Eq. 27
c_i = concentration of cation i in liquid, meq/mL
c_{0i} = initial concentration of cation i in liquid, meq/mL
C_i = dimensionless concentration of cation i in liquid, c_i/c_{0i}
C_{di} = dimensionless concentration of cation i in bulk liquid
C_{pi} = dimensionless concentration of cation i in liquid in macropores
C_{si} = dimensionless concentration of cation i in liquid at the particle surface
D_{ci} = micropore diffusivity for cation i, cm^2/s
D_{c0i} = corrected micropore diffusivity for cation i, cm^2/s
D_{gi} = $3\rho(1-\epsilon)q_{0i}/\epsilon c_{0i}$
D_{li} = liquid diffusivity for cation i, cm^2/s
D_{pi} = macropore diffusivity for cation i, cm^2/s
D_{si} = surface diffusivity for cation i, cm^2/s
D_{s0i} = corrected surface diffusivity for cation i, cm^2/s
D_{0i} = corrected diffusivity for cation i, cm^2/s
k_{fi} = film mass-transfer coefficient for cation i, cm/s
k_{gi} = $3k_{fi}(1-\epsilon)/\epsilon R_p$ or $3k_{fi}(1-\epsilon)/\epsilon r_c$
q_i = concentration of cation i in solid phase, meq/g
q_{si} = saturation concentration of cation i in solid phase, meq/g
q_{0i} = concentration of cation i in equilibrium with c_{0i}, meq/g
$\underline{Q}_i$ = dimensionless concentration of cation i in solid phase, q_i/q_{0i}
$\overline{Q}_i$ = dimensionless average concentration of cation i in zeolite crystal
$\overline{\overline{Q}}_i$ = dimensionless average concentration of cation i in solid phase
r = radial coordinate for microparticle, cm
$\bar{r}$ = dimensionless radial coordinate for zeolite crystal, r/r_c
r_c = microparticle radius, cm
$\underline{R}$ = radial coordinate for macroparticle, cm
$\overline{R}$ = dimensionless radial coordinate for zeolite particle, R/R_p
R_p = macroparticle radius, cm
t = time, s

Greek letters

ϵ = voidage in bed
ϵ_p = fraction in binder in particle
ξ_i = $c_{0i}\epsilon_p/(1-\epsilon_p)q_{0i}\rho$
ρ = density of particles, g/cm^3

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